iCOM

5th International Conference on the Physics of Optical Materials and Devices

BOOK OF ABSTRACTS

Igalo, Montenegro
27th to 31st August 2018

The 5th International Conference on the Physics of Optical Materials and Devices

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ICOM 2018

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Dear Colleagues and Friends,

It is our great pleasure to welcome you for the fifth time to The International Conference on the Physics of Optical Materials and Devices – ICOM 2018. The conference is organized by the Vinča Institute of Nuclear Sciences, University of Belgrade (Serbia), Laboratoire de Chimie de la Matière Condensée de Paris (France), Institut de Chimie de Clermont-Ferrand (France) and the Institute of Low Temperature and Structure Research Polish Academy of Sciences, Wrocław (Poland). This meeting is the continuation of a series of ICOM conferences organized every three years starting with Herceg Novi, Montenegro in 2006 and 2009; Belgrade Serbia in 2012 and Bečići, Montenegro in 2015.

The ICOM Conference brings together scientists and technology users who investigate or develop materials for optical applications. The conference presents the state of the art in preparation methods, optical characterization, and usage of optical materials and devices in various photonic fields. This year 2 plenary, 9 keynote, 21 invited lectures, 95 oral and 146 poster presentations will be presented in the following sections: Luminescent materials: new luminescent materials, new synthesis techniques, new phenomena; Hybrid optical materials (organic/inorganic); Low-dimensional systems, quantum dots, single molecule and single-particle spectroscopy; Characterization techniques of optical materials; Luminescence mechanisms and energy transfers; Theory and modelling of optical processes; Ultrafast-laser processing of materials; Luminescence thermometry; Physical, chemical and biological sensing using optical methods; Optical sensors; Medical imaging and bioimaging; Advanced optical materials in photovoltaics and biophotonics; Devices: lasers and amplifiers, LED and OLED, plasmoniclight sources, photovoltaics; Photothermal and photoacoustic spectroscopy and phenomena.

We hope that ICOM 2018 will be fruitful in terms of scientific exchange and that it will reinforce the existing collaborations between the participants and promote new ones in the future. We would like to acknowledge financial support given by numerous organizations.

Organizers of the ICOM 2018 wish you a nice time during the conference!

Conference Chairpersons:

Prof. Dr. Miroslav D. Dramićanin
Prof. Dr. Bruno Viana
Prof. Dr. Wiesław Stręk
Prof. Dr. Rachid Mahiou

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A. Meijerink[a], P.T. Prins, P. Villanueva-Delgado, M. Castelijns, R. G. Geitenbeek, Z. Wang, F.T. Rabouw

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It is not often that 0.5 is a perfect number but in case of upconversion (UC) materials 0.5 represents the perfect quantum yield. The best that can be achieved is emission of one high energy photon for every two low energy photons absorbed. Where ‘normal’ (downshifting) phosphors in lighting and displays have quantum yields close to the ideal 1, UC phosphors are still far from their perfect 0.5. For microcrystalline materials the highest UC quantum yields are just over 0.1 but in UC nanocrystals quantum yields are much lower [1,2]. In this presentation several causes for the low UC quantum yields will be discussed. An important tool is quantitative modelling of energy transfer and (for UC nanocrystals) ligand quenching. A new microscopic ligand-quenching model will be presented and applied to understand multi-phonon vibrational quenching in $NaYF_4$: Er,Yb UC nanocrystals. It takes into account cross-relaxation at high doping concentration as well as Förster energy transfer from lanthanide excited states to vibrational modes of molecules surrounding the NCs. Our model provides insight in the inert-shell thickness required to prevent solvent quenching in NCs. Overall, the strongest contribution to reduced UC efficiencies in core–shell NCs comes from quenching of the near-infrared energy levels (Er^{3+}: $^4I_{11/2}$ and Yb^{3+}: $^2F_{5/2}$), which is likely due to vibrational coupling to OH^- defects incorporated in the NCs during synthesis. Finally the role of the photonic environment will be discussed in relation to avenues to enhance upconversion efficiencies [3].

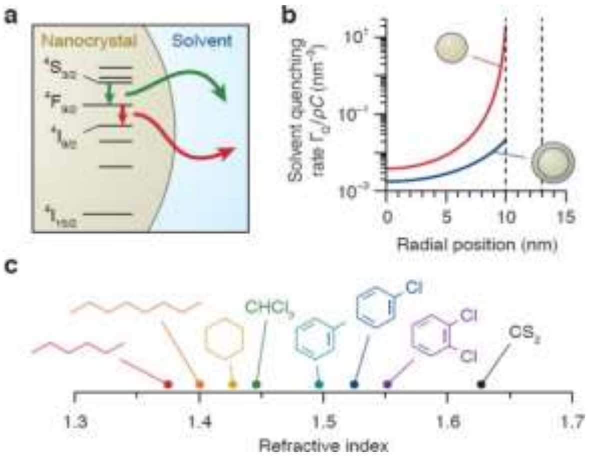

Figure 1. (a) Schematic of solvent quenching for green and red emission from Er^{3+}, (b) Dependence of quenching rate on the position of the Er^{3+} dopant in the NC and the role of shell growth, (c) Solvents with different refractive index used to investigate the role of photonic effects [2,3].

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ADVANCES IN HIGHLY DOPED UPCONVERSION NANOPARTICLES AND EMERGING APPLICATIONS

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Lanthanide ions doped upconversion nanoparticles (UCNPs) are capable of converting near-infrared light into visible and ultraviolet one. Their unique optical properties have advanced a broad range of applications, such as fluorescent microscopy, bio imaging, nanomedicine, optogenetics, security inks, and volumetric displays. The restraint of concentration quenchinghas been long challenging the community for the development of brighter UCNPs with a large amount of dopants. This review surveys the mechanism and strategies that bypass the concentration quenching effect to produce highly doped UCNPs, followed by a detailed discussion of new optical properties and some emerging applications introduced by these nanoparticles.

UPCONVERSION NANOPARTICLES IN NANOBIOMEDICINE

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The field of upconversion in ion doped system can be traced back to an idea of Bloembergen in 1959. Bloembergen proposed that IR photons could be detected and counted through sequential absorption (ESA) within the levels of a given ion in a solid. Role of energy transfer in upconversion was recognized by Auzel in 1966. Medical science has begun to focus their attention on the use of nanomaterials to improve diagnosis and treatment of diseases with the ultimate goal of moving into personalized medicine. The need to develop more efficient drug delivery procedures motivated us to propose novel nano-carrier based on lanthanide upconverting nanoparticles (UCNPs). They offer significant advantages in biological applications, particularly the extension of the system applicability to deep tissue regions of the body, a reduced scattering of the excitation wavelength, reduction of autofluorescence, and decrease in photodamage to the system under study. We will discuss relevant biological applications of these upconverting nanoparticles as a platform for drug delivery, photodynamic therapy, optogenetic and XPDT.

BIG CHANGES IN PERSISTENT LUMINESCENCE CHARACTERISTICS AND ELECTRONIC STRUCTURES OF Ce-DOPED GARNETS BY HYDROSTATIC PRESSURE

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Luminescence properties of phosphors are generally varied with pressure because the electronic structures of the host material including Ln^{3+}:4*f*, 5*d* and trap levels depends on pressure. We have reported compositional variation of electronic structures such as the conduction band (*CB*) bottom and Ce^{3+}: 5*d* levels in $Y_3Al_{5-x}Ga_xO_{12}$: Ce^{3+} (YAG*G*:Ce) phosphors as well as their persistent luminescence of Cr^{3+} codoped samples (YAG*G*:Ce-Cr)[1]. We have also reported Ga-content (x) dependence of quantum efficiency of Ce^{3+} in GYAG*G*, which rapidly drops in compositions above x>3.0 [2]. By using a diamond anvil cell (DAC) Prof. Grinberg in Gdansk and our group have reported large pressure dependence of photoluminescence (PL) in YG*G* (x=5)[2]. According to the results, non-luminescent YG*G*: Ce^{3+} at *RT* becomes luminescent and its lifetime, thermail quenching temperature increase with increasing pressure because of increasing *CB* bottom, which is close to the Ce^{3+}: $5d_1$ level. In this study, the pressure dependence of PL and persistent luminescence (PersL) in Ce^{3+}-M^{3+} codoped $Y_3AlGa_4O_{12}$ (x=4) phosphors were investigated, in which M^{3+} ions (*M* = Yb or Cr) act as an electron trap for persistence. The PL intensity of $Y_3AlGa_4O_{12}$: Ce^{3+}-M^{3+} was increased by pressure because the nonradiative rate due to thermal ionization decreases due to the increase of energy gap between the *CB* bottom and the $5d_1$ state of Ce^{3+}. With increasing pressure, the slope of PersL decay curve in the Yb-codoped system decreases. This result indicates the pressure increases the energy gap between *CB* and trap level of Yb^{2+}, the electronic configuration of which is $4f^{14}$. On the other hand, in the Cr^{3+} phosphor, the persL decay slope of Ce^{3+} were increased with increasing pressure. This discrepancy is due to different nature of 3*d* orbitals of chromium, which are split in a crystal field and more largely under higher pressure. In the garnet structrure, the Cr^{3+} ions ($3d^3$) occupy the octahedral site, which accept one more electron to be Cr^{2+} during charging as a result of photo-ionization of Ce^{3+}. As a high-spin configuration under a moderate 10*Dq*, this 4th electron occupies the e_g-state with higher energy. Increasing 10*Dq* under high pressure can decrease the trap depth of Cr^{2+}.

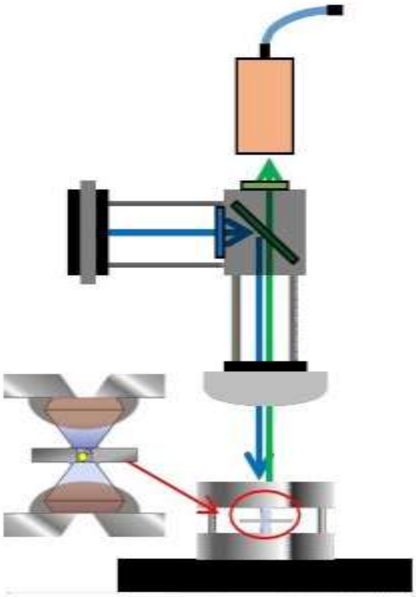

Fig.1. Measurement setup of persistent luminescence under high pressure with DAC.

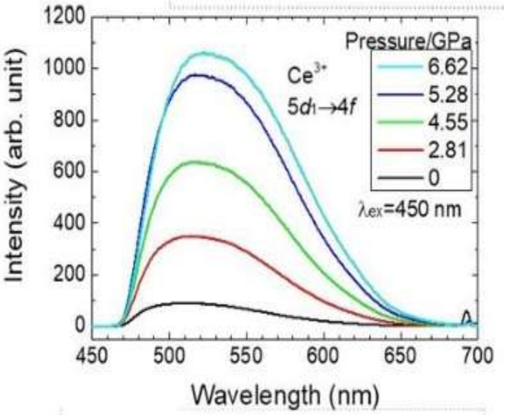

Fig.2. Pressure dependence of PL spectra of YAGG:Ce^{3+}. The PL intensity increases with pressure.

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RED PHOSPHORS FOR MAKING “GOOD” WHITE *LED* - A THEORETICAL INSIGHT

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The growing demand for the white light emitting diodes with low color correlated temperature and high color rendering index drives the intensive search for the narrow-band efficient red phosphors with high efficacy. If such phosphors are added to the InGaN blue LED chip in a combination with yellow YAG: Ce^{3+} phosphor, a warm white LED can be fabricated. The best candidates for this purpose are the Mn^{4+}-containing fluorides or oxyfluorides. The blue LED light can be utilized for the Mn^{4+} ions excitation with subsequent emission of red light in the 620-720 nm range, depending on the host material [1-2].

One of the most important drawbacks of the Mn^{4+}-based phosphors is a weak intensity of the zero-phonon line, which decreases the overlap of the phosphor emission spectrum with the human eye sensitivity curve resulting in lower lumen/watt content.

In the present paper we give a general overview of the Mn^{4+} spectroscopic properties, both in a free state and in solids. The crystal field theory and the first-principles calculations were used to gain a better understanding of the structural, optical and electronic properties of the studied compounds. Several trends across the considered compounds (related to the structure of the host materials, local symmetry of the dopant sites, and chemical bonds properties) were classified. Derivation of the empirical linear relation between the position of the emitting ^2E energy level of the Mn^{4+} ions and recently introduced nephelauxetic parameter β_1 [3] will be presented [4].

Based on our recent publications, we also suggest a key strategy on how to enhance the zero-phonon line intensity [3, 5], which can serve as a useful guide in a smart search for new phosphor materials with improved characteristics.

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CONTROLLING THE SPECTROSCOPIC AND LASING PROPERTIES OF RARE EARTH DOPED CRYSTALS BY SURFACE PLASMONS

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Currently, the extraordinary properties of surface plasmons to control and manipulate light are being exploited to demonstrate lasing in nanoscopic volumes. Commonly, plasmon lasers combine metallic nanostructures with optical gain media, based on organic dyes or semiconductors, to provide coherent radiation at the nanoscale with sub-wavelength confined modes [1]. Recently, these systems have been extended by the demonstration of lasing at the nanoscale from plasmon-assisted Rare-Earth (RE)-based Solid State Lasers (SSLs) [2, 3]. In this context, the incorporation of SSLs into the new class of plasmon lasers is of great interest since it allows exploiting the inherent properties of SSLs in nanoscopic systems.

In this talk, the effect of different plasmonic arrangements on the spectroscopic properties and laser action of different RE^{3+} ion doped crystals will be shown. We will analyze i) the effect of linear chains of silver nanoparticles on the properties of a Nd^{3+} doped SSL, and ii) the effect of disordered plasmonic networks on the optical performance of a Yb^{3+} doped SSL. Depending on the specific architecture, different and novel performances, such as a strong threshold reduction or a plasmon induced dual wavelength lasing, can be obtained.

The results are promising to extend the relevant features of SSLs to the nanoscale and demonstrate the potential of new RE-based plasmon-lasers to achieve novel functionalities not demonstrated yet at the nanoscale.

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DEFECTS IN ENERGY STORING PHOSPHORS: THE GOOD, THE BAD AND THE UGLY

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In most impurity doped luminescent materials, the defects responsible for the absorption and emission characteristics of phosphors are deliberately doped ions, often substituting for specific ions in the crystal lattice. The emission typically occurs within milliseconds after the excitation and can essentially be described by electronic transitions within the defect. To obtain a high quantum efficiency, the emission behavior of those Good defects should not be perturbed by Bad defects, bringing for instance non-radiative decay paths [1]. In that sense, phosphor optimization is driven by avoiding unwanted impurities and clusters of luminescent ions within the lattice.

A specific class of luminescent materials are those phosphors which are able to store excitation energy in their lattice, in such a way that the time between excitation and emission can be extended up to minutes, hours or even many thousands of years. They find applications in geological dating and as x-ray storage phosphors (via optically stimulated luminescence [2]), in persistent phosphors (via thermally driven release [3, 4]) or in mechanoluminescent phosphors (via pressure driven release, [5]).

Quite surprisingly, it is for many of those energy storing phosphor systems still largely unclear what the nature of the defect(s) responsible for the energy storage is. Often specific analytical techniques (such as XANES [6] or EPR [7]) or quantum mechanical calculations [8] are required to probe their role. It is however commonly the case that those defects are playing a role which goes beyond the mere energy storage reservoir which we would like them to be. In this presentation, the focus will be on those Ugly defects, bringing the desired energy storage, yet also being susceptible for occasionally strong interactions with the Good defects and the excitation light intended to store energy [9].

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PLASMONIC MATERIALS/METAMATERIALS AND OTHER NOVEL PHOTONIC MATERIALS OBTAINED BY CRYSTAL GROWTH TECHNIQUES

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In recent years, two different types of materials are developed in the area of photonics: metamaterials [1] and plasmonic materials [2]. These novel fields of photonics need new fabrication techniques. We will demonstrate how to utilize the melt-based crystal growth methods for manufacturing of such advanced photonic materials. Two novel approaches towards materials with unusual electromagnetic properties will be presented: (i) directional solidification of eutectics (DSE) [3, 4, 5] and (ii) NanoParticle Direct Doping (NPDD) [6, 7].

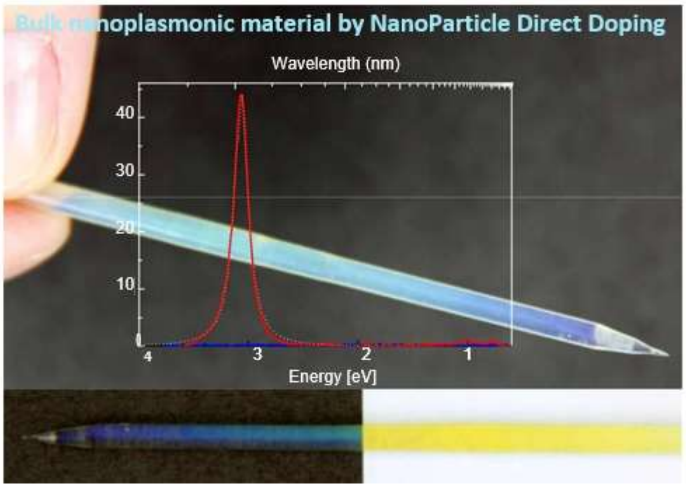

Figure 1. Demonstration of nanoplasmonic bulk materials obtained utilizing the NanoParticles Direct Doping with the micro-pulling down method.

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TO WHAT EXTENT THE DEVELOPMENT OF CHALCOGENIDE GLASSES CAN LEAD TO INNOVATIONS IN ENVIRONMENTAL INFRARED DETECTION?

[1]J. Ari, [1]N. Abdellaoui, [1]E. Baudet, [1,2]F. Starecki, [1]C. Boussard-Pledel, [3]J. Charrier,
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A review of our current research on chalcogenide materials contributing to the development of optical sensors will be presented.

The 3-15 μm range is a key region for a large number of optical sensor applications in various fields such as biology and medicine, molecular spectroscopy or environmental monitoring. Infrared spectroscopy is a powerful tool for detecting and determining the composition of complex samples. It is a simple, reliable, fast, economical and non-destructive method.

In order to further develop this technique especially for on-site real time monitoring, it is crucial to provide suitable infrared materials covering the mid-infrared spectral range. It is in this context that we intensified our efforts to develop chalcogenide glasses that meet the specific requirements for the development of optical sensors dedicated to environmental issues.

On the one hand, the detection of molecules at low concentrations down to a ppm or ppb level is often necessary and on-chip chalcogenide devices can provide motivating insights. On the other hand, infrared sources are a key entry point for optical sensors. Oxides generate at the best near-infrared light, whereas mid-infrared emissions of 3 to 8 μm are allowed in chalcogenide matrices with lower phonon energy. The down-wavelength conversion mechanism could be adapted in the mid-infrared range to develop incoherent light sources to replace blackbody sources for remote sensing or spectroscopy applications, for example.

Aknowledgement: V. Nazabal is thankful to Brittany region, Intercarnot IFREMER/BRGM, ANR SEED CGSμLAB, ANR LOUISE, ANR OPTIGAS and ADEME for financial support.

GO FOR RED TO BE AHEAD! HIGH PERFORMANCE RED- AND *NIR*-EMITTING MATERIALS FOR OPTICAL SENSING

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Optical sensors became increasingly popular in the last decades due to many advantages compared to conventional analytical techniques. Among optical sensors and probes, those based on luminescent materials are probably the most numerous ones. Unfortunately, application of many luminescent materials in high-performance sensors is limited by several factors such as inferior photophysical properties (low brightness, low photostability), poor selectivity for the analyte of interest, laborious synthesis etc.

The materials operating in the red and near-infrared parts of the electromagnetic spectrum are of particular interest due to compatibility with the biological “optical window” and low interference from background fluorescence and light scattering. Here we will provide an overview of our recent research activities which have been focused on preparation of high performance optical sensors based on red- and NIR-emitting fluorescent dyes, phosphorescent metal complexes and inorganic phosphors. A broad palette of (metal)organic indicators for detection of oxygen, pH, basic and acidic gases, metal ions and temperature has been prepared. Although most of these systems are based on porphyrins and related systems (BODIPYs and azaBODIPYs), some other dye classes (such as perylenes) yielded promising results as well.

We also demonstrate applicability of the new sensors in several fields such as oceanography, medicine and biotechnology. Importantly, due to similar spectral properties, most of the new materials show compatibility with a palette of compact phase fluorometers, making low-cost multi-parameter sensing possible.

MULTI-MODAL HYBRID NANOSTRUCTURES BASED ON RARE EARTH DOPED NANOPARTICLES

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The surge of recent interest in near-infrared (NIR) excited nanoparticles stems from their potential in a number of applications with diagnostic and therapeutic medicine leading the charge. In this regard, rare earth doped nanoparticles (RENPs) are at the vanguard since they possess multiple absorption and emissions in the three NIR "biological windows" (ca. 700-990, 1050-1350, and 1550-1870 nm) allowing for their excitation within one window and observe emission in another. Given the multitude of their 4*f* electronic states (with corresponding long lifetimes), it is also conceivable to induce upconversion where the NIR excitation light is converted to higher energies spanning the UV-visible-NIR regions.

By combining RENPs with other optically active nanostructures (oxides, semiconductors, plasmonic nanomaterials, etc.), it becomes possible to develop multi-modal nanoplatforms and thus expand the functionality of these nanoparticles. Here, we present the synthesis and surface functionalization of various NIR excited RENP, their assembly with other nanostructures and demonstrate how they can be used for biological applications.

HIGHLY DOPED RARE EARTH PHOSPHORS FOR SOLID STATE LIGHTING

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Rare earth doped phosphors are always popular as their substantial energy levels can provide various color emissions. However, weak absorption in near-UV region, ascribed to the parity-forbidden transitions of some trivalent rare earth typically Tb^{3+} and Eu^{3+} ions makes it difficult to fully use the exciting light of LED chips. More luminescence centers are expected to be doped in crystal lattices to enlarge the absorption but a low emission efficiency due to the inextricable contradiction between doping concentration and cross relaxation might follow.

Our previous works reveal that energy transfer would not easily occur in identical ions in some special cases like $K_2Ln(PO_4)(WO_4)$(Ln = Y, Gd and Lu), $Ca_8MgLu(PO_4)_7$ and $Ca_3Y(GaO)_3(BO_3)_4$ and $YGa_{1.5}Al_{1.5}(BO_3)_4$. These materials have the similarity in structure that sites available for the substitution of rare earth ions are highly isolated. The isolation in the space can damp of concentration quenching in both Tb^{3+} and Eu^{3+} ions. We believe highly doped rare earth phosphors are far more superior and potential for solid state lighting.

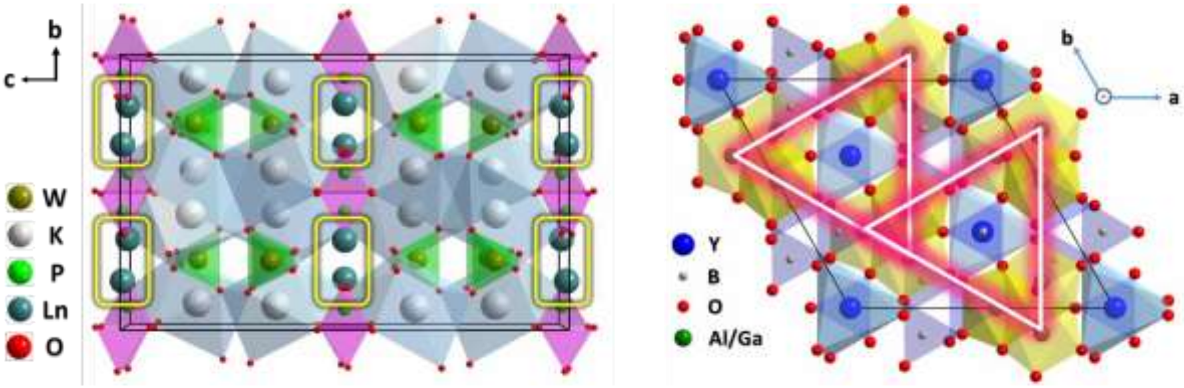

Figure 1 The highly isolated sites available for the substitution of rare earth ions in $K_2Ln(PO_4)(WO_4)$ (Ln = Y, Gd and Lu) and $YGa_{1.5}Al_{1.5}(BO_3)_4$.

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THEORETICAL INSIGHTS INTO THE EMPIRICAL MODELS USED IN LANTHANIDE AND TRANSITION-METAL SPECTROSCOPY

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In the past decades, the lanthanide and transition-metal (TM) activated phosphors have attracted more interest due to their outstanding performance on the white and colored light generation for the lighting application. And the empirical models, such as Dorenbos's "zigzag" model for lanthanides [1] and the β_1 model proposed by Brik and Srivastava for Mn^{4+} and Cr^{3+} [2], have made it possible to form a fast and computationally simple design strategy for the optimization of the optical properties of those phosphor materials from the experimental point of view. However, so far the empirical models actually remained to be purely empirical, based on the analysis of a larger amount of experimental data with their possible extrapolation. Therefore, it should be desirable to outline the theoretical basis of the empirical models in terms of more fundamental quantum mechanics knowledge in order to get a deep insight into the validity of the models.

In this talk, we will reveal the completely theoretical understanding on the β_1 model of Brik and Srivastava and Dorenbos's "zigzag" model by employing the combined *ab* inito and crystal-field (CF) methods. Three aspects will be referred as follows: 1) the empirical linearity of the spin-forbidden emission energies of TM ions with respect to the nephelauxetic ratio parameter is confirmed by considering the Tanabe-Sugano matrices for the corresponding electronic configurations [3], as shown in Fig. 1; 2) the empirical 4f-5d transition energy expression of trivalent lanthanide ions in solids [4] can be reproduced by using the effective Hamiltonian theory of $4f^{N-1}5d$ configuration in combination with the results of the *ab* initio free ion calculations; 3) the trend of the 4f single-electron energy level positions in the band gap of cubic Cs_2NaYF_6 across the whole lanthanide series is given by the HSE06 DFT calculations and further compared with the empirical results of Dorenbos [1].

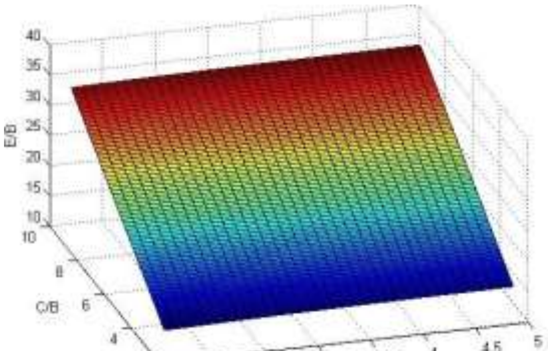

Figure 1. Dependence of the $^2E \rightarrow {}^4A_2$ transition energy in unit of B on the two parameters Dq/B and C/B.

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HANDLING LARGE AMOUNTS OF DATA. APPLICATIONS IN APPLIED FLUORESCENCE SPECTROSCOPY

Rasmus Bro,
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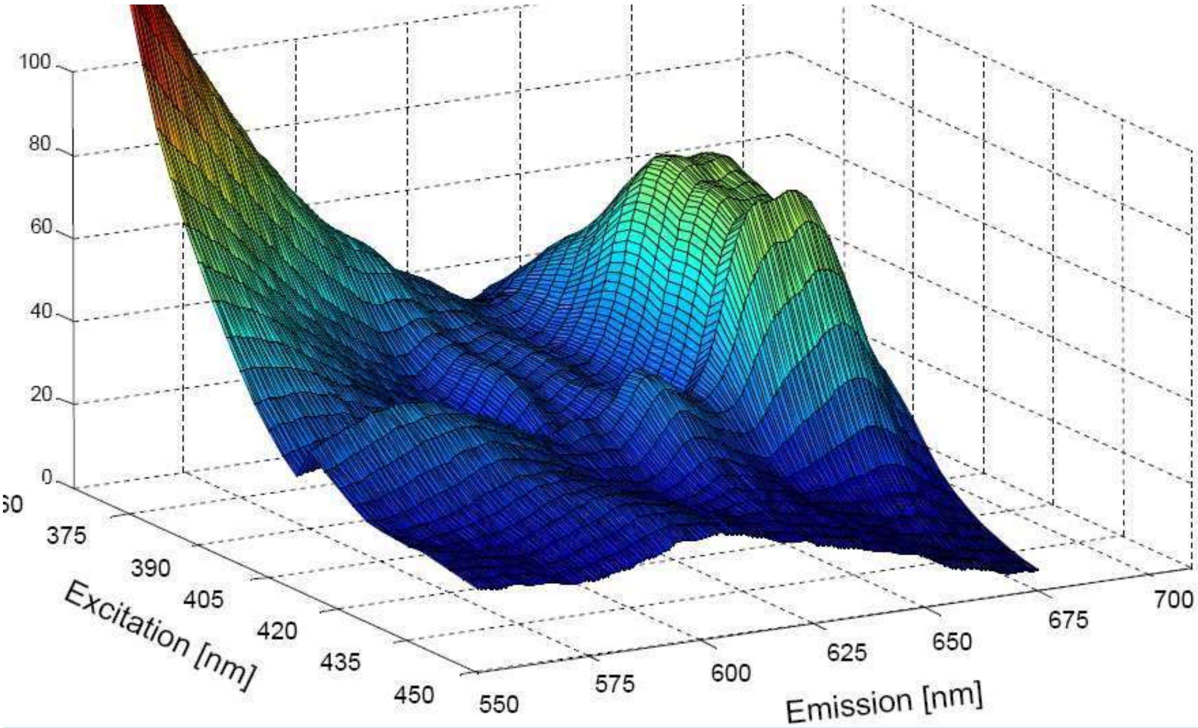
When measuring complex samples, complex data will be obtained. To get the most information from such data, it is necessary to have data analytical tools that allow to understand, visualize and analyze the data comprehensively.

We will show that such tools exist and that they are really easy to use. The field of chemometrics (data generation and analysis in chemical sciences) is a field that has existed for more that forty years and that provides simple solutions to understand measurements of millions of data points in simple manners.

We will show how methods like principal component analysis and parallel factor analysis can be used to analyze fluorescence data in a variety of problems related to food, pharma and health.



Example of complex data. Fluorescence EEM of a butter sample

PIONEERING DIVALENT LANTHANIDES FOR UPCONVERSION

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In contrast to the 4f-4f transitions in general observed for trivalent lanthanides, the intense emissions of the parity-allowed 4f ↔ 5d transitions of divalent rare earth ions depend strongly on the surrounding. The luminescence of the most stable one, Eu^{2+}, has been described in numerous host lattices, while other divalent lanthanides are rather sparsely investigated due their lower stability. In fact, the number of publications correlates on the reduction potential Ln^{3+}/Ln^{2+}. While some works of Yb^{2+} and Sm^{2+} doped materials are available, the number of publications concerning Tm^{2+} are rare [1-3]. Materials containing more unstable divalent lanthanides, like Dy^{2+} and Ho^{2+}, are very scarcely described. The general procedure is doping with trivalent lanthanides, the reduction was achieved afterwards by γ-rays or alkaline earth vapor. This procedure is by far not suitable for the preparation of high quality samples, because it leads to numerous defects which influences the optical properties, and, moreover, the stability of the samples is very poor.

In this talk, we present the investigation of the luminescence properties of Tm^{2+}, Dy^{2+}, Ho^{2+} doped in different chloride host lattices (MCl_2 (M = Ca, Sr, Ba); $AMCl_3$ (A = K, Rb, Cs; M = Ca, Sr)) and the Matlockite type compounds (MFCl (M = Ca, Sr). For the first time samples of good quality was achieved by direct doping with $LnCl_2$ (Ln = Tm, Dy, Ho), which are very convenient for measurements of optical properties.

At room temperature, $AMCl_3$ (A = K, Rb, Cs; M = Ca, Sr) and $CaCl_2$ doped with Tm^{2+} showed a very intensive emission located at 8770 cm^{-1} assigned to $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. From the lowest 5d level a spin-allowed (LS) and a spin-forbidden transition (HS) into the $^2F_{7/2}$ state (ground state) was detected at 10 K as well as at room temperature at around 13400 cm^{-1} (750 nm) and 12400 cm^{-1} (806 nm), respectively. These chlorides are good candidates for up-conversion materials because the 5d level can be reached by a two photon absorption process ($4f^{13}(^2F_{5/2}) \rightarrow 4f^{13}(^2F_{7/2}) \rightarrow 4f^{13}5d^1$). Tm^{2+} doped into fluoride host lattices cannot be used as up conversion material because of the high energy of the 5d level. In $CaFCl:Tm^{2+}$ we observed the first excitation band of the 5d state at around 20000 cm^{-1} (500 nm).

New activator ions for up conversion process could be Dy^{2+} and Ho^{2+}. These ions doped into MCl_2 (M = Ca, Sr) shows only one sharp parity-forbidden band at around 7000 cm^{-1} (1430 nm; $^5I_6 \rightarrow {}^5I_8$) and 5450 cm^{-1} (1835 nm; $^4I_{13/2} \rightarrow {}^4I_{15/2}$) for Ho^{2+}, respectively. In Matlockite host lattices a second sharp emission band were detected for both ions at low temperature. The emission band for Dy^{2+} at around 9200 cm^{-1} (1087 nm) can be assigned to the transition $^5I_5 \rightarrow {}^5I_8$, and the emission line for Ho^{2+} at around 8650 cm^{-1} (1156 nm) can be assigned to the transition $^4I_{11/2} \rightarrow {}^4I_{15/2}$. Consequently, in contrast to Tm^{2+}, only fluorides host lattices could be used as an up conversion material for Dy^{2+} and Ho^{2+}. The possible pathway for the up conversion process of Dy^{2+} is the two step excitation $4f^{10}(^5I_8) \rightarrow 4f^{10}(^5I_6) \rightarrow 4f^95d^1$ followed by a non-radiative transition into the $4f^{10}(^5I_5)$ state. The pathway for Ho^{2+} can be described as an: excitation $4f^{11}(^4I_{15/2}) \rightarrow 4f^{11}(^4I_{13/2}) \rightarrow 4f^{10}5d^1$, followed by a non-radiative transition into $^4I_{11/2}$.

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IONIC LIQUIDs FOR PHOTOLUMINESCENT AND PHOTONIC APPLICATIONS

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The development of modern technologies forces the search for new materials that not only meet the application requirements, but are also environmentally friendly. Thus, in recent years there has been a growing interest in studies of ionic liquids (ILs). ILs are considered to be generally ionic salts with a melting point below 100°C, many of them are already liquid at room temperature (RTILs). The physicochemical properties of ILs as thermal stability, viscosity, density, melting temperature can be modify by selecting appropriate cations and anions. The extremely low vapor pressure and non-flammability of most ionic liquids makes them good candidates to replace some organic solvents and ILs are often called green solvents. It has been shown that ILs are very efficient media for nanoparticles synthesis, as they can act as in-situ stabilizer and the template for forming particles. Moreover, by the changing in the anionic or cationic part of ILs it is possible to influence the materials morphology and particles size, thus the spectroscopic properties of the nanomaterials can be tuned. The low temperature process allows also for better control of the quality of the material obtained, and the synthesis parameters including the ionic liquid structure contribute to the morphology and particles size, thereby modifying the spectroscopic properties. Modelling of the morphology of the phosphate nano-sized due to the fact that the substances are hardly soluble is particularly difficult in conventional synthesis reactions, therefore the use of ionic liquids serve as a template for forming grains opens the way to synthesize materials with controlled characteristics.

We already presented the using of ILs based method for the synthesis of luminescent efficient nanophosphors – fluorides and phosphates. Our recent studies of application of ILs in photonic was also devoted to polimerizable ILs, which could replace currently using polymers. Low vapour pressure makes ILs good candidates to use in vacuum techniques and consequently put a substrate with an ionic liquid layer into a chamber of SEM (scanning electron microscope) equipped with FIB (focused ion beam) source. Moreover, a thin layer of this material can be obtained without using a solvent, which might be crucial in many technological processes.

The ILs role as in-stabilizer and reactant for nanopraticles synthesis as well as the useful photonic materials will be shown and discuss.

CHIRAL THIN FILMS FOR NEW OPTICAL DEVICES

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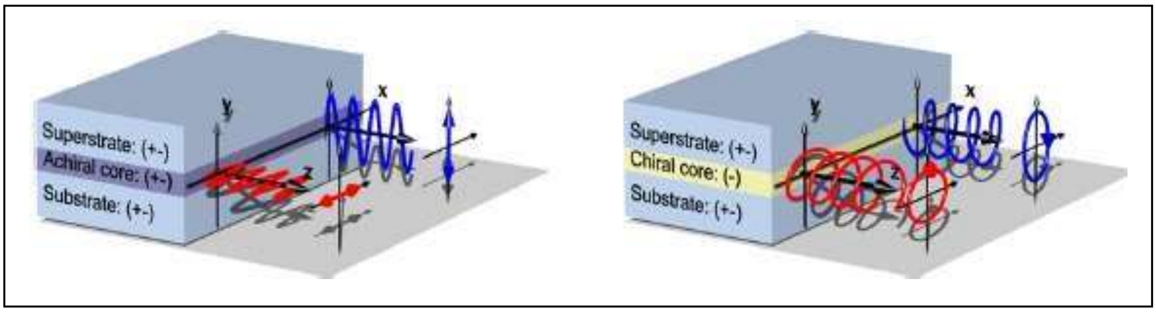
Chirowaveguides are planar waveguides with an isotropic chiral core. These waveguides theoretically proposed in 1989 [1] open new perspectives in planar guided optics because they allow the propagation of any polarization from linear to circular [2] (Figure 1). Many theoretical works have been done dealing with the unique properties of these waveguides and their potential applications (TE/TM convertor, switches [3] or chiral sensors [4]).

Organic materials made of molecules exhibiting high chiroptical activities are good candidates for such devices. Deposition of these materials requires techniques which are able to conserve the chirality and allow elliptically polarized light propagation. In this talk, we will give an overview of the main properties of planar chirowaveguides and their potential applications. Emphasis will be made on the requirements to build such structures. We will then present our last results concerning the coating of thin films of high optical rotary power based on different chiral organic molecules. Two deposition techniques are investigated: Pulsed Laser Deposition and dip coating of hybrid Si-binaphtyl molecules [5-7]. Elliptical to quasi-circular polarizations propagation is demonstrated in optical planar chirowaveguides with optimized refractive index contrast [8].



(a) (b)

Figure 1: Propagation of eigen modes: linear in planar waveguides (a) and elliptic in chirowaveguides (b).

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PHOTONICS GLASS-CERAMICS

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Transparent glass ceramic are nanocomposite systems that exhibit specific morphologic, structural and spectroscopic properties allowing to develop interesting new physical concepts, for instance the mechanism related to the high observed transparency and to the peculiar thermal properties, as well as novel photonic devices based on the enhancement of the luminescence and photons management. At the state of art, the fabrication techniques based on bottom-up and top-down approaches appear to be viable although a specific effort is required to achieve the necessary reliability and reproducibility of the preparation protocols. In particular, the dependence of the final product on the specific parent glass and on the employed synthesis still remain an important task of the research in material science. Looking to application, the enhanced spectroscopic properties typical of transparent glass ceramic activated by rare earth ions, in respect to those of the amorphous structures constitute an important point for the development of integrated optics devices, including optical amplifiers, monolithic waveguide laser, novel sensors, coating of spherical microresonators, and up and down converters for solar energy exploitation. The more important point to be resolved now is to develop a specific protocol for the patterning of the glass-ceramic avoiding worsening of the optical properties induced, for instance by the reactive ion etching process. In the case of oxide glasses exploitation of photorefractive properties is recently attempted with promising preliminary results. The excellent flexibility of the physical vapor deposition technique could be employed to deposit the material into suitable channels and layouts previously fabricated on the substrate. This lecture presents a short overview of the state of art in transparent glass ceramics focusing the discussion on photonics application and evidences the capital scientific and technological interest of this kind of two-phase materials, which require and allow common multidisciplinary research involving scientists coming from a large spectrum of disciplines.

The research activity is performed in the framework of ERANET-LAC FP7 Project RECOLA - Recovery of Lanthanides and other Metals from WEEE (2017-2019) and Centro Fermi MiFo project. Lam Thi Ngoc Tran acknowledges the scholarship of the Ministry of Education and Training, Vietnam International Education Development

BIOCOMPATIBLE LANTHANIDE MATERIALS FOR TUMORS TARGETING, IMAGING AND INHIBITION TARGETING *EBV* ASSOCIATED CANCER DISEASES

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Epstein-Barr virus (EBV) infects human B-cells as well as epithelial cells and immortalizes and transforms them into malignant cancer cells under some circumstances. During the transformation process, EBV expresses a handful number of viral proteins to support the tumor growth. Epstein-Barr nuclear antigen 1 (EBNA1), is the only viral protein expressed in all EBV-associated tumors, it plays a critical role in replication and maintenance of the viral genome in the host cells, and EBNA1 can also function as a transcription factor to activate the expression of the other viral genes required for the cellular immortalization and proliferation. Several small molecules as their inhibitors have been reported; however, those reported inhibitors are not emissive and cannot directly evaluate their effectiveness, such as real time imaging, biodistribution and pharmacokinetic studies. Over the recent two decades, luminescent lanthanide materials have shown extensive applications in the detection of various bioactive molecules and for in vitro/in vivo imaging, addressing the problem of autofluorescence. For this reason, one of our driving forces for synthesizing new lanthanide materials for imaging these cell cycle regulated protein relates to their unique photophysical properties, such as long emission lifetimes (effective elimination of biological auto-fluorescence in time-resolved spectroscopy) and characteristic hypersensitive emissions, (providing real-time information about the effect on coordination environment by surrounding entities, especially with europium) which are attractive substitutes to the more commonly used organic fluorophores.

In this seminar, I would like to share our development recently on emissive lanthanide upconversion nano- materials as dual bioprobes for in vitro/in vivo imaging and inhibition of overexpressed tumor regulator proteins on EBV associated cancer- EBNA1. It is hoped that the success in research could also lead to the success in practice, thereby providing more powerful tools for ending EBV cancer.

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RATIOMETRIC OPTICAL THERMOMETRY USING DEEP RED LUMINESCENCE
FROM $^4T_2$ AND ^2E STATES OF Cr^{3+} IN $ZnGa_2O_4$ HOST

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$ZnGa_2O_4:Cr^{3+}$ is a well-known deep red (persistent) phosphor with *R*-lines due to the $^2E \rightarrow {}^4A_2$ spin-forbidden transition of Cr^{3+} ions between 690 and 750 nm. Recently, this system has attracted a great deal of interest for *in-vivo* bio-imaging[1]. In this study, we investigated the temperature dependence of photoluminescence (PL) spectrum of $ZnGa_2O_4:Cr^{3+}$ and the possibility of using this material for thermometry. At 100 K, the zero-phonon lines and phonon-side bands of the $^2E \rightarrow {}^4A_2$ transition were observed in the PL spectrum as shown in Figure 1. At higher temperatures above 250 K, a broad PL band was observed at around 720 nm in addition to the sharp $^2E \rightarrow {}^4A_2$ luminescence. After determination of the Stokes shift energy between the PL and PL excitation spectra and the increase of broad luminescence band intensity with increasing temperature, we attribute this additional broad luminescence band to the spin-allowed $^4T_2 \rightarrow {}^4A_2$ transition of Cr^{3+} ions as shown in Figure 1. The fluorescence intensity ratio of these emission transitions ($^4T_2 \rightarrow {}^4A_2$)/($^2E \rightarrow {}^4A_2$) shows good linearity from 270 K to 700 K in the Arrhenius plot. Thus, the population of $^4T_2$ and ^2E follows Boltzmann distribution. The activation energy needed for excitation from the ^2E state to the $^4T_2$ state of Cr^{3+} was estimated to be 1744 cm^{-1}. Based on our results, we suggest that the $ZnGa_2O_4:Cr^{3+}$ system can work well as a ratiometric thermometer with a high relative sensitivity of 2.8 $\%K^{-1}$ (at 310 K) in a wide temperature range.

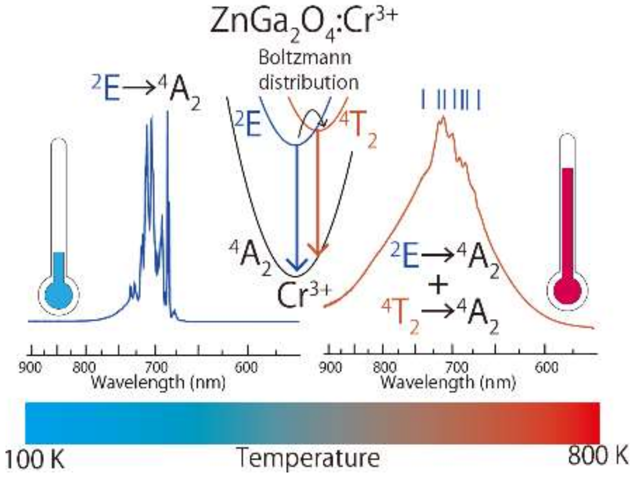

Figure 1. PL spectra at 100 K and 700K and configuration coordinate diagram.

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LOCAL SYMMETRY AT CATIONIC SITES IN RHOMBOHEDRAL PYROCHLORES $M_2La_3Sb_3O_{14}$ (M = Mg OR Ca): A STRUCTURAL AND SPECTROSCOPIC INVESTIGATION

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$Mg_2La_3Sb_3O_{14}$ and $Ca_2La_3Sb_3O_{14}$ are rhombohedral pyrochlores. A detailed powder X-ray Diffraction (XRD) investigation shows that, as a consequence of the larger difference in the ionic radii of La^{3+} and Mg^{2+} with respect to La^{3+} and Ca^{2+}, in the former compound there is an ordered distribution of the cations and a local inversion symmetry for La^{3+} sites. On the contrary, because of the cationic disorder observed in $Ca_2La_3Sb_3O_{14}$, a break of the local inversion symmetry of La^{3+} is observed. This very peculiar structural behavior has a big impact on the Eu^{3+} luminescence spectroscopy of the doped materials $Mg_2La_3Sb_3O14$:1%Eu^{3+} and $Ca_2La_3Sb_3O_{14}$:1%Eu^{3+}. Moreover, first-principles calculations were implemented in order to confirm the structural evidence stemming from XRD, acquire the electronic properties of two studied hosts, such as their bandgaps, and elucidate the structure-spectroscopy relationships of these Eu^{3+}-doped materials.

SPECTRAL SIGNATURES OF RANDOM LATTICE DEFORMATIONS IN RARE-EARTH-DOPED CRYSTALS

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This talk summarizes the studies on a spectroscopic detection of random lattice deformations in crystals doped with rare-earth (RE) ions, which were carried out in the Institute of Spectroscopy during the last seven years, in collaboration with a theoretical group of Prof. B.Z. Malkin in Kazan' Federal University and with several crystal-growth groups.

In real crystals, defects are always present causing a local perturbation of the crystal lattice structure and inducing long-range strain fields. Very often, point defects dominate; they generate fields that decrease as $\sim r^{-3}$ with the distance r from the defect. Random strains substantially modify magnetic, dielectric, elastic, and optical properties of crystals. In particular, random strains can affect incoherence processes in systems used in quantum informatics. In optical spectroscopy of crystals, a well-known effect originating from crystal-lattice defects is inhomogeneous broadening. Within the *isotropic* continuum approximation and for a low concentration of point defects inhomogeneously broadened spectral lines corresponding to the transitions between *nondegenerate* states of localized electrons in crystals, as well as the distribution function of random strains have a Lorentzian shape [1].

We have shown that in the case of optical transitions that involve orbitally *degenerate* electronic states of rare-earth impurity ions random lattice deformations result in very specific inhomogeneous line shapes with a sharp dip at the line center [2-4]. This line shape has been explained and satisfactory modeled on the basis of the generalized distribution function of strains produced by point defects in the *isotropic* elastic continuum, derived in Ref. [3]. The widths of the strain distribution for various host – rare-earth impurity pairs were extracted from this modeling representing a characteristic of the crystal's quality.

Quite recently, a theory was developed that took into account an elastic anisotropy of real crystals. A generalized distribution function of all six independent components of the strain tensor induced by point defects in an elastically *anisotropic* continuum was constructed [5]. Multidimensional distribution functions were obtained for cubic and tetragonal crystals. The developed approach was applied to estimate defect strengths of impurity Tm^{3+} ions in essentially anisotropic ABO4 (A = Y, Lu; B = P, V) crystals with zircon structure, on the basis of modeling the observed specific fine structure in the high-resolution optical spectra.

This work was supported by the Russian Academy of Sciences under the Research Program "Topical problems of photonics".

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INFLUENCE OF Al $^{3+}$ and P^{5+} ION CONTENTS ON BOTH THE VALENCE STATE AND THE DISPERSION EFFECT ON Yb^{3+} LASER IONS IN SILICA GLASS

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In recent years, Yb^{3+}-doped silica fiber lasers have become a hot research area [1–6] because of the demand of high-power fiber lasers for Inertial Confinement Fusion (ICF) [7] and laser processing. High-power fiber sources that maintain a good output beam quality are often realized by using a Yb^{3+}-doped silica large-mode-area photonic crystal fiber (LMA PCF) (i.e., large core and low NA) to reduce optical intensity in the core while guiding single-mode or only a small number of mode at certain designed PCF structures [8−9]. Therefore, Yb^{3+}-doped LMA PCF can be applied to high-power single-mode laser devices. Generally, high Yb^{3+} doping concentration is necessary to reach sufficient pump absorption even in a cladding pumped configuration. This reduces the fiber length and increases the threshold for undesirable nonlinear effects in the fiber [8]. In this regard, co-doping with Al^{3+} or P^{5+} ions in silica glass is the most effective way to increase Yb^{3+} solubility in silica glass and avoid clustering due to their good dispersion effect on Yb^{3+} ions [10−13].

In this work [14], three series of Yb^{3+}-doped silica glasses containing different amounts of Al_2O_3 and P_2O_5 were prepared successfully by using sol-gel method. It is found out that the addition of Al^{3+} or P^{5+} ions has a great influence on the redox state of ytterbium ions. Absorption, excitation and fluorescence spectra of Yb^{2+} and Yb^{3+} ions in these glasses were measured and analysed systematically. With increasing Al^{3+} ions content, more trivalent Yb^{3+} ions are reduced to divalent Yb^{2+}. On the contrary, the increase of P^{5+} ions content greatly promotes divalent Yb^{2+} ions to be oxidized into trivalent Yb^{3+}. The possible redox mechanisms have been explored and discussed in detail. Both the near-infrared luminescence intensity of Yb^{3+} ions and the cooperative luminescence of Yb^{3+} pairs decrease gradually with increasing Al^{3+} and P^{5+} ions contents. The decrease of cooperative luminescence of Yb^{3+} ions pairs indicates good dispersion effect of Yb^{3+} ions by Al^{3+} and P^{5+} ions and we have observed that P^{5+} ions have a better dispersion effect on Yb^{3+} ions than Al^{3+} ions.

The results are helpful to solve some important problems in Yb^{3+}-doped silica fiber laser such as high background optical loss and photodarkening which were partly due to the existence of Yb^{2+} ions and Yb^{3+} ions pairs in Yb^{3+}-doped silica glass.

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MICROREFRACTOMETRY BY FLUORESCENCE NANOSCOPY WITH SINGLE PROBE EMITTERS

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The refractive index n is one of the most important materials parameters of solids and has, in recent years, become the subject of significant interdisciplinary interest, especially in nanostructures and meta-materials. It is, in principle, a macroscopic quantity, so its meaning on a length scale of a few nanometers, i.e., well below the wavelength of light, is not clear a priori and is related to methods of its measurement on this length scale. Here we introduce a novel experimental approach for mapping the effective local value $\tilde{n}$ of the refractive index in solid films and the analysis of related local-field enhancement effects.

The approach is based on the detection and spectroscopy of single chromophore molecules at cryogenic temperatures. Since the fluorescence lifetime T1 of dye molecules in a transparent matrix depends on the refractive index due to the local density of the electromagnetic field (i.e., of the photon states), one can obtain the local $\tilde{n}$ values in the surroundings of individual chromophores simply by measuring their T1 times. Spatial mapping of the local $\tilde{n}$ values is accomplished by localizing the corresponding chromophores with nanometer accuracy. We demonstrate this approach for a polycrystalline n-hexadecane film doped with terrylene. Unexpectedly large fluctuations of local-field effects and, hence, effective $\tilde{n}$ values (the latter varying between 1.1 and 1.9 over distances which can be as short as 100 nm) were observed and mapped.

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WHITE LIGHT GENERATION VIA ENERGY TRANSFER MECHANISM AMONG MULTIPLE INORGANIC DOPANTS IN ZINC BORATE GLASSES

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Energy transfer mechanism among multiple dopants in a host material has been intensively studied for efficient, robust, and durable white light generations, where the energy transfer mechanism has not been clearly understood yet. Because selection rules in a triplet exciton material prohibit direct transition to the ground state, energy transfer among dopants harvests the triplet excitons and yields efficient light emissions useful for OLEDs. Here, we investigate inorganic dopants in zinc borate (ZnB) glasses, where the inorganic dopants are rare-earth ions of Tm^{3+}, Tb^{3+}, and Eu^{3+}. We have experimentally observed efficient and tunable luminescence in blue green and red regions when the sample is excited by UV light. This combined luminescence in three color regions is due to energy transfer among three dopants and applicable to white LEDs in the field of solid state lightening as well as tunable solid state lasers.

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OMCVD GOLD NANOPARTICLES FOR SENSING: A WAVEGUIDE TRANSMISSION SENSOR AND AN ENSEMBLE LINEWIDTH NARROWING EFFECT

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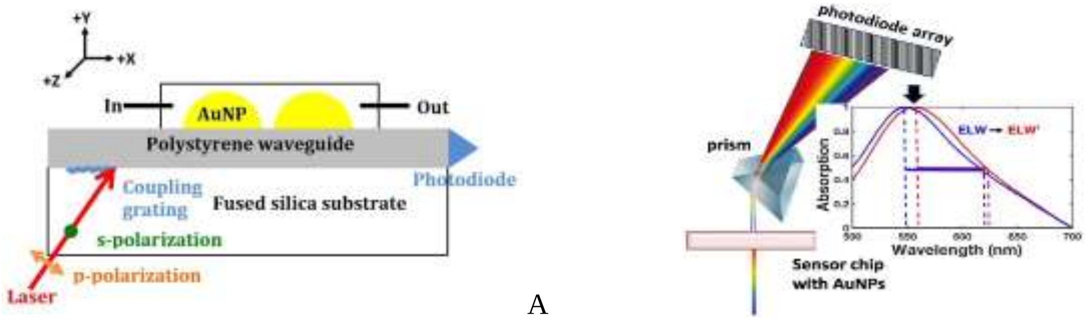
Gold nanoparticles (AuNPs) are successfully used for biosensing. Typically, the absorption feature, the localized surface plasmon resonance (LSPR), and its spectral shift upon binding of an analyte is implemented. Here we show a new approach where AuNPs are grown via an OMCVD process onto a polystyrene slab waveguide leading to covalently attached NPs. The sensing signal is deducted from the waveguide transmission intensity. The operation wavelength of the device and the spectral position of the LSPR need to be carefully chosen. A waveguide-mode dependent figure of merit was found, highest for the TM1 mode with 7.744 RIU^{-1} and a limit of detection for streptavidin binding to a biotin functionalization in the order of 10^{-14} M.

We have discovered an ensemble linewidth narrowing (ELWN) effect with the very small OMCVD AuNPs when immersed in a solvent with higher refractive index and when functionalizing the NPs. This narrowing/broadening effect is reversible with refractive index changes. A simple theory was developed from which a linear relationship between LSPR peak position shift and the ELWN is found. A novel AuNP sensor platform is proposed.



A B

Figure 1 A) Schematic of the waveguide sensor. A substrate (white) carrying a coupling grating (blue) supports a polystyrene waveguide (grey) with AuNPs (yellow) covalently bound on top. A flow cell is fixed to cover a circular sensing area where AuNPs are deposited. Mode-selective coupling is conducted outside the flow cell to ensure constant coupling conditions. The intensity of a transmitted waveguide mode is detected by a photodiode (blue triangle) at its end-face. B) Proposed sensing platform without moving components based on the ensemble narrowing effect. A white light beam is incident on the sample carrying the AuNP. The transmitted light is dispersed by a prism and collected by a diode array delivering both ELW and spectral peak position.

COMPOSITE MATERIAL OPTICAL FIBRES – FUNCTIONALISATION WITH METALS, ELECTRODES, SEMICONDUCTORS AND 2D MATERIALS

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Over the past decade a new field of semiconductor-based optical fibre has emerged. Using high pressure chemical deposition technology developed by our groups at Penn State and ORC Southampton, semiconductors have been grown inside hollow silica glass fibres, allowing the properties of these materials to be exploited for applications such as all-fibre optoelectronics. The high-pressure technique is simple, low cost, and flexible so that it can be modified and extended to fill the large number of micro- and nanoscale pores in microstructured optical fibres, including the latest generation of Hollow-core Antiresonant (ARF) fibre to create a novel class of Composite Material ARF (CM-ARF) waveguide, thus providing flexibility to enhance the potential application base of these devices. Recent work has seen the integration of bulk semiconductors such silicon and even more recently, 2D TMD materials such as MoS_2 inside CM-ARFs. I will discuss the optical fibres we have fabricated to date and the prospects for using them in the manipulation and generation of light.

In parallel with this effort, more recently we have begun to re-examine the well-established technique of thermal poling of optical fibres, which allows for the creation of an effective second order nonlinearity in centrosymmetric materials, such as glasses, which naturally lack any second order susceptibility. This has led to the discovery of novel experimental poling methods as well as numerical simulations to overcome some of the apparently intrinsic limits shown by the thermal poling technique so far, such as for example the length of the nonlinear devices and the complexity of the geometrical structure of microstructured optical fibre. A new poling method, based on electrostatic induction, has been developed and numerically modelled which allows for poling an optical fibre without any physical contact between the source of the electric potential and the electrode embedded into the fibre. Finally, I will discuss the prospects for merging semiconductor fibre fabrication and thermal poling with the aim of exploiting the high intrinsic nonlinearities of semiconductors to potentially increase the effective second order nonlinearity of an all-fibre nonlinear device.

MULTICONFIGURATIONAL AB INITIO CALCULATIONS ON LUMINESCENCE: TESTING MODELS AND HYPOTHESES

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Multiconfigurational ab initio methods of quantum chemistry are used nowadays to calculate complex manifolds of excited states of luminescent materials [1]. They are not tuned to fit any experiment, which makes them unbiased and suitable to check models and hypotheses of luminescence. Here we report ongoing explorations of several widespread assumptions.

i) Quenching of the greenish-blue emission of Pr^{3+} in $CaTiO_3:Pr^{3+}$ in favor of the red one was attributed to charge transfer states (CTS) that enable non-radiative decay from $^3P_0$ to $^1D_2$ [2]. These CTS were tentatively assumed to be Pr-to-Ti metal-to-metal ones (MMCT). Multiconfigurational ab initio calculations support the CTS hypothesis and indicate the involvement of O-to-Ti ligand-to-metal CT states (LMCT) rather than MMCT [3]. These LMCT states provide direct host-to-dopant energy transfer that selectively populates $^1D_2$ after interband excitation.

ii) A very broad band centered at around 20000 cm^{-1} in the diffuse reflection spectrum of $SrTiO_3:CeAlO_3(0.5\%)$ is considered an archetype of MMCT absorption (Ce-to-Ti) in lanthanide compounds [4]. However, a multiconfigurational ab initio calculation on the embedded $(CeTiO_{15})^{23-}$ cluster could not support this interpretation. Other hypotheses involving perturbed LMCT transitions are being explored at this moment in our lab.

iii) Two hypotheses are used to interpret the anomalous NIR luminescence in $KZnF_3:Mn^{2+}$ at high concentrations: Mn-Mn exchange interactions [5] and a strongly perturbed Mn^{2+} center [6]. We explore both of them with multiconfigurational ab initio calculations on the embedded $(Mn_2F_{11})^{7-}$ cluster.

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BULK CRYSTAL GROWTH OF Ce DOPED Gd$_3$(Ga,Al)$_5$O$_{12}$ SINGLE CRYSTAL FROM THE MELT IN THE COLD CRUCIBLE

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The GAGG:Ce scintillator - Gd$_3$(Ga,Al)$_5$O$_{12}$:Ce, was developed in 2011 [1], become well known to be attractive material for application in many fields such as nuclear science, industry, environmental monitoring, gamma ray astronomy, and medical imaging [2]. The scintillators are known to have high density (6.63 g/cm^3), good light output - between 40.000 and 55.000 ph/MeV - and fine energy resolution, even as good as 3.7% at 661.7 keV, [3].

Recently, it is found that the Mg^{2+} codoping in GAGG:Ce improve the light yield and acceleration of decay time [4]. This effect is starting to be understood [5,6]. In the discussion, fine discussion is carried out using small amount of co-doping, defects, charge valence. However, so far, all the crystals were grown in Ar or N$_2$ atmosphere and this atmosphere generate large amount of oxygen vacancy and Ga vacancy. The atmosphere is selected not for the nature of the GAGG, but for protecting the iridium crucible from oxidation.

In this study, iridium crucible was NOT used and GAGG:Ce were grown in AIR. Cold crucible pulling (CCP) method is used for the single crystal growth. This method is the fusion of skull method and Czochralski method. Higher frequency was used to heat the GAGG melt directly and crystal were pulling from the melt. In the presentation, detail of CCP method will be reported. The luminescence and scintillation properties of GAGG:Ce grown in air will be presented comparing the GAGG:Ce, GAGG:Ce,Mg grown in Ar or N$_2$ atmosphere.

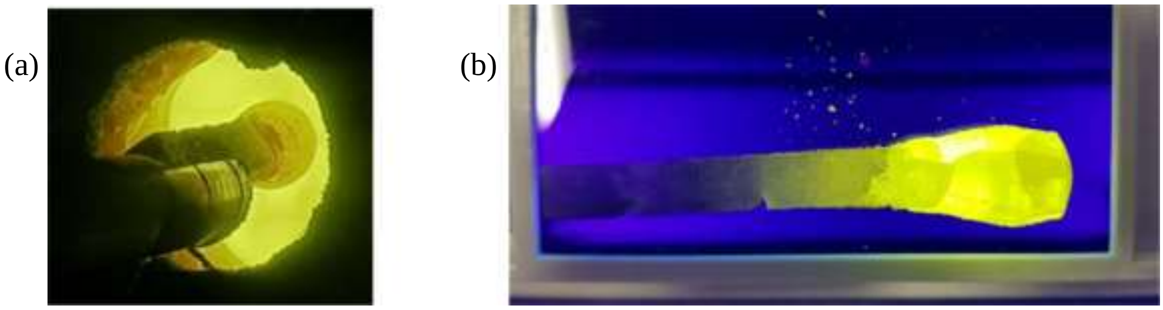

Figure 1 (a) Photo of crystal growth with CCP method. (b) GAGG:Ce grown from the CCP method. Yellow emission is observed by UV exitation.

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THE PHASE DIFFERENCE OF SPONTANEOUS AND STIMULATED EMISSION BY ATOMS INTO AN ELECTROMAGNETIC FIELD

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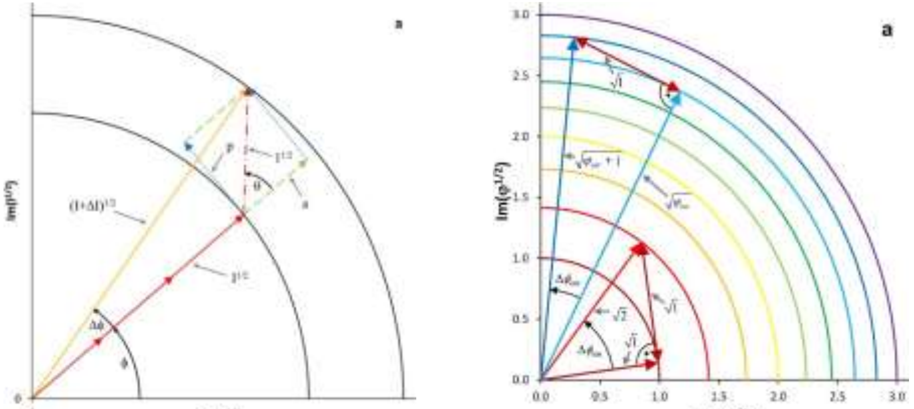
At the fundamental end of the physics of optical materials and devices lies the emission of light by atoms, ions, molecules, or electron-hole pairs. At the application end of our efforts lies the fabrication of sophisticated and efficient light sources, such as lasers. Understanding the fundamental processes of spontaneous and stimulated emission is key to optimizing optical materials and device performance.

In 1917 Einstein exploited a semi-classical rate-equation approach [1] including the rates of stimulated and spontaneous emission and absorption to provide the physical foundation of Planck's law of blackbody radiation, thereby predicting the existence of stimulated emission and quantifying its relation with spontaneous emission. Einstein did not specify the phase difference between the incident and emitted electromagnetic field. It is widely believed that stimulated emission occurs in phase, whereas spontaneous emission occurs under an arbitrary phase difference with respect to an incident electromagnetic field [Fig. 1(a)]. This interpretation has served as a basis for explaining quantum- mechanically [2] the Schawlow-Townes laser linewidth [3], as well as its narrowing and broadening effects. Assuming the validity of Maxwell's equations, both processes would, thus, violate the law of energy conservation [4]. In semi-classical approaches, we investigate stimulated emission in a Fabry-Pérot resonator [5], analyze the Lorentz oscillator model [6], apply the Kramers-Kronig relations to the complex susceptibility, understand the summation of quantized electric fields, and quantitatively interpret emission in the amplitude-phase diagram. In all cases, we derive [4] that the phase of stimulated and spontaneous emission is 90° in lead of the incident field [Fig. 1(b)]. These semi- classical findings question the physical explanation of the laser linewidth and its narrowing or broadening.



(a) (b)

Figure.1. (a) Amplitude-phase diagram visualizing the common interpretation of quantum noise and laser linewidth [2]. (b) Emission, absorption (dark-red arrows pointing toward upper left and lower right, respectively) conserving energy [4].

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ENHANCED ANTI-STOKES' EMISSIONS AT ELEVATED TEMPERATURE FOR ULTRASENSITIVE NANOTHERMOMETRY

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The key to advancing optical nanothermometry is to significantly improve their sensitivity and to cover a large temperature range. The bottleneck exists when increasing the temperature, known as thermal quenching effect. Thermal quenching is commonly caused by the increased activity of phonons that leverages the competing non-radiative relaxation pathways. Here we discovered a kind of heat-favorable phonons existing at the surface of luminescent nanomaterials with the right frequency of vibration energy to combat thermal quenching. We probe such a surface phonon by using a nanoscale energy transfer system, e.g. lanthanide- doped upconversion nanoparticles. We identify that the oxygen moiety of surface ligand, as the source of the surface phonon, generates vibrations to modulate the excited state of sensitizer ions, so that the barrier of energy mismatch to their neighborhood activator ions can be managed through increasing the temperature. As a result, at 453 K we observed the up- converted blue emission enhanced by ~2000 folds for a sub-10 nm Yb^{3+}/Tm^{3+} co-doped β- $NaYF_4$ nanocrystal, under near infrared excitation. This corresponds to an enhancement in upconversion quantum yield by two orders of magnitude for the ultra-small upconversion nanoparticles. This strategy, by activating surface phonons in a thermal field, suggests a new pathway to build photon-plus-phonon energy upconversion systems.

We further extend this principle to enable a heat-favorable phonon assisted anti-Stokes' emissions from $NaYF_4$:Yb^{3+}, Nd^{3+} system, that is, one lower-energy excitation photon at 980 nm can be converted into one higher-energy emission photon at 800 nm. When increasing the temperature, bright emissions with the characteristic spectrum profile of Nd^{3+} were observed, standing in stark contrast to the thermal quenching effect. This allows us to design and synthesize a nanorod structure, by sandwiching $NaYF_4$: Yb^{3+}, Nd^{3+} between the traditional material $NaYF_4$: Yb^{3+}, Er^{3+} using an inert spacer $NaYF_4$. This results in new records in both sensitivity, up to 9.5%/K around room temperature, and dynamic range, up to 413 K where its sensitivity remains above 2.7%/K.

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Pr^{3+} LUMINESCENCE FOR TEMPERATURE READING

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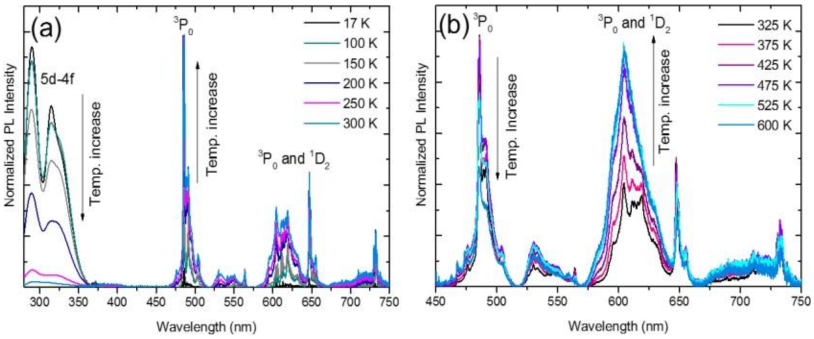
Development of novel and evolving technologies raised the interest in elaboration of non-contact thermometry. Nowadays, pyrometry is the technique of choice for such purposes. Yet, it has important limitations – sensitivity to stray light or reflected radiation and to flame interferences. Its accuracy (<~2 K) is also not always satisfactory. Furthermore, today technologies do not fulfill the needs of temperature sensing in microelectronics, microoptics, photonics, microfluidics, nanomedicine. These require alternative solutions.

Among promising approaches, overcoming the limitations of other techniques, luminescent methods are of rising interest. While the idea is not new [1], a real breakthrough using this technique was not yet achieved. Combining a high sensitivity and accuracy as well as broad range of temperature usability within one temperature sensor appeared challenging [2,3].

In this presentation we shall prove that Pr^{3+} luminescence may offer a lot in this field. We explored the possibility to use all its three luminescent components: 5d→4f, $^3P_0 \rightarrow {}^3H_J$ and $^1D_2 \rightarrow {}^3H_J$ to sense the temperature accurately and in a broad range. Intensity of the three emissions depends differently – a basic requirement to read temperature by means of luminescence technique. Our presentation will show validity and effectiveness of this approach on the example of Sr_2GeO_4:Pr and its chemical modifications. The figure below presents profound changes in emission spectra of Sr_2GeO_4:Pr in the range of 17-600 K [4].



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CHARGE TRANSPORT IN BRANCHED CONDUCTING POLYMERS: QUANTUM GRAPHS BASED APPROACH

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Conducting polymers has attracted much attention recently in the context of organic electronics. Some types of such polymers can have supramolecular (macroscopic) branching. Branched polymers occur when groups of units branch off from the long polymer chain [1-3]. These branches are known as side chains and can also be very long groups of repeating structures. Branching polymers can be further categorized by how they branch off from the main chain. Polymers with many branches are known as dendrimers, and these molecules can form a webbing when cooled. This can make the polymer strong in the ideal temperature range. Such branched polymer chains can be modeled in terms of so-called quantum graphs, which are the set of nanoscale bonds connected at the vertices. The connection rule is called topology of a graph [4,5]. Modeling of wave dynamics in branched conducting polymers require developing of effective methods allowing to take into account transition of the waves from one to another branches via the branching points. One of such approaches is based on the use of metric graphs as the models of the branched polymers. Within such approach, exciton dynamics can be modeled in terms of the Schrodinger equation on metric graphs.

In this work we use solve the problem of exciton dynamics and charge separation (via splitting of exciton into electron and hole) by modeling the whole system in terms of quantum graph. The main problem we studied is splitting of exciton from transmission from one branch to another one. Charge separation probability is explicitly calculated.

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FLUORESCENCE RESPONSE ON OXYGEN FROM TiO_2:Sm^{3+} FILMS DECORATED BY Au/ SiO_2 NANOPARTICLES

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Control of oxygen concentration both in technological processes and in living environment is important for preservation of goods, fire safety, ecology of atmosphere, health care and proper life quality [1]. Traditional electrochemical and chemi-resistive oxygen sensors are based on the electrical effects. At the same time changes in optical, namely fluorescent, response of materials at different oxygen concentrations can be also used for O_2 sensing. This idea attracted both scientific and applied attention during recent decades. Optical fluorescent sensing has such benefits as absence of heated elements, low power consumption, possibility for non-invasive and remote control of optical data.

Contact of emitting centers with oxygen usually causes quenching of their fluorescence [2]. In contrast to this, increase of fluorescence intensity detected for TiO_2:Sm^{3+} films in oxygen-containing atmospheres has certain novelty. Some authors [3] point that oxygen absorbed on lattice defects in the TiO_2 host can block non-radiative energy transfer to them and, by such a way, keep fluorescence from rare earth ions at sufficiently high level. As far as we know, there were no detailed investigations about such type of energy transfer processes.

Here stationary and time-resolved fluorescence spectra from sol-gel derived TiO_2:Sm^{3+} films are examined in the O_2:N_2 atmospheres with different concentrations of O_2. Influence of oxygen on the schemes of energy transfer between titania lattice defects and Sm^{3+} ions is discussed on the basis of obtained results corroborated by X-ray diffraction, transmitted electron microscopy, electron paramagnetic resonance and micro-luminescence data from the samples. Fluorescence decay kinetics for Sm^{3+} are fitted by quite complicated equation, in which Förster -type quenching of Sm^{3+} ions is combined with their delayed excitation by excitons released from shallow traps in TiO_2 host. Such traps can be formed at O^{2-} and Ti^{3+} defects in titania lattice detected by means of electron paramagnetic resonance. It is proposed (see also our articles [4, 5] recently published) that oxygen can work as a switch blocking non-radiative acceptance of energy by these defects and increasing Sm^{3+} fluorescence intensity by such a way. Decoration of TiO_2:Sm^{3+} films by gold-coated nanoparticles increases amount of defects controlling the intensity of Sm^{3+} fluorescence. As a result, sensitivity of films to oxygen can be increased up to 10 times in the samples decorated by gold-coated nanoparticles in comparison with referent TiO_2:Sm^{3+} films.

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DETERMINATION OF TRAPPING PARAMETERS IN Y_2O_3 NANOPARTICLES BY LOW TEMPERATURE THERMOLUMINESCENCE MEASUREMENTS

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Yttrium oxide is a rare earth material becoming focus of interest in many research field due to its physical and chemical properties. The material can be used for LEDs and MOS transistor applications. In this study, luminescence centers in Y_2O_3 nanoparticles were explored using thermoluminescence (TL) measurements in the below room temperature region (10–250 K). TL spectrum obtained at constant heating rate of 0.4 K/s presented overlapped seven peaks around 19, 62, 91, 115, 162, 196 and 215 K. $T_{\max}$–T_{stop} experimental method was used to determine the number of peaks consisting in whole TL curve and characteristics of trapping centers associated with these peaks. Analyses of TL curves obtained at different stopping temperatures resulted in presence of one quasi-continuously distributed trap within the forbidden gap and six discrete single trapping centers. Activation energies of traps responsible for observed peaks were revealed using initial rise method for TL curves obtained with various T_{stop} values. Activation energy of distributed trap centers was found as increasing from 18 to 24 meV as a function of T_{stop} in the range of 10–16 K. Activation energies of six single trap centers were determined as 49, 117, 315, 409, 651 and 740 meV. Heating rate dependence of TL curves was also studied in the various ranges 0.4–0.8 K/s. The increase of heating rate resulted in decrease of TL intensities and increase of peaks maximum temperatures. Furthermore, structural characterizations of Y_2O_3 nanoparticles were accomplished using X-ray diffraction and scanning electron microscopy measurements.

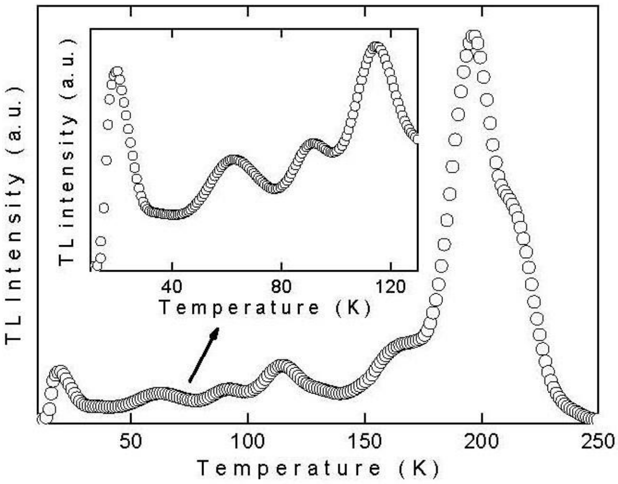

Figure 1. TL glow curve of Y_2O_3 nanoparticles with heating rate of 0.4 K/s.

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CHARACTERIZATION OF TRAP CENTERS IN GALLIUM SESQUISULFIDE CRYSTALS BY LOW TEMPERATURE THERMOLUMINESCENCE MEASUREMENTS

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Thermoluminescence (TL) experiments were performed for Ga_2S_3 crystals to obtain information about trapping parameters. TL measurements were carried out from 10 to 300 K with varying heating rates in the range of 0.2–0.8 K/s. Two TL glow peaks centered at T_{max} = 44 and 91 K were observed at heating rate of β = 0.5 K/s. For low-temperature peak A, TL intensity decreased whereas that for high-temperature peak B increased with elevating the heating rates, which means anomalous heating rate behavior occurred for high-temperature peak. Distribution of trap centers was investigated using T_{max}–T_{stop} method. TL measurements were conducted with varying illumination temperature (T_{stop}) from 10 to 60 K. For both peaks, TL intensity values decrease and T_{max} values shift to higher temperatures with increase of T_{stop}, which means that traps are distributed quasi-continuously. For each TL curve for different T_{stop} values, initial rise method was used to find activation energies of traps. Thermal activation energies increased from 40 to 135 meV by increasing T_{stop} values from 10 to 30 K for A peak and those for B peak increased from 193 to 460 meV by elevating T_{stop} values from 40 to 60 K. The increase of the activation energies with the rising T_{stop} values is consistent with the gradual emptying of shallowest trapping levels during each preheating treatment. Moreover, frequency factors and capture cross sections for revealed traps were evaluated.

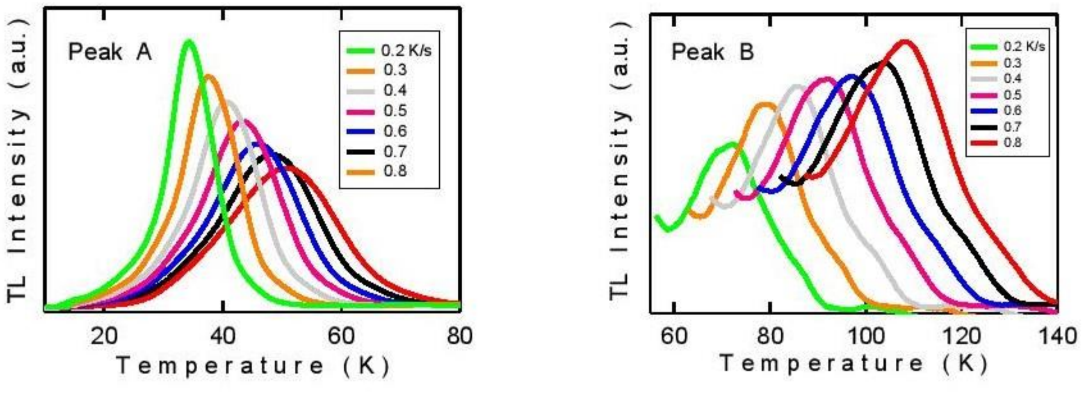

Figure. TL glow curves of Ga_2S_3 crystals with various heating rates.

THIRD ORDER OPTICAL NONLINEAR CHARACTERIZATION OF GRAPHENE QUANTUM DOTS

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We consider commercially available fluorescent blue GQDs in water at a concentration of 1 mg/ml [1]. Quantum dots are composed of few-layer of graphene with a maximal thickness of 100 nm and a diameter lower than 5 nm. Strong quantum confinement of excitons in these quantum dots allows the opening of bandgap in the electronic structures. To confirm this behavior, we first characterize the linear optical properties of these GQDs. Then, we have characterized, the NL response of GQDs suspension in water. We have observed that the Kerr refractive index and the nonlinear absorption are significant only in the UV domain at 355 nm, very close to the linear absorption band. Moreover, we have brought out a clear saturable absorption effect (see Table 1). No NL response is present in the visible at 532 nm and in the infrared at 1064 nm.

Thanks to a simple model, we have estimated the nonlinear refractive index and nonlinear absorption values of a single graphene nanosheet constituting the GQDs, $n_{2nano} = (2.4 \pm 0.6) \times 10^{-15}$ m^2/W and $C_{2nano} = (-5.9 \pm 1.2) \times 10^{-8}$ m/W, respectively. The obtained Kerr index value is in the order of magnitude of bulk materials. More interestingly, it corresponds to a focusing effect and it is three orders of magnitude lower than the values found in the literature for monolayer graphene in the infrared domain.

In contrast with the large and broadband nonlinear response of graphene [2], the three-dimensional confinement of excitons in the quantum dots modifies largely the electronic configuration and therefore the NL optical properties of graphene which behave mostly as semiconducting carbon nanotubes [3]. The NL properties of GQDs are therefore found to be significant only in the region close to the absorption band in the UV.

As the sharp resonances exhibited by the GQDs are directly related to the size of the quantum dots, it is therefore expected that the position of the maximal GQDs NL response can be spectrally shifted, in function of the desired applications. The obtained experimental measurements are summarized in table 1.

Table 1: Average values of the measured NL coefficients. The third column shows the range of incident intensity. α, n_2 and C_2 denote the linear absorption, the NL refractive index and the NL absorption coefficients respectively.

λ (nm)	Material	I_0 (GW/cm^2)	L (mm)	α (m^{-1})	$n_2 \times 10^{-20}$ m^2/W	C_2 (cm/GW)
355	GQDs	2.5 - 26	1	2525	57 ± 12	-1.4 ± 0.4

We expect the present study can foster several others and to be useful for numerous future fundamental interest or potential applications.

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A MODEL FOR 1500- TO 980 nm PHOTON UPCONVERSION IN TRIVALENT ERBIUM

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Photon upconversion, in which two- or more low-energy photons are converted into one of higher energy, is a promising way of optimizing the efficiency of solar cells [1]. Trivalent erbium ions are suitable for photon upconversion due to their absorption band in the near-infrared region below the band gap of typical PV materials, and due to their ladder-like energy spacing which is important for efficient energy conversion [2].

The low absorption cross section of trivalent erbium limits the conversion efficiency. In previous work of our group this limiting factor has been overcome by introducing electron-beam-lithography written plasmonic gold-nanostructures on top of magnetron-sputtered TiO_2: Er thin films to increase the near-field around the erbium ions, and hereby, utilize the non-linear nature of the upconversion process [3].

To increase the efficiency even further the dynamics in the upconversion process should be understood better. In general, a complex interplay of radiative-, non-radiative transitions as-well-as energy transfer and cross relaxation determines the upconversion efficiency. To study the dynamics in the upconversion process we have proposed a simple rate-equation model including the four lowest energy levels of trivalent erbium: $^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$, and $^4I_{9/2}$. Our model can be solved analytically to give a measure of the upconversion luminesce (UCL) yield in terms of rate-equation parameters. This result has been compared to measured UCL yield and decay times of the excited states: $^4I_{13/2}$ and $^4I_{11/2}$ for samples with varying quality where good agreement was found over several orders of magnitude [4].

Moreover, we have studied the saturation of the UCL by accounting for the experimental detection and hereby obtained saturation curve. It is well known that the upconversion scales non-linearly with intensity. In the extreme low excitation regime the UCL scales with the number of photons involved (two in this case) but this behavior will of course saturate as the intensity is increased. From the saturation curve we are able study rate-equation parameters among other the absorption cross section for the $^4I_{15/2} \rightarrow {}^4I_{13/2}$-transition which so far has been in-accessible due to the extreme low value and the thin thickness of the investigated samples.

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WATER COLLOIDS OF Nd^{3+} DOPED FLUORIDE NANOCRYSTALS FOR BIOIMAGING IN THE FIRST BIOLOGICAL WINDOW

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Water colloids of the Nd^{3+}:LaF_3 nanocrystals (NCs) synthesized with PVP as biocompatible surfactant by hydrothermal - microwave treatment (HTMW) have proven themselves as promising fluorescent probes for near IR imaging in the first biological window (750 – 950 nm) [1, 2], because of their high fluorescence brightness and high stability of aqueous colloidal solutions. One of the reasons of high fluorescence brightness is high crystallinity of the Nd^{3+}:LaF_3 nanoparticles (NPs) synthesized by HTMW, i.e. small amount of defects like clusters of Nd^{3+} ions and OH^- groups in their volume comparing to those synthesized by co-precipitation method [3]. Here we discuss another advantage of the Nd^{3+}: LaF_3 NCs, their low fluorescence quenching. To understand this fact we found simple criteria for choice of crystal host for synthesis of NPs for Nd^{3+} doping for fluorescent bioimaging in the first biological window. It is large ratio of intensity parameters $\Omega_4/\Omega_6 \sim 1$ [4] used in Judd-Ofelt theory, which increases fluorescence branching ratio β to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition lying in the first biological window, and low value of intensity parameters $\Omega_6 = 2.50\ 10^{-20}$ cm^2, which makes weaker the Nd-Nd fluorescence self-quenching and quenching by the OH^- molecular groups. We checked this with the concentration series of highly dispersible aqueous colloidal solutions of the Nd^{3+}: LaF_3 and Nd^{3+}: KY_3F_{10} [5] NCs synthesized by HTMW treatment with PVP. In so doing the dependence of relative fluorescence quantum yield (FQY) and fluorescence brightness (FB) on Nd^{3+} concentration connected with nonradiative energy transfer to the quenching acceptors is found from the measured fluorescence kinetics. We observed smooth decrease in FQY and pronounced maximum in FB with increasing neodymium concentration in both systems. However, for Nd^{3+}: KY_3F_{10} NCs the fall of fluorescence brightness begins at a concentration four times lower than for Nd^{3+}: LaF_3, which is due to a stronger energy transfer to the quenching acceptors in the former. At the same time the fluorescence branching ratios to the first and the second biological windows are almost equal for the Nd^{3+}: LaF_3, while for Nd^{3+}: KY_3F_{10} it is higher to the second biological window. The result is in line with twice larger the Ω_4/Ω_6 ratio and three times smaller Ω_6 intensity parameter in Nd^{3+}: LaF_3.

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W-O EMISSION CENTERS IN DIFFERENT PHOSPHORES

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In recent years oxygen containing materials having high light output of an emission in optic region and short time decay have been extensively used as phosphors, laser materials, scintillation detectors in tomography, as a phonon-scintillation cryogenic detectors in dark matter investigation and so on.

The present study aims to investigate the effects of the phosphor matrix structure on the optical characteristics of the emission center containing tungsten oxide in $ZnWO_4$ and $CdWO_4$ crystals, or being a dopant in LiF crystal and MgF_2 ceramics.

All materials except ceramics were grown by the Czochralski method in the Institute for Single Crystals of NAS of Ukraine (Kharkov). MgF_2-WO_3 ceramics microcrystals of (2^x7) μm^2 were obtained by sintering the charge under the action of an electron beam in air.

In the report the results of the investigation of absorption spectra, emission and excitation spectra of the emission, luminescence time decay, light output in all phosphors exposed to 250 MeV electron flux in absorbed doses interval of 0−10^{5}Gy were observed.

- All as-grown materials were not transparent above 4 eV. (The absorption coefficient at region 4−6 eV in LiF-WO_3 and $ZnWO_4$ crystals could reach 100 cm^{-1}).
- Emission spectrum in all phosphors consists of a band with FWHM of 0.6−0.7 eV with position of the maximum in interval of 2.5−2.7 eV and emission time decay equal to 18−20 μs in MgF_2 ceramics and 25−30 μs - in the tungstates of Zn and Cd and LiF crystals at 300 K. The excitation spectra of 2.5−2.7 eV emission in all phosphors has a threshold about 4 eV and a plateau in the interval 4−6 eV.
- Light output (LO) at 300 K in the band at 2.7 eV in as-grown LiF-0.3 wt. % WO_3 is comparable with LO in $ZnWO_4$ and reaches 60% of LO in $CdWO_4$. In the MgF_2-WO_3 ceramics LO is an order of magnitude lower because of the volatility of fluoride compounds of tungsten.
- Unlike $ZnWO_4$, $CdWO_4$ and MgF_2, the LiF-WO_3 phosphor has low radiation resistance. The accumulation of color centers in the lattice leads to a loss of transparency in the region of the emission band and to the reabsorption of the emission by the matrix itself. The latter leads to a drop in LO at 2.7 eV band.

Thus, it was found no effect on the phosphors emission properties: of the following internal and external parameters:

- the value of matrix E_g (6, 13, 12 eV in tungstates, LiF and MgF_2, respectively),
- lattice type (wolframite, alkali halide metal, rutile),
- spectral position of threshold in excitation spectrum of emission,
- method of obtaining a phosphor (sintering or growth in air).

This result may indicate the presence in all investigated phosphors a WO_3 phase with inherent defects and band gap Eg about 4 eV [1], which defines both the transparency boundary of all PP and the position of the threshold in the excitation spectra of the PP emission in region 2.7−2.5 eV.

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PHOTOTRANSISTOR AND PHOTOVOLTAIC EFFECT IN NANOCRYSTALLINE PHOSPHORS UNDER INFRARED LASER EXCITATION

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The subject of this work is a phototransistor based on nanocrystalline ytterbium aluminum garnet (YbAG). The insulating YbAG nanocrystals constitute the optically active material, while the 975 nm 2W laser diode is used as an excitation source. With proper focusing of the beam the power of the light source translates to an optical density of up to 17 W/cm^2. Observation of a strong photocurrent under IR excitation was realized via DC current measurement in range of +/- 150 V of applied voltage.
The measured current exhibited a very strong gain, up to 10^5-fold in the highest optical power regimes. Furthermore, the relationship between the excitation power and photocurrent was found to be non-linear. As such, high control of electrical signal can be achieved and thus a phototransistor based on this phenomenon can be proposed for this class of materials. Nanocrystalline phosphors can be prepared in a mass production process, with costs drastically lower than in the case of conventional semiconductors used in the construction of phototransistors. Furthermore, being insulators, they possess a higher dielectric strength, resulting in a much wider range of voltages available for their operation, creating another potential use for the nanocrystalline-based phototransistors in high-voltage switching. What is more, significant potential lies also in the fact that nanocrystalline insulators can have their properties greatly manipulated by introducing changes in their structure, chemical composition of the dielectric matrix or by doping with rare earth ions. In addition to the laser- driven electrical signal control, a photovoltaic effect was also observed in a modified construction of the device, where one of the electrodes is separated from the optically active material by a vacuum gap. As a conclusion, based on the newly found aspects of optoelectronic phenomena observed in the investigated structures, numerous applications are discussed.

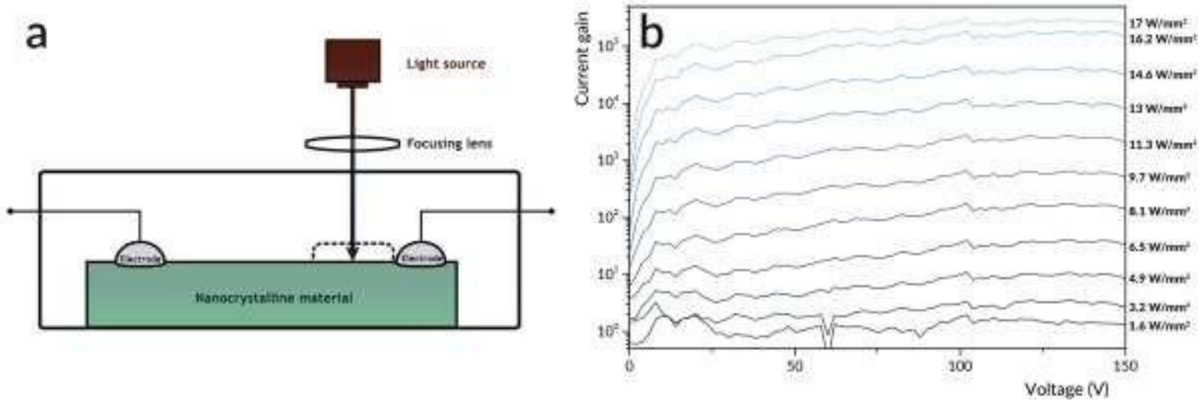

Fig. 1. (a) Operational schematic of an insulating nanocrystal-based phototransistor (b) Current gain of the YbAG phototransistor as a function of voltage in a series of excitation optical density

FLUORESCENCE SPECTROSCOPY OF Cr^{3+} IONS IN LASER MOLECULAR BEAM EPITAXY-GROWN OXIDE FILMS

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Two-dimensional insulating oxide epitaxial nanostructures (layers and superlattices) produced by laser molecular beam epitaxy (LMBE) technique can be promising candidates for realizing beyond state of the art molecular electronic, electro-optic and pure optical sensors and devices.

MgO and $MgAl_2O_4$ films and superlattices doped with Cr^{3+} ions were grown with the use of LMBE system based on KrF excimer laser. Surface morphology of the samples was studied using atomic force microscopy (AFM). Crystalline structure of the layers was studied by reflection high-energy electron diffraction (RHEED) technique.

The crystalline $MgO:Cr^{3+}$ hosts a few types of Cr^{3+} centers (multisites) with different symmetry and thus provides a selection of fluorescent centers for probing the structure of the surrounding matrix. The zero-phonon magnetic dipole R-line (^2E - $^4A_2$) of cubic Cr^{3+} centers lacking local charge compensation and electric dipole N-lines of locally compensated tetragonal Cr^{3+} centers are most attractive for this kind of studies. The ^2E - $^4A_2$ fluorescence spectra of probe Cr^{3+} ions in MgO nanolayers of different thickness deposited on Al_2O_3 and GaN substrates were studied. The spectra revealed the strong inhomogeneous broadening that prevents observation of spectral shifts and splittings due to lattice distortions. The measurements of the ^2E state radiative lifetimes, which are sensitive to energy interval Δ between the ^2E and $^4T_2$ states, provided an indication of lattice distortions and may be used for diagnostics of the epitaxial oxide films.

The fluorescence spectra of Cr^{3+} ions in $MgAl_2O_4$ spinel films and superlattices containing $MgAl_2O_4$ layers were measured. These spectra are dominated by the $^4T_2$ - $^4A_2$ fluorescence of Cr^{3+} in low-field sites. The fluorescence spectroscopy and radiative lifetime measurements revealed the role of interfaces in Cr^{3+} fluorescence.

REACTIVE AGENTS USAGE IN SYNTHESIS OF THE $SrSi_2O_2N_2$:Eu^{2+} PHOSPHOR POWDERS AS A STRUCTURAL AND OPTICAL CHARACTERISTICS CONTROL FACTOR

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$Sr_{0,96}Eu_{0,04}Si_2O_2N_2$ phosphor has been obtained via solid state reaction method in nitrogen flow. Various concentrations of carbonate or fluoride reactive agents have been added to initial powders in order to impact the crystallization of the oxynitride phase. The XRD analysis revealed the presence of a triclinic $Sr_{1.02}Si_2O_2N_2$ phase. For some reactive agents concentration, additional phases could be observed as well. The SEM and particle size distribution analysis indicate that reactive agents affected powders morphology. The resultant powders were characterized by light-green to brownish emission under UV excitation. Significant differences in excitation and emission range, quantum efficiency (QE) and luminous efficacy were identified. Thermal quenching measurements in 280 – 500 K and thermoluminescence analysis in 280 – 700 K range were performed also.

The conducted studies proved that optimization of a proper reactive agent concentration results in getting bright, green phosphor with broad excitation range, characterized by 86% of QE and an excellent thermal stability (15 % emission intensity decrease by 500 K).

OPTICAL SPECTROSCOPY OF Yb^{3+} CENTERS IN YAM

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Over the past several years there has been an ongoing research for Yb^{3+} activated materials for lasers, phosphors and quantum memories. Oxide crystals from the Y_2O_3-Al_2O_3 binary system are one of the most studied groups of optical materials, owing to their good optical, mechanical and chemical properties. The monoclinic $Y_4Al_2O_9$ (YAM) phase is the least studied one and only limited information is available on the spectroscopic properties of this system so far. YAM is more complicated than YAG and YAP crystals due to the existence of four distinct Y^{3+} sites which could be substituted by active ions [1-4]. YAM samples with Yb^{3+} activator concentrations of 0.1, 1, 5 and 10 at.%, used in this study were grown by micro-pulling down (μ-PD) method in the Institute of Electronic Materials Technology (ITME) in Warsaw. The main aim of this work is to characterise the new Yb^{3+} system and to extend our general knowledge on site occupancy. In Fig.1 transmission spectrum corresponding to the intra-configurational $^2F_{7/2}(0) \rightarrow {}^2F_{5/2}(0')$ transition of Yb^{3+} ions in YAM is presented. It could be seen that the spectrum exhibits existence of five different Yb^{3+} related centers, four major ones associated with Yb^{3+} in regular positions substituting yttrium and one other additional center.

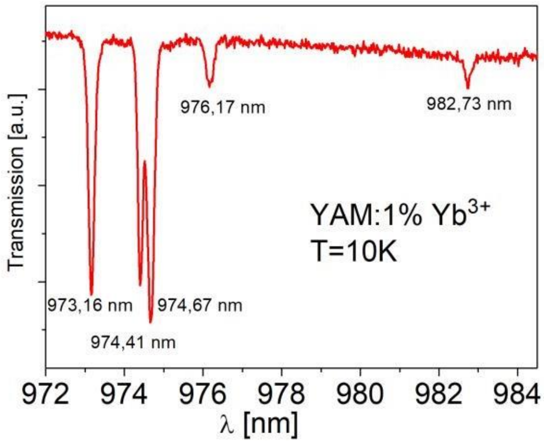

Fig.1 Transmission spectrum of 1% Yb^{3+}:YAM for the $^2F_{7/2}(0)$ to $^2F_{5/2}(0')$ transition at 10 K.

In the work reported here, new results on the number of ion sites, site preferences for Yb^{3+} ions, their relaxation dynamics and energy transfer in YAM are presented and discussed in a function of temperature and activator concentration.

Acknowledgment
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$Gd_3Li_3Te_2O_{12}$:U^{6+},Eu^{3+}: A RED EMITTING GARNET SHOWING AN U^{6+} TO Eu^{3+} ENERGY TRANSFER AT ROOM TEMPERATURE

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Warm-white LEDs comprising Eu^{2+} activated nitrides such as $(Sr,Ca)AlSiN_3$:Eu^{2+} or $Sr[LiAl_3N_4]$:Eu^{2+} as a red emitting component have some drawbacks like low luminous efficacy (LE) and demanding syntheses conditions. Due to the broad band emission, a significant part of the emission is located in the deep red or even in the NIR region and thus lowers the overall efficacy of the w-LED.[1] Mn^{4+} activated red phosphors show line emission with high LE, but require hydrofluoric acid in the syntheses process and often exhibit a reduced stability against humidity and high photon fluxes. Instead, Eu^{3+} activated phosphors have typically a very high LE, but the absorption in the blue spectral range is by far to low.[2] Thus, sensitizers such as Tb^{3+} and Bi^{3+} are required to enhance the absorption cross section in near UV to blue spectral range. As Blasse *et. al* demonstrated a long time ago, hexavelent uranium can be applied as well in order to sensitize the Eu^{3+} ion.[3] To this end, the luminescence and energy transfer properties of the garnet compound $(Y,Gd)_3Li_3Te_2O_{12}$ doped with U^{6+} or Eu^{3+} were investigated. To the best of our knowledge, the energy transfer behaviour of U^{6+} to Eu^{3+} was not investigated in this material so far. Although the energy transfer of U^{6+} to Eu^{3+} at low temperatures is well known in several other compounds.[4,5]

A solid solution of $Gd_3Li_3Te_2O_{12}$ was prepared with different doping concentrations of U^{6+} and Eu^{3+}. Phase formation and particle morphology were investigated by powder diffraction and scanning electron microscopy. Optical measurements at temperatures ranging from 3 to 500 K were conducted to entangle the energy transfer behavior. Diffuse reflectance and quantum yields measurements were used to further investigate the optical properties of the red emitting phosphor. Figure 1 depicts the emission and excitation spectra of $Gd_3Li_3Te_2O_{12}$:U^{6+},Eu^{3+}. The uranate emission coincides among others with the Eu^{3+} excitation transitions $^7F_{0,1} \rightarrow {}^5D_1$. We could demonstrate that this compound class exhibtis efficient energy transfer from U^{6+} to Eu^{3+} even at room temperature. Due to co-doping with U^{6+} the photoluminescence intensity of Eu^{3+} could be enhanced drastically. However, the $O^{2-} \rightarrow U^{6+}$ charge transfer band is peaking at 340 nm and therefore not suitable for the conversion of blue light. Though, the insight given by our research can be used for further investigations of red emitting phosphors using U^{6+} as a sensititzer for Eu^{3+}.

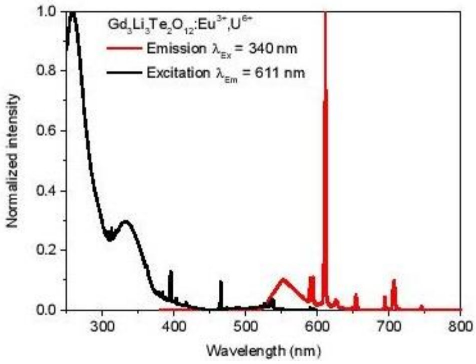

Figure 1: Emission and excitation spectra of $Gd_3Li_3Te_2O_{12}$:U^{6+},Eu^{3+}.

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LASER-INDUCED BREAKDOWN SPECTROSCOPY AS AN EFFECTIVE APPROACH FOR DISTINGUISHING OF DIAMONDS

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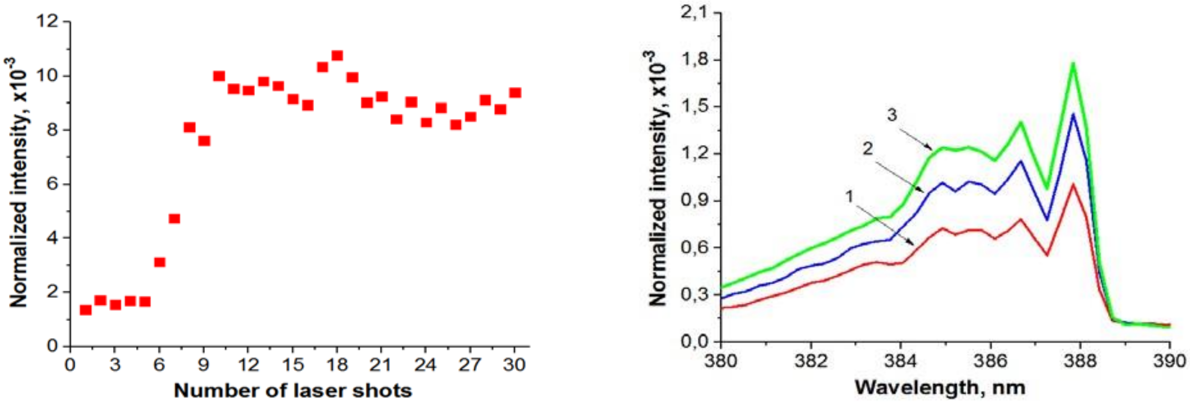
At present, large high-quality single crystal synthetic diamonds for photonics can be grown by HPHT-method. LIBS is a suitable express spectral technique for multi-elemental analysis. Single- and multi-sectoral plates of the yellow synthetic single-crystal diamonds with dimensions 5x5 mm^2 were studied. A Q-switched Nd^{3+}:YAG laser with a repetition rate of the frequency 2 Hz, the pulse duration 17 ns and the pulse energy 230 mJ was used. The plasma spectra of diamonds were recorded in argon atmosphere by the AvaSpec-ULS2048L-USB2 spectrometer using our own software [1]. The Raman spectra of the initial and irradiated diamond plates were measured using a micro-Raman system (InVia, Renishaw).



a) b)

Fig. 1. a) Normalized intensity of C_2 emission band vs number of laser shot; b) Normalized intensities of CN emission band averaged for: 1 - 1-5th shots, 2 – 6-10th, 3 – 14-30th.

The rapid graphitization of the sample surfaces and the steady-state plasma emission were observed after 10-12 laser shots (Fig. 1a). The Raman spectrum of graphitized surface consisted of the wide diamond D-band (1332 cm^{-1}) and G-band (1600 cm^{-1}) which characterizes sp^2 hybridized carbon atoms. The sharp increase in the number of C=C double bonds led to increase of the C_2 Swan bands emission intensity up to five times. A weaker rise of the CN emission intensity also was observed (Fig. 1b). Changes of intensities of C_2 and CN emission bands are related to changes in bonding structure of the atoms [2] and have been observed for the different samples and the different sectors of each diamond plate. The changes in the intensity of the plasma emission have been increased significantly by the surface graphitization of diamonds.

As a result, the laser-induced graphitization is a suitable process, which leads to an increase in the LIBS technique sensitivity for the recognition of diamonds. This sensitivity varies with other impurities due to selective evaporation in laser ablation.

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TERBIUM COMPLEX DECORATED SILICA PARTICLES AS LUMINESCENT BIOMARKER FOR CELL IMAGING

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The breakthrough in the study of functional silica particles (SiO_2) was achieved by controlling size, shape, insertion/adsorption, and adjustable surface properties that have greatly expanded their application potential in medical fields[1]. SiO_2 holding lanthanide complexes form a hybrid material that exhibits luminescence under appropriate excitation and therefore can be exploited as a biomarker for cell imaging purposes[2], for labeling and probing cells. In the present work, we developed a luminescent biomarker composed of silica particles decorated with terbium complexes (Fig. 1a) and investigated its use in imaging tests of living CHO-k1 cells. Firstly, spheroidal aminofunctionalized particles (~220 nm) were prepared via the sol- gel method, then a Schiff base was formed on these particles surface to serve as an anchoring site for the Tb^{3+} ions. Benzoic acid (benzac) was then used to complete the coordination sphere of Tb^{3+}. The obtained biomarker is non-toxic, and showed green luminescence (Fig.1b). It was also characterized by scanning electron microscopy (SEM), ^{29}Si-NMR, and zeta potential. Internalization of the particles by the cells was verified by transmission electron microscopy (TEM), Fig. 1c, from where we could see particles in the cytosol and in the perinuclear membrane; no further functionalization with any specific biomolecule was needed to allow the internalization. Confocal microscopy images, Fig. 2a-c, reveal that the particles are in higher concentration around the nucleus. This result demonstrates the success of the produced biomarker for cell imaging with specificity to delineate the nucleus.

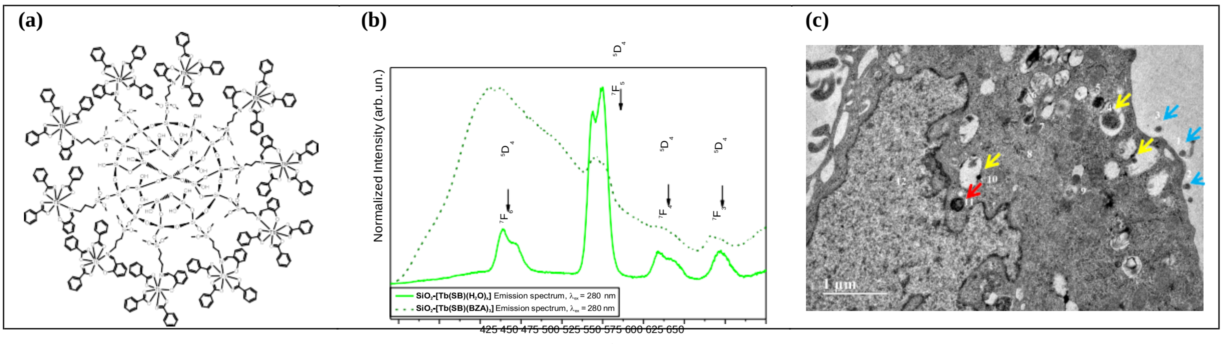

Fig.1 – (a) Scheme of the decorated biomarker (not in scale). (b) Biomarker emission spectra before and after the benzoic acid addition. (c) TEM images of a CHO-k1 cell exposed to the biomarker. Yellow arrows: particles inside endosomal vesicles distributed in the cytoplasm; red arrow: particles around the nucleus; and blue arrows: extracellular medium.

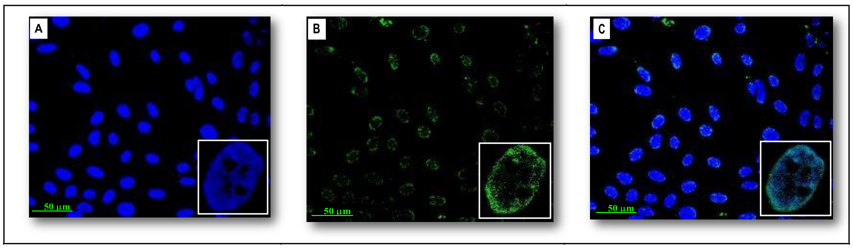

Fig.2 - Confocal Microscopy images of CHO-k1 cells exposed to the biomarker. (a) Excitation with DAPI channel; (b) Green channel indicating the Tb^{3+} emission; (c) superposition of both.

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STUDY OF THE ORIGIN OF THE DEFECTS IN $La_3Ga_{5,5}Ta_{0,5}O_{14}$ SINGLE CRYSTALS

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Lanthanum - gallium tantalate ($La_3Ga_{5,5}Ta_{0,5}O_{14}$, LGT) crystals were first grown in the 1980 for application in laser physics. However, the insufficient crystal quality and rather small boule size at that time prevented LGT application in this field. In the past decade the optical quality of LGT crystals was significantly improved. This makes them an attractive alternative as nonlinear crystals for tunable lasers, as rare-earth-doped phosphors, upconversion materials, laser media, and scintillating crystals [1-3]. The main problem that still limits application of these crystals is undetermined origin of the defects.

We performed a comprehensive study of the properties of LGT crystals grown in different atmospheres before and after the post growth treatments (annealings in air and vacuum) using different methods in order to clarify origin of defects.

All investigated samples were cut from boules grown in JSC "Fomos-Materials" using Czochralski method in Ir crucibles, growth atmosphere – Ar and Ar + (2%) O_2.

The optical properties and elemental composition of the crystals have been shown to depend on the growth atmosphere and the atmosphere of annealing The absorption spectra of the colored crystals contain two strong bands in the UV spectral region (~290 and ~370 nm), one band in the visible range (~480 nm), and two bands in the IR spectral region (1750–1950 and ~2920 nm). The spectra of the colorless crystals show a weak band at ~290 nm. The data obtained by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy indicate that there is a difference in the ratio of the main elements in dependence on the growth atmosphere and that the composition of the samples varies from their surface to their bulk. The binding energies evaluated from XPS data are in the range of reference data reported for the constituent oxides and correspond to the chemical state of La^{3+}, Ga^{3+}, and Ta^{5+} ions coordinated by oxygen. Diffuse X-ray scattering results indicate that the crystals contain two types of defects: planar shape interstitial defects and nearly spherical shape vacancy-type defects [4].The defect structure has been also studied using luminescence spectroscopy, that allowed to obtain deeper insight to their origin.

On the base of the results of our study we propose self-consistent model of the defect origin in LGT crystals. The main defects are Schottky type defects. With add of oxygen in the atmosphere, F-centers are formed. During annealing in air, the concentration of the F-centers increases, and annealing in a vacuum leads to the destruction of F-centers. The defect origin data will allow to affect their concentration to reduce it to an acceptable level and may return LGT to the laser materials family.

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EXPLORATION OF RARE EARTH ELEMENTS AND ABSORPTION-EMISSION FEATURES IN RARE EARTH (La-Lu) ORTHOPHOSPHATES

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Mining of rare earth elements (REEs) followed by application of mined REEs to wide range of application, has been of immense interest for both, geologists and phosphor engineers. In the present contribution, we will focus on *a*) exploring laser-induced fluorescence (LIF) for REE exploration in our project “inSPECtor”; and *b*) combining absorption-emission characteristics to understand *f-f* and *f-d* transitions in rare earth orthophosphates (La-Lu)PO_4.

Orthophosphate deposits in nature are important for technological and environmental challenges faced by high-tech industry. It has been shown recently that the phosphorites can be considered as the primary source of REEs to solve the global rare earth supply shortage [1]. The existing technologies in rare earth exploration are based on diffuse-reflectance measurements (for example, Hyperspectral Imaging). However, the spectral features of REEs are due to sharp 4*f*-4*f* *intraconfigurational* transitions, which are sufficiently distinct to enable spectral classification. LIF is an important technique which records REE features in spectral as well as the time domain. Recently, we started a project “inSPECtor” to develop a single sensor system, which combines hyperspectral imaging (or diffuse reflectance spectra) with laser induced fluorescence (for spectral and time resolution from ns to ms).

From an application point of view, the Rare earth orthophosphates ($REPO_4$) are important compounds for application in light emitting diodes (LEDs), plasma display panels (PDPs) and fluorescent lamps [2]. The lower atomic number lanthanides (La-Gd) based orthophosphates crystallise with monoclinic structure (P_21/n space group) at moderately high temperatures; while the higher atomic number lanthanides based orthophosphates possess tetragonal xenotime-type structure (I_41/amd space group). The luminescence properties in a lattice of orthophosphates are expected to be controlled by the type of REEs and their coordination around PO_4^{3-} tetrahedra. However, PO_4^{3-} (which forms host valence and conduction band), is transparent itself in visible-UV region and does not absorb, up to approximately 175 nm [3]. Hence, the type of rare earth ion, which increases in ionic radii by approximately 22% from La-Lu, control the electronic structure and optical properties therein. Some of the $REPO_4$, for example-$LaPO_4$, $GdPO_4$, YPO_4 and $LuPO_4$; have been explored recently for their charge carrier trapping and relevant applications in storage devices [4]. However, information for other $REPO_4$ is limited and no clear information, relevant to their absorption-emission features, charge storage/release could be found. We present results on our extensive investigation in both these directions; the new sensor and fundamental properties.

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OPTICAL PROPERTIES OF Tb^{3+}-BASED CRYSTALS FOR VISIBLE LASER APPLICATIONS

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The development of commercially available blue semiconductor pump sources in recent years has attracted research interest of utilizing the well-known visible emissions of lanthanide ions to generate visible lasers. C. Kränkel and coworkers demonstrated laser operations on the green and yellow emissions in Tb^{3+}-doped fluoride crystals in 2016 [1]. Nevertheless, visible laser performance using Tb^{3+}-doped oxide crystals as gain medium has not been reported to date, whereas oxides are much easier to fabricate than fluorides. Investigations of Tb^{3+}-based oxide crystals regarding their optical properties are necessary to achieve this goal.

A preliminary investigation into the oxide materials of $Ba_3Tb(PO_4)_3$, $Sr_3Tb(BO_3)_3$, $TbAl_3(BO_3)_3$, $Li_6Tb(BO_3)_3$, and $TbCa_4O(BO_3)_3$ shows that they feature relatively small crystal field depression values, which can reduce the possibility of detrimental excited-state absorption during the laser operation. Their bulk single crystals were grown by Czochralski or TSSG method. The optical properties of electron paramagnetic resonance, refractive index, absorption and emission spectra, and fluorescence dynamics were characterized. The absence of electron paramagnetic resonance signals in the as-grown or post-treated crystals at room temperature indicates that they are free from unwanted Tb^{4+}. Ground-state absorption spectroscopic measurements reveal that $TbAl_3(BO_3)_3$ yields the highest cross-section of 1.0×10^{-21} cm^2 of the $^7F_6\rightarrow{}^5D_4$ transition which is suitable for pumping. This value is larger than that of Tb:$LiLuF_4$ which gives the best laser performance. The measured energetic position of the energetically lowest $4f^8\rightarrow4f^75d^1$ transitions are in good agreement with the expected values. The emission cross-sections of the green $^5D_4\rightarrow{}^7F_5$ transition range from ca. 5×10^{-22} to 1×10^{-21} cm^2. The broaden emission bands in $Ba_3Tb(PO_4)_3$ and $Sr_3Tb(BO_3)_3$ provide the output wavelength tunability [2]. Fluorescence lifetimes of the $^5D_4$ excited state were measured to be typically around 3 ms. Such long lifetimes, in spite of the large concentrations of Tb^{3+} in these matrices, are favorable to store pump energy for the purpose of Q-switched laser operation. Judd-Ofelt analysis was performed based on the experimental data. The calculated oscillator strengths are overall in good agreement with the experimental values and the resulting radiative lifetimes are closed to the measured fluorescence lifetimes. This indicates that the $^5D_4$ state is free from detrimental non-radiative processes or multiphonon relaxation in these crystals.

In conclusion, the studied Tb^{3+}-based oxide crystals show comparable spectroscopic properties to the fluorides in terms of the optical transitions in the visible. Light amplification as well as laser measurements are in progress and the results will be presented in the conference.

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THERMAL QUENCHING OF Mn^{4+} LUMINESCENCE IN Sn^{4+}-CONTAINING GARNET HOSTS

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Mn^{4+} doped compounds are considered as suitable red phosphors for obtaining warm white phosphor converted (pc) LEDs. For practical applications, especially in high-power pc-LEDs, the high thermal stability of Mn^{4+} luminescence is an extremely important property. Thermal quenching temperature of Mn^{4+} luminescence varies in a very wide range for Mn^{4+} phosphors with different host compositions [1, 2] but the origin of such different temperature behavior of Mn^{4+} luminescence in different hosts is still not well understood.

Spectral properties and thermal quenching of Mn^{4+} luminescence have been studied in several multi-component garnet hosts comprising Sn^{4+} ions at octahedral sites. It has been found that these Mn^{4+} phosphors exhibit very poor thermal stability of Mn^{4+} luminescence with $T_{1/2} \leq 100$ K. On the other hand, thermal quenching is observed at rather different temperatures for the studied Mn^{4+} phosphors with almost equal energies of the emitting Mn^{4+} ^2E state.

Multi-phonon relaxation from the excited ^2E state to the $^4A_2$ (^4F) ground state of Mn^{4+} doesn't appear to be the real mechanism of thermal quenching. Moreover, no direct correlation is observed between the energy of the emitting Mn^{4+} ^2E state and thermal quenching temperature. A possible influence of thermally stimulated ionization of electrons from Mn^{4+} excited states on thermal quenching of Mn^{4+} luminescence, similar to the case of Ce^{3+} luminescence [3], cannot be analyzed on the basis of available data and thus needs further dedicated studies.

The thermal quenching temperature of Mn^{4+} luminescence in the studied phosphors always correlates with the energies of the Mn^{4+} $^4T_2$ and O^{2-} - Mn^{4+} charge transfer states which can serve as quenching states for Mn^{4+} luminescence. The available experimental data is not sufficient yet for establishing the dominant mechanism of thermal quenching in the studied phosphors. However, at least a general rule for increasing thermal stability of Mn^{4+} phosphors can be formulated: A higher thermal stability of Mn^{4+} luminescence can be predicted for matrices in which Mn^{4+} ions substitute for host cations with a lower charge or smaller size.

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COOPERATIVE ENERGY TRANSFER IN Bi^{3+}-Yb^{3+} CODOPED Y_2O_3 PHOSPHORS

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Y_2O_3 co-doped with Bi^{3+} and Yb^{3+} has been considered as an efficient downconversion candidate because of the broadband absorption of Bi^{3+} in UV-visible spectrum region and the possibility of photon splitting by cooperative energy transfer from Bi^{3+} to two Yb^{3+} neighbors. However, evidence for the occurrence of photon splitting is lacking. If photon splitting occurs, this can strongly enhance the efficiency of *c*-Si solar cells.

In present work we investigate the energy transfer mechanism for Bi^{3+} to Yb^{3+} energy transfer by temperature dependent luminescence and luminescence decay measurements. For cooperative energy transfer the Yb^{3+} concentration dependent decay curves are expected to show the signature of cooperative dipole-dipole transfer. Analysis of the concentration and temperature dependent decay curves however demonstrates that the energy transfer mechanism between Bi^{3+} and Yb^{3+} is single-step energy transfer through a Bi^{4+}-Yb^{2+} charge transfer state (CTS). The temperature dependence of the energy transfer efficiency is unique as the efficiency strongly decreases with increasing temperature. This is a signature of transfer via exchange interaction for which the transfer rate does not depend on donor and acceptor oscillator strengths. Upon raising the temperature, the Bi^{3+} donor emission changes from $^3P_0 \rightarrow {}^1S_0$ (forbidden) to $^3P_1 \rightarrow {}^1S_0$ (allowed) and overtakes the constant energy transfer rate at higher T. Based on our findings, we construct a configuration coordinate model depicting the energy transfer mechanism from $^3P_0$ and $^3P_1$ levels on Bi^{3+} to Yb^{3+} (Fig. 1).

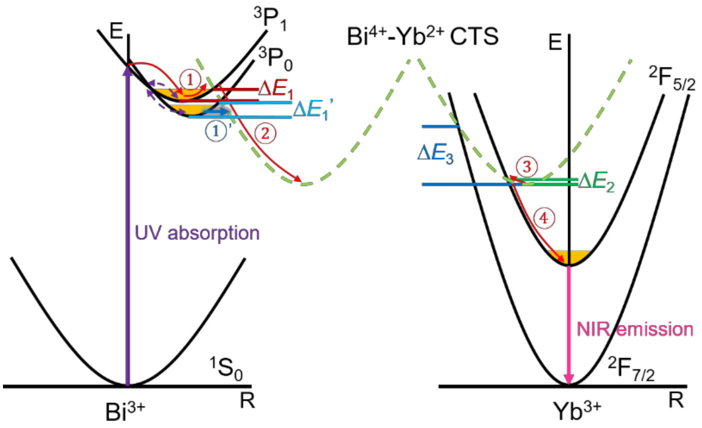

Fig. 1. Configuration coordinate model shows the $^1S_0$, $^3P_0$ and $^3P_1$ states of Bi^{3+}, the $4f^{13}$ state of Yb^{3+} (solid parabolas) and the Bi^{4+}-Yb^{2+} CTS (dashed parabolas), illustrating the single-step energy transfer via Bi^{4+}-Yb^{2+} CTS.

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STRUCTURAL AND OPTICAL PROPERTIES OF COMPOSITE MATERIALS BASED ON TTF-AZINE ORGANIC CHROMOPHORES

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Composite systems based on organic chromophores embedded into polymeric matrix are intensively studied because of their potential applications in optoelectronic and laser devices. These systems possess many advantages over inorganic compositions as a low production cost and new arbitrarily changes in optical properties [1]. The nonlinear optical (NLO) properties of composite materials depend primarily on the chromophore hyperpolarizabilities and the intermolecular interactions between components of the system. The occurrence of these interactions can drastically change the NLO properties of the embedded chromophore. It is crucial, for the rational design of composites that are tailored for specific applications, to access to physical explanations helping to construct accurate guest- host materials [2]. In this ground, molecular simulations and quantum chemical calculations can help to explain the nature of the guest-host interaction and to separate the different contribution of the each component of the composites to the final optical signal.

Organic chromophores involving a conjugated π-electron system terminated with donor and acceptor groups usually show large hyperpolarizabilities which are important for the NLO applications [3]. In the present work, the optical and structural properties newly synthetized tetrathiafulvalene-appended azine derivatives [4] incorporated in poly(methyl- methacrylate) (PMMA) matrix were studied. Electronic properties of the chromophores were calculated via *ab initio* methodology and density functional theory (DFT) applying B3LYP and LC-BLYP functionals. Effect of polar solvent on the electronic properties of the chromophores was taken into account applying the PCM model. The polymer effect on the optical properties of chromophores was modelled taking into account the molecular dynamic simulations with respect to the all-atom consistent valence force field (CVFF) model within GROMACS program package. Additionally, the discreet local field model was applied. Moreover the influence of the chromophores aggregation in the polymeric matrix on the NLO composite properties as well as electrostatic and multipole interaction between its components will be discussed.

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ADVANCED UV-CONVERSION MATERIALS BASED ON GADOLINIUM OXIDE

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Gadolinium oxide doped with rare-earth ions are of interest as a new type of material for energy conversion devices, in particular, for solar cells [1]. Improvement of functional characteristics of convertors based on rare-earths requires the optimization of synthesis technologies which determine the atomic and electronic structure of materials and, ultimately, their optical properties. In present work, we summarize the basic requirements for the crystal structure type and defectiveness of Gd_2O_3 matrix as well as the concentration of dopant ions to achieve the enhanced energy conversion efficiency.

Pure and erbium-doped Gd_2O_3 nanoparticles with cubic and monoclinic crystal structures were synthesized by chemical precipitation and self-propagating combustion, respectively. XRD, SEM and Raman spectroscopy data confirmed the obtaining of stable low-dimensional monophasic erbium-doped gadolinium oxide with an average particle size of 50 nm. XPS measurements and DFT calculations provided experimental study and theoretical modeling of Gd_2O_3:Er electronic structure. The luminescent properties were studied with an optical spectroscopy technique in the 8-300 K temperature range.

In cubic Gd_2O_3, point defects of anionic sublattice (oxygen vacancies) are responsible for the change in the cation energy structure and the appearance of additional Gd^{3+} electronic states in the Gd_2O_3 band gap region [2]. The Gd^{3+} ions become optically active and can be excited in the UV spectral region with the following energy transfer to the dopants. This provides an additional channel for energy conversion without deliberate introduction of donor ions into the lattice, since this role is played by host lattice cations – Gd^{3+} ions. It is especially promising for increasing the efficiency of Si-based solar cells because the additional quanta with UV energy will participate in the solar energy conversion. In monoclinic Gd_2O_3, impurity hydroxide ions arising at the synthesis stage completely quench the emission, so this polymorph is not suitable as a luminescent material, and we focused on the Gd_2O_3 nanoparticles with a cubic structure to search for the optimal Er^{3+} concentration.

Optical reflection spectroscopy we found the effect of giant phonon softening in Gd_2O_3 doped with 1% of Er^{3+} ions [3]. Analysis of temperature dependence of Er^{3+} luminescence confirmed that minimal non-radiative losses are observed in nanoparticles with this concentration of activator. Minimization of thermal losses leads to enhanced quantum efficiency of erbium luminescence under UV radiation conversion. The basic requirements for Gd_2O_3 matrix and Er^{3+} dopant for achieving the improved characteristics of energy conversion are listed in Table 1.

Table 1. The requirements for Gd_2O_3 matrix and Er^{3+} dopant for achieving the improved parameters of UV-visible conversion.

Crystal lattice of matrix	*Er^{3+} concentration*	*$Gd^{3+} \rightarrow Er^{3+}$ energy transfer efficiency*	*Quantum efficiency of emission*	*Decay time of emission*
cubic	1%	50%	26%	107 μs

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SYNTHESIS AND DURABILITY INVESTIGATION OF InP/ZnE (E = S, Se) QUANTUM DOTS FOR *LED* LIGHTING APPLICATIONS

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In the race for miniaturization of optical systems like lighting or display devices, the development of luminescent nanoparticles with high quantum yields represents a tremendous issue. The fluorescent semiconductor nanocrystals, commonly called "Quantum Dots" (QDs), seem to meet all the conditions for such applications. QDs have generally a diameter lower than 10 nm and exhibit size-tuneable optical properties. QDs having currently the best stabilities and optical performances contain cadmium (Cd), a strongly toxic chemical element. The purpose of this work was to develop a Cd-free QDs family by thermal decomposition method allowing an accurate control of the stoichiometry and the final diameter of QDs with a narrow size distribution. To this aim, we have synthesized indium phosphides (InP) QDs from indium halide and aminophosphine precursors [1]. Two types of shell were grown onto InP cores, i.e. ZnS and ZnSe, in order to enhance their stability and their optical efficiency. By modifying the cores growth time, the nature of halide precursors and the shell type, several visible emitting QDs were achieved (Fig 1).

Figure 1: InP/ZnS QDs upon UV light excitation (λ_{exc}=365 nm)

The different samples of QDs were characterized structurally (XRD, IR, XPS), morphologically (TEM and DLS) and optically (quantum yields, excitation and emission spectra, fluorescence decays). Furthermore, the durability of QDs and thus the long-term stability of their optical performances were assessed upon photonic and thermal stresses in order to identify the most promising compositions for an integration in LEDs based lighting or display devices. To this end, luminescent composites were prepared by incorporating QDs in polymeric films. Finally, the photometric parameters (CRI, CCT, color coordinates) and the luminous efficiency (in lumen per Watt) of the emitted white light upon blue and/or UV LEDs excitation were determined.

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RADIO- AND CATHODOLUMINESCENCE STUDY OF $Sr_4Al_{14}O_{25}$:Eu,Dy

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Phosphors are generally studied through photoluminescence (PL) experiments. When exciting by means of X-rays or electrons, many phosphors also show radioluminescence (RL) and cathodoluminescence (CL), respectively. Because of the different excitation energies and pathways that are now available, additional information can be gathered.

For this work, RL and CL experiments are performed on the persistent phosphor $Sr_4Al_{14}O_{25}$:Eu,Dy, which show the emission of the Dy^{3+} ions next to of the typical broad Eu^{2+} emission that is found in PL [1,2]. Studying RL and CL thus allows to track the luminescence of both ions simultaneously, providing insight on the interactions between Eu and Dy.

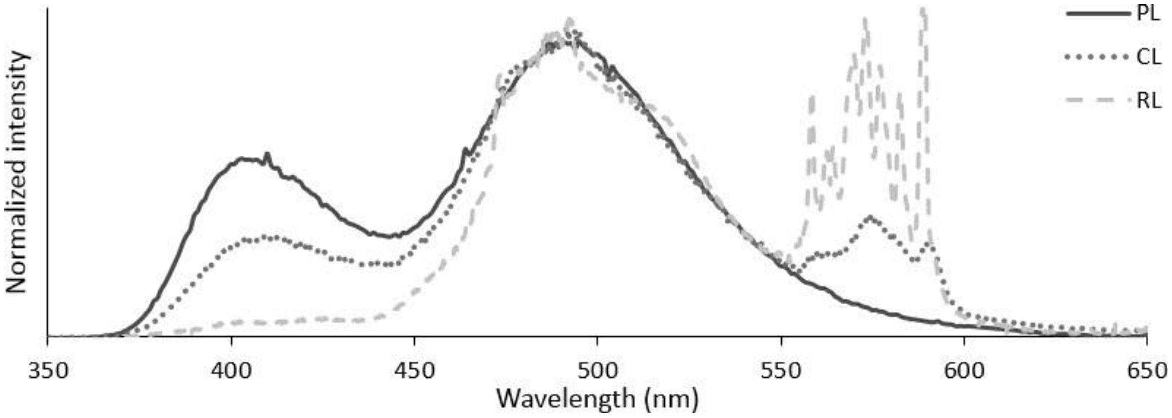

Figure 1: Comparison of PL, CL and RL spectra for $Sr_4Al_{14}O_{25}$:Eu,Dy

Since the cathodoluminescence experiments are performed in a scanning electron microscope (SEM-CL) it is possible to obtain emission maps with a high spatial resolution [4]. Equipped with an energy-dispersive X-ray detector, this setup additionally yields the interesting combination of luminescent and chemical information for micrometer-sized areas. To study the afterglow on this scale, a beam blanker is added, which allows to switch the electron beam on and off during short time intervals. Local afterglow curves are then obtained, providing insight in both inter- and intraparticle characteristics of the persistent luminescence.

Furthermore, all of the above is executed using a heating stage, which allows to control the sample temperature between -25°C and 160°C. This way, thermally resolved CL spectra and afterglow curves are investigated, as well as local thermal quenching behavior [5].

This comprehensive technique offers a wide variety of non-averaged data and is bound to reveal more details about the relevant luminescent mechanisms in $Sr_4Al_{14}O_{25}$:Eu,Dy and persistent phosphors in general.

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ELECTRONIC, ENERGETIC AND OPTICAL PROPERTIES OF THE Cu AND THE Ag SUBSTITUTIONAL DEFECTS IN THE $Li_2B_4O_7$ SCINTILLATOR

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$Li_2B_4O_7$ (LTB) is a wide-gap material which is used in acoustoelectric, linear and nonlinear optic, laser frequency-conversion, piezoelectric and pyroelectric applications [1,2]. Besides, the LTB is also well known host material for Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) dosimetry applications [3]. When enriched with ^{6}Li and ^{10}B isotopes, it is also used as a neutron detector. With objective to improve its luminescent characteristics, the LTB has been doped with a number of chemical elements, but, from the standpoint of the TL and OSL, the best results are obtained with the Cu and Ag transition-metals [4].

The present work analyses quantum-mechanical effects of incorporation of the Cu [5] and the Ag [6] ions at the Li sites within the $Li_2B_4O_7$ crystal matrix, investigated by means of the first-principles calculations on density-functional-theory level. The isolated Cu and Ag defects are considered in various charge states with objective to simulate situations of the capture of an electron or a hole when the crystal is irradiated. In all cases the defective crystal is computationally relaxed, Cu-O and Ag-O chemical bonds are carefully analyzed and local structure around the defects precisely determined. It is found that both defects vastly perturb their O neighborhoods and suffer significant off-site dislocation from initial Li position in theirs +1 and 0 charge states, while the Cu^{2+} and Ag^{2+} stabilize approximately at the Li site. Resulting defect formation energies demonstrate that the Cu^{1+}, Cu^{0}, Ag^{1+} and Ag^{0} centers are the most stable ones. Electronic structure calculations reveal that both the Cu and the Ag introduce their d- and s-states within the gap and their energies and occupation depend strongly on the charge state of the defect. Experimental optical absorption spectra for the LTB:Cu are well reproduced by the sole Cu^{1+} defect spectra, leading to the conclusion that in the as-grown material just Cu^{1+} centers are formed, with possible presence of small concentration of the Cu^{2+} centers. In the case of irradiated material, present study predicts formation of the interstitial Cu^{0} defects, whose presence should significantly change the optical absorption and emission of the material. Considering the LTB:Ag, the optical spectrum of the non-irradiated sample is also well reproduced by the sole Ag^{1+} defect spectrum. When irradiated, the spectrum is dominated by the Ag^{0} and Ag^{2+} centers, indicating formation of exactly these charge states of the defects.

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COUPLING $ZnGa_2O_4$:Cr^{3+},Bi^{3+} LUMINESCENT NANOTHERMOMETER AND GOLD NANORODS HEATER FOR LOCAL TEMPERATURE MEASUREMENT

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$ZnGa_2O_4$:$Cr^{3+,}Bi^{3+}$ nanoparticles (NPs) have been demonstrated as a relevant luminescent nanothermometer because of its very strong temperature dependence of luminescence lifetime of chromium(III) and its high sensitivity on a large temperature range [1]. In order to demonstrate the possibility to use these NPs as local thermal nanoprobe, gold nanorods are synthesized [2] and used as nanoheater to be coupled with the NPs. Indeed, under an appropriate excitation, gold nanoparticles may induce heat due to their plasmonic properties. Anisotropic shape is chosen because of the suitable wavelength excitation in the longitudinal band, which is not absorbed by the $ZnGa_2O_4$:$Cr^{3+,}Bi^{3+}$ nanothermometer (at about 960 nm). The heat generation can be highlighted by thermal camera pictures. The aim of this work is to analyze and quantify the local temperature increase. Lifetime measurements were performed in solution but also on powder. A study on the influence of the distance between nanosensors and nanoheaters and the measured temperature has been carried out by coating with tunable thickness of silica layer the nanosensors. The variation of the optical nanosensor response is relevant and promising and could further be envisioned as a potential candidate to be use in hyperthermia treatment with a precise and controlled temperature.

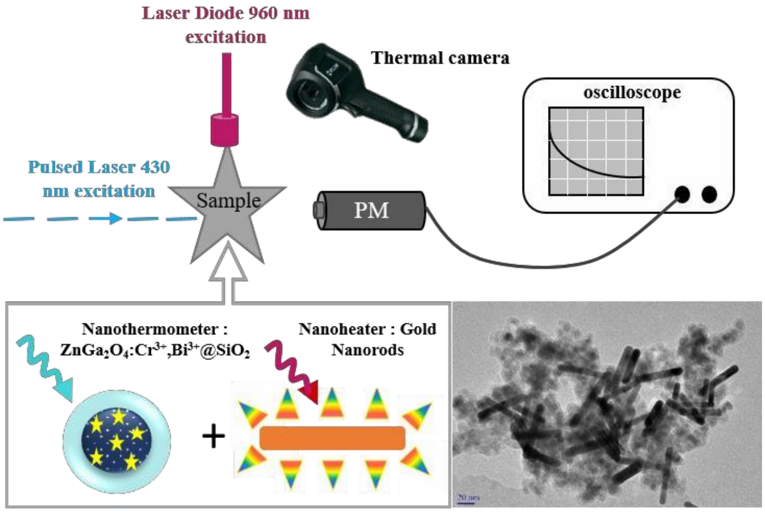

Figure 1. Schematic representation of experimental setup used for local temperature determination induced by plasmonic effect

DGA, Matisse and ANR PEPSI are acknowledged for the support of the work

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TWO-PHOTON ABSORPTION SPECTRA OF BENZOXAZOLES UNDERGOING EXCITED STATE INTRAMOLECULAR PROTON TRANSFER: TDDFT CALCULATIONS

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Two-photon absorption in organic materials is considered to be a useful process for applications in 3D micro-fabrication and micromachining, 3D data storage, optical power limiting, two-photon induced photopolymerization and two-photon pumped laser. 2-(2'- hydroxyphenyl)benzoxazole (HBO), 2,5-bis(2-benzoxazolyl)phenol (DBP) and 2,5-bis(2- benzoxazolyl)hydroquinone (BBHQ) (Fig. 1) are benzoxazole derivatives with single and double hydrogen bonding undergoing photoinduced excited state intramolecular proton transfer (ESIPT). The ESIPT converts enol structure of the molecules with the OH…N hydrogen bonds into keto structure with the O…HN hydrogen bonds and causes appearance of fluorescence with an anomalously large Stokes shift.

Two-photon absorption cross sections of transitions in molecules of HBO, DBP and BBHQ were evaluated by a TDDFT method using the B3LYP functional and 6-31G(d,p) basis set for the structures of the molecules obtained in the ground state by DFT calculations. All calculations were performed with the GAMESS program package.

It has been calculated that the largest two-photon absorption cross sections of DBP and BBHQ are about 50 times as much as the cross section of HBO (Fig. 1). In contrast to the one-photon absorption spectra where the transitions to the lowest excited states S_1 and S_2 dominate, in the two-photon absorption spectra the transitions to the higher excited states are significant. For a centrosymmetric molecule of BBHQ the cross section of the transition to the excited state S_3 is predicted to be an order of magnitude greater than the cross sections of the transitions to other states possessing A_g symmetry (Fig. 1d).

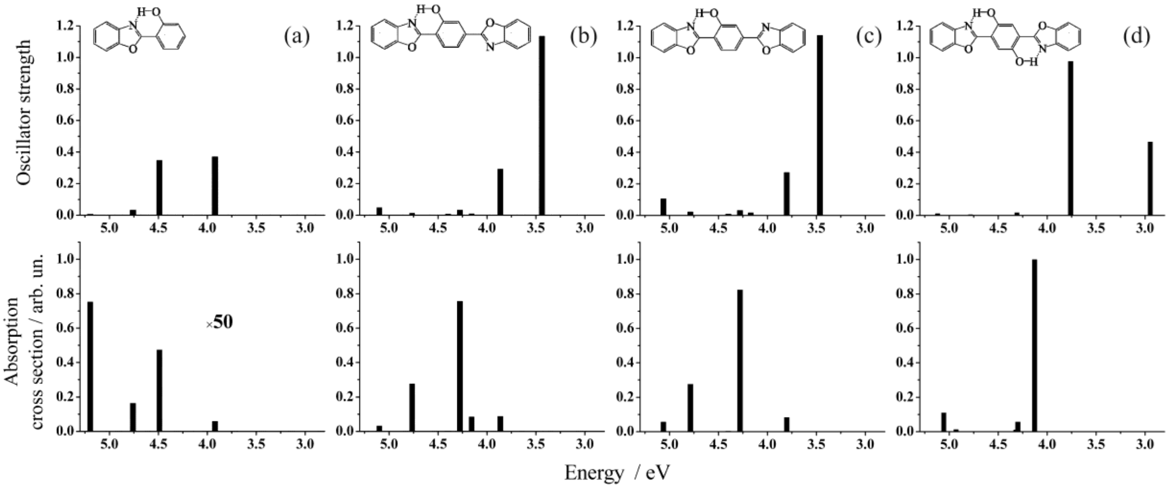

Fig. 1. Energy, oscillator strength and two-photon absorption cross section of electronic transitions in molecules of HBO (a), two rotameric structures of DBP (b, c) and BBHQ (d). The cross sections are calculated for linear polarization of the incident light and equal frequencies of the two photons.

RARE EARTH LUMINESCENCE IN HYDRIDES

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Usually, the material class of the hydrides is connected to energy applications such as hydrogen storage or ion conduction [1, 2]. Even though there is a large interest in rare earth doped materials and many different compounds, from halides to oxides, sulfides and nitrides have been studied and *RE* ions can also serve as local probes, hydrides had not been considered for many years. About five years ago, we were able to quantitatively analyze the strength of the ligand field and the nephelauxetic effect of the hydride anion for the inverse perovskite hydrides $\mathrm{Li}M\mathrm{H}_3$ and $\mathrm{Li}M\mathrm{D}_3$ (M= Sr, Ba) doped with divalent europium [3]. Eu^{2+} usually shows the parity-and spin-allowed $4f^65d^1$-$4f^7$ transition. The 5d shell is only insufficiently shielded, which leads to a strong dependence of the emission energies on the chemical environment. Even though the hydride anion was known to be a soft and polarizable anion, the exact strength of the ligand field and nephelauxetic effect had before never been quantified.

We also studied a series of other Eu^{2+}-doped hydrides and for the first time investigated thermoluminescence in europium-doped hydrides [4 and unpublished results]. Currently, we are studying mixed hydride halides, such as hydride fluorides and hydride chlorides. For Eu^{2+}-doped compounds, the emission wavelength can be tuned by adjusting, for example, the hydride fluoride content. We also use rare earth ions as EPR probes and are exploring suitable hosts for RE^{3+}-doping. At the present conference, rare earth doping of this original family of compounds will be discussed, for example as local optical and EPR probes.

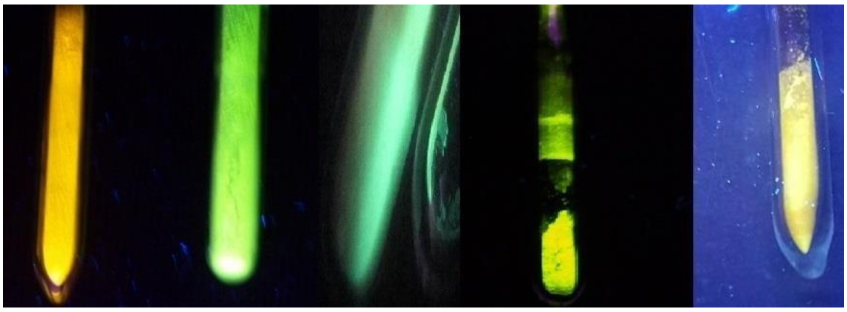

Fig. 1: From left to right: $\mathrm{LiSrH_3{:}Eu^{2+}}$, $\mathrm{LiBaD_3{:}Eu^{2+}}$, EuHCl, $\mathrm{KMgH_3{:}Eu^{2+}}$, $\mathrm{RbMgH_3{:}Eu^{2+}}$ under UV light.

Acknowledgments: The author thanks the FCI and the DFG for financial support. Furthermore, a number of co-workers were involved in measurements and discussions of the results presented herein. The author especially likes to thank Rolf Böttcher, Victor Castaing, Pieter Dorenbos, Philippe Goldner, Andries Meijerink, Andreas Pöppl, Daniel Rudolph, Adlane Sayede, Thomas Schleid, Atul Sontakke, Bruno Viana, Sacha Welinski, and Thomas Wylezich.

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OPTICAL PROPERTIES OF LOW-DIMENSIONAL CUPRATES

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Strongly correlated low-dimensional cuprates form a large group of materials from monoxide CuO to quasi-1D ($CuGeO_3$, $LiCu_2O_2$, $LiVCuO_4$, …), and quasi-2D parent and superconducting cuprates (La_2CuO_4, $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{6+x}$, …) with a large variety of exceptional properties such as high-Tc superconductivity, multiferroicity, quantum magnetism, helical magnetism, and unusual linear and nonlinear optical properties. The CuO_4 clusters with nominal Cu^{2+}-ion are the basic element of their crystal and electronic structure, however, the cuprates provide opportunity to explore the role played by the Cu^{1+}- and Cu^{3+}- centers. An extremely strong, sharp, and highly anisotropic optical feature with $\mathrm{Im}\varepsilon_{xx}=26$ was observed in $LiCu_2O_2$ at 3.27 eV and assigned to an exciton-like transition in the O^{2-}-Cu^{1+}-O^{2-} dumbbells [1], challenging opportunities to explore optical response of the Cu^{3+}-centers are in $La_2Cu_{0.5}Li_{0.5}O_4$. Fundamental absorption band or dielectric gap in cuprates is shown to be formed by a superposition of intracenter *p-d* charge transfer (CT) transitions and two-center *d-d* CT, or Mott-Hubbard, transitions near 1.5-2.0 eV [2-4]. In other words these should be classified as compounds intermediate between CT and Mott-Hubbard insulators. A large body of experimental data points toward a CT instability of parent insulating cuprates to be their unique property. It is argued that the true (thermal) CT gap in these compounds is as small as 0.4-0.5 eV rather than 1.5-2.0 eV as usually derived from the optical gap measurements. The true CT gap is associated with the non-Franck-Condon counterpart of the Franck-Condon transition near 1.5-2.0 eV. As a result, we deal with a competition of the conventional $Cu^{2+}(3d^9)$ ground state and a CT state with the formation of electron-hole dimers which evolves under doping to an unconventional bosonic-like system with high-Tc superconductivity [5].

To interpret the optical data in insulating cuprates we developed a semi-quantitative embedded cluster approach applied to describe the electron-hole excitations. The theory includes the complete set of Cu *3d* and O *2p* orbitals forming bonding as well as nonbonding molecular orbitals and predicts a rather wide (2-13 eV) spectral range of the main dipole- allowed *p-d* and *d-d* CT transitions, whose positions are in a good quantitative agreement with the experimental spectra [2-4]. The approach does provide a unified standpoint on the main experimental findings for parent cuprates including linear and nonlinear optical, EELS, Raman, photoemission, photoabsorption, and transport properties related with the CT excitations. Furthermore, we demonstrate how the optical properties of the parent cuprates can be used to describe unconventional properties of the hole- or electron-doped compounds, in particular, the mechanism of high-Tc superconductivity and optical properties of superconducting cuprats.

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SOURCES OF OPTICAL RADIATION BASED ON SCINTILLATORS ACTIVATED BY ALPHA- RADIOACTIVE ISOTOPES

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The idea of converting the energy released in the result of radioactive decay into electricity, heat or optical radiation seems very attractive. This is due to the possibility of long-term use of such a device without the need for replacement or recharging. The time of use of such radioactive source is determined by the half-life of the radioactive isotope and can be up to tens and hundreds of years.

If the radionuclide as the source of alpha radiation is immobilized as an impurity in a crystal lattice containing active optical luminescence centers the crystal becomes self-glowing. The time of its self-glowing is determined by the lifetime of the radionuclide and can be up to tens and hundreds of years. The content of the radionuclide will be selected in such a way as to ensure ecologically safe and technically simple handling of self-glowing materials. The most promising radionuclide for this task is radionuclide mainly with alpha decay. This is due to the fact that most of the energy of the alpha particles will be absorbed in the scintillator itself. The mileage of the alpha particles, if they penetrate outside the scintillator, is a few microns and can easily be blocked, for example by a thin layer of glass. This makes it possible to make the source based on the alpha-isotope safe to use and minimize the effect of radiation on other elements of the structure. In connection with the need to activate scintillators with radionuclides, the scintillator matrix must possess high mechanical, chemical and radiation resistance. Therefore, the high-temperature oxide crystalline materials and ceramics were used.

The first self-glowing crystals based on orthophosphates (YPO_4) and zirconates ($ZrSiO_4$) with red and green luminescence were glow. The crystal YPO_4: Eu^{3+} with a 238-Pu content of 0.1% wt. with volume of 0.02 cm^3 can generate the electric power of 0.1 microwatt.

Autonomous sources of optical radiation can be used as the main element of a battery in combination with a converter of optical energy into electric current. Silicon photodiodes or photoelectric converters based on AIIIBV semiconductor compounds that show high efficiency (about 50%) and possess high radiation resistance can be used as such converters. Also, autonomous sources of optical radiation can be used in sensors consisting of a radiation source-a receiver for identifying the contents of various gases in the atmosphere. The possibility of using such sources of optical radiation in robotics as an element of an optoelectronic pair also seems promising. The long life and reliability of the proposed sources of optical radiation makes it possible to use these elements in conditions where regular monitoring of the serviceability of the source is impossible (conditions of the Far North, space, expeditions, etc.). This idea was first proposed and partially implemented in Ioffe Institute and Khlopin Radium Institute.

CHARACTERISATION OF PHOSPHOR PARTICLES FOR TEMPERATURE IMAGING IN FLUID FLOWS

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Laser-based measurement techniques are essential for fundamental studies of fluid-mechanical turbulence, convective heat transfer and reacting flows. In recent years, new optical techniques to measure temperature in liquid and gas flows using thermographic phosphors have emerged as a robust tool with a broad range of applications [1]. Micron-size phosphor particles are seeded into the flow as a tracer, and their temperature-dependent luminescence properties are probed using lasers and detectors for remote thermometry. The validity of this concept is based on the fact that temperature of the micrometre-size particles closely matches that of the surrounding fluid [1].

It is evident that the choice of phosphor is crucial to perform accurate measurements in fluids. Desirable luminescence properties are: a) high number of luminescence photons emitted per particle , which is linked to the absorption cross section and quantum efficiency b) a short luminescence lifetime (µs range) to allow short measurement duration in fast gas flows c) a high sensitivity of the exploited luminescence properties to temperature in the desired range d) a high thermal quenching temperature to measure at elevated temperatures e) a low cross-sensitivity of the luminescence properties to other parameters e.g. the fluid pressure, composition and phase, the laser excitation intensity, etc to minimise error sources.

Characterisation experiments are therefore necessary to qualify a phosphor for fluid thermometry. However traditional studies of bulk powder are unsuitable due to phenomena which are specific to the state of agglomeration and not encountered with dispersed particles. Examples are multiple scattering, re-absorption, amplified spontaneous emission, and laser induced heating and degradation under repeated illumination. We have therefore developed a methodology to probe a known quantity of dispersed particles in a fluid, allowing quantitative luminescence measurements on a per particle basis. From such studies we have identified 3 suitable commercial phosphors: $BaMgAl_{10}O_{17}:Eu^{2+}$, ZnO, $(Sr,Mg)_3(PO_4)_2:Sn^{2+}$. The observed properties for particles of 1-2 µm are summarised in Table 1. The signal levels are similar, but the best compromise is found with $(Sr,Mg)_3(PO_4)_2:Sn^{2+}$ as it shows a high temperature sensitivity, a high quenching temperature and a low cross-sensitivity to excitation fluence. In terms of future development, it is important to note that the commercial phosphors tested here are not optimised for our specific use as fluid sensors. Therefore we seek to identify, synthesise, test and even design phosphor particles with new and improved sensing capabilities.

Phosphor	$BaMgAl_{10}O_{17}:Eu^{2+}$	ZnO	$(Sr,Mg)_3(PO_4)_2:Sn^{2+}$
Intensity (photons/particle/pulse) at 300 K	$2.6x10^6$	$3.0x10^6$	$2.1x10^6$
Lifetime at 300 K	1 µs	<1 ns	26 µs
Temperature sensitivity at 300 K Quenching	0.2 %/K	0.7 %/K	0.6 %/K
temperature T_{50}	~600 K 3 K	~400 K 6 K	~600 K
Temperature error per 10% change in excitation intensity at 300 K			0.6 K

Table 1: Key luminescence parameters of three different commercial phosphor particles in dispersed form under 266 nm laser excitation, with a fluence of 20 mJ/cm^2 and a pulse duration of 10 ns.

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MID-INDFRARED PHOTOACOUSTIC SPECTROMETER FOR ATMOSPHERIC NO_2 MEASUREMENTS

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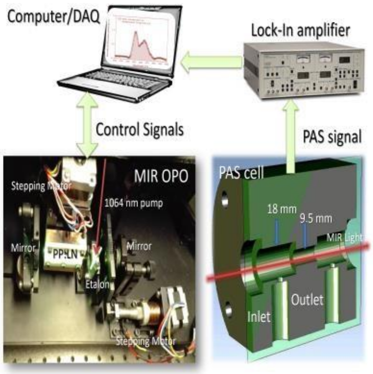
NO_2 is a very toxic gas and a regulated air pollutant that possess a serious risk for human health. Atmospheric NO_2 is primarily a manmade problem and is related to combustion processes, such as the emissions from cars, power plants and factories. The EU Directive 2008/50/EG provides a lower assessment hourly limit value for the protection of human health of approximately 50 ppbV at 1 atm pressure and 20°C. Conventional methods for NO_2 (and other NO_x and SO_x) measurement include chemiluminescence and wet chemical analysis, which are widely employed for atmospheric monitoring. However these methods have minutes to hour's response time and are very sensitive to cross interference with other molecules, especially at low concentrations in the ppbV range [1].

We therefore foresee that photoacoustic spectroscopy (PAS) will be a very promising method for monitoring of many other environmental gasses [2,3]. A miniaturized photoacoustic (PA) sensor for spectroscopic measurements of NO_2 is demonstrated. The PA sensor is pumped resonantly by a nanosecond pulsed single-mode mid-infrared optical parametric oscillator (MIR OPO). Explicit spectroscopic measurements in the 3250 nm to 3550 nm wavelength region with a resolution bandwidth of 5 cm^{-1} and a single-shot detection limit of 1.6 ppmV is demonstrated. The acquired spectrum is compared with data from the Hitran database and a very good agreement is found. An Allan deviation analysis shows that the detection limit at optimum integration time for the PAS sensor is 14 ppbV@170 seconds.



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GRAPHENE-BASED LIQUID CRYSTAL DEVICES ON RIGID AND FLEXIBLE SUBSTRATES

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Liquid-crystal displays (LCDs) are electro-optical devices that use light-modulating ability of the liquid crystals to control the phase and intensity of light. Nowadays, they play a key role in modern photonic devices being technologically responsible for human to machine interaction. Moreover the rapid progress requires LCDs to overcome the challenges as super- fast response time, lower power consumption, broader viewing angles and high contrast ratio. Besides, simple fabrication procedure in large area and uniform process ability are crit ically important in both rigid and flexible substrates. In this aspect graphene is considered as an excellent candidate due to its outstanding properties as high electronic mobility, exceptionally low absorbance and bent ability on the flexible substrates [1].

In this paper we demonstrate the fabrication of large scale high-performance liquid-crystal displays (LCDs) devices based on graphene conductive electrodes. We use high quality multilayer graphene synthesized by low pressure CVD method. Due to the graphene's nature (atomically thin carbon layer), graphene face high risk of damage or de-attachment during conventional mechanically rubbing treatment in comparison with ITO film, being much thicker and mechanically robust. Therefore photoalignment method instead of commercial mechanical rubbing technique was use to prevent graphene detachment from the substrate.

The measured voltage-transmittance characteristics, response time and high modulation values of several graphene-based LC cells are competitive with the reference LC cell using ITO contacts and conventional mechanical rubbing technique. Detailed mapping of graphene- based LC device operating on large working area opens a great potential for next generation ITO-free electrodes on rigid and flexible substrates.

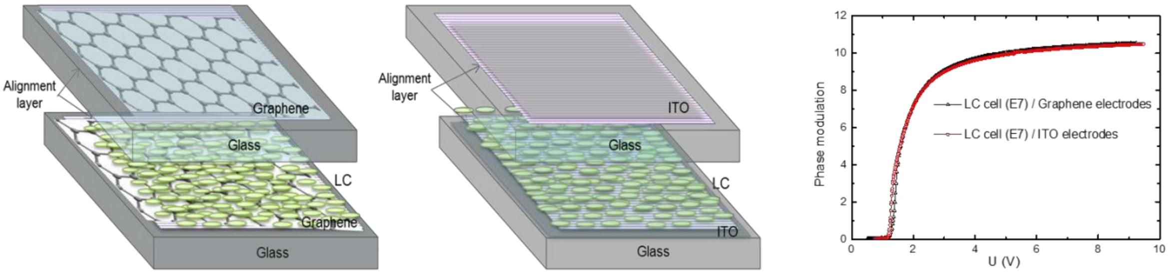

Fig.1. Schematic structure of graphene –based and ITO-based LC devices and phase modulation behavior.

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Nd^{3+}/Ho^{3+}-CODOPED GERMANATES FOR NEAR-INFRARED LASER APPLICATIONS

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Infrared lasers operating in the 2.0–3.0 μm spectral range find a wide application in laser radar systems, laser imaging, biomedical systems, remote sensing, monitoring and communication systems [1–3]. Luminescence in this wavelength region can be caused by the 4*f*–4*f* transitions in lanthanide ions (Ho^{3+}, Er^{3+}, Tm^{3+}, Dy^{3+}, etc.). Since these ions have no absorption bands or have a small cross section at 808 or 980 nm, commercial laser diodes cannot be used as pump sources. In order to achieve strong emission in the near-infrared region, codoping of other active ions as sensitizer ions, e.g. Nd^{3+} or Yb^{3+}, has been used. Different energy transfer processes occurring between lanthanide ions can greatly enhance the absorption of excitation energy by Er^{3+} or Ho^{3+} ions. The above-mentioned lanthanide ions can either be introduced in an optical host as codopants in form of the corresponding individual educts directly in the synthesis procedure or exist already in a lanthanide-containing initial reagent of interest according to stoichiometric relation for the chosen method of preparation. These both variants have been experimentally considered in the present study in which the residual concentration of holmium ions has been accurately defined to propose the model of excitation mechanism in various germanate compounds doped with neodymium ions such as $CaLa_2Ge_3O_{10}$ trigermanates, $Sr_3La_2(Ge_3O_9)_2$ cyclogermanates, $NaLa_9(GeO_4)_6O_2$ oxyapatites and $Ca_3Y_2Ge_3O_{12}$ garnets. Our report is focused on the synthesis, the crystal structure and luminescence properties of new infrared phosphors based on the listed germanates studied by means of powder X-ray diffraction and optical spectroscopy.

The emission spectra of these germanates in the range from 0.85 to 3.0 μm under 808 nm laser diode excitation exhibit the infrared emission bands, which correspond to a series of 4*f*– 4*f* transitions of the lanthanide ions. The most intensive lines centered at 2.1 and 2.7 μm are associated with the $^5I_7 \rightarrow {}^5I_8$ and $^5I_6 \rightarrow {}^5I_7$ transitions in Ho^{3+} ion. The lines in the range 0.9–1.9 μm assigned to the $^4F_{3/2} \rightarrow {}^4I_J$ (J = 9/2, 11/2, 13/2 and 15/2) transitions in Nd^{3+} ion exhibit low intensity. The mechanism for multistage process of energy transfer between the active centers, which involves the participation of Nd^{3+} ions as sensitizers of infrared luminescence of Ho^{3+} ions was proposed from analysis of the near-infrared emission, the visible upconversion luminescence, the diffuse reflectance spectra and the decay curves. The results indicate that the studied germanates can be considered as promising materials for near- infrared laser applications.

The work was supported by the Russian Science Foundation (project No. 16–13–10111). The crystallographic study was carried out at the multiple–access center for X–ray structure analysis at the Institute of Solid State Chemistry, UB RAS (Ekaterinburg, Russia).

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SOLUTION PROCESSING OF HYBRID ZnO NANOPHOSPHORS ASSEMBLED IN MESOSPHERE FOR LED APPLICATION

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An important economic improvement of white light emitting diode is based on the use of lanthanide-free phosphors that are supposed to convert UV light into visible one, thanks to down-conversion (DS) process. ZnO nanoparticles (NPs) have aroused an increasing interest since they possess a variety of intrinsic defects that provide light emission in the visible range without the introduction of any additional impurity. However, high photoluminescent quantum yield (PLQY), green/yellow emission, stable dispersion and easy scale–up process are expected for industrial applications. Li-doping and polymer surface modifications of ZnO nanoparticles are mainly used in order to reach high PLQY (>30%) but PLQY decay over few days, uses of sophisticated polymers or multi-step reactions are the main issues for industrial implementation. Recently, we developed and patented an industry-capable (in terms of legislation concerns) and cost effective chemical solution process to get unique mesospheric self-assembly hybrid ZnO system with intense (PLQY = 40-75%) and stable visible emissions. [1,2] (Figure 1). This hierarchical structure revealed to be efficient scatterer, resulting in a significant increase of the light-harvesting capability. We also demonstrate that the use of mixture of commercial polyacrylic acid-based polymers can provide scalable amounts of ZnO NPs clear water suspensions that can be dried and dispersed again in water without compromising the functional performance (e.g. transparency and PLQY) of the final DS layer. Herein, we will address the effects of the ZnO NPs surface functionalization - such as nature, molecular weight, concentration, ratio of the PAA-based polymers and self-assembly process- but also the impacts of transition metal dopings (nature and content) on the enhancement of the efficiency and on the control of the emission colour light of DS thin films in LED technology.

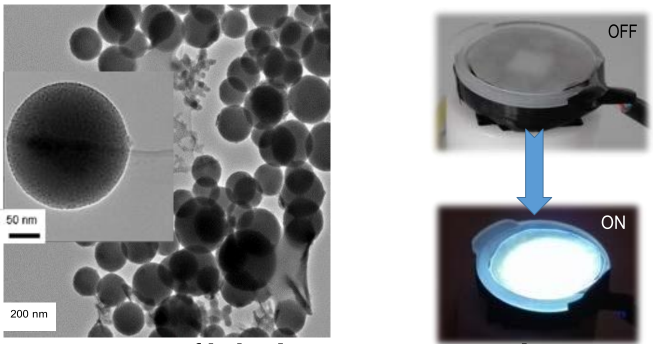

Figure 1. TEM Images of hybrid ZnO aggregates and LED prototype

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Mo AND W CO-DOPING EFFECTS ON Ce DOPED GARNET SCINTILLATORS

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Scintillator materials combined with photodetectors are used to detect high energy photons and accelerated particles in medical imaging techniques, high energy and nuclear physics detectors, high-tech industrial applications and most recently also in the advanced homeland security related techniques. The Ce-doped $Lu_3Al_5O_{12}$ (Ce:LuAG) single crystal was shown to be a prospective scintillator material with a relatively high density of 6.7 g/cm^3, a fast scintillation response of about 60–80 ns, and light yield of about 12–14,000 phot/MeV. Recently, in the silicate, perovskite and garnet scintillators the slow tunneling-driven radiative recombination between Ce emission centers and nearby lying electron traps can deteriorate scintillation performance. Improvement of scintillation performance by co-doping with alkali earth AE^{2+} ions in Ce activated scintillators such as, Ce,Ca:LSO [1], and Ce,Mg:LuAG. In these scintillators, light yield and scintillation decay time were enormously improved and accelerated and the presence of Ce^{4+} was clearly identified by its characteristic charge transfer (CT) absorption in the near UV range below 350 nm [2].

The aim of this work is to investigate and compare the Group 6 elements such W and Mo ions co-doping effects on luminescence and scintillation properties of garnet scintillators such Ce:LuAG and $Y_3Al_5O_{12}$ (YAG) single crystal scintillator. Ce0.5mol.% doped LuAG and Ce:YAG with 500 mol.ppm W and Mo co-doing were grown by the μ-PD method with an RF heating system. All of the grown crystal showed Ce^{3+} emission band at 520nm. Light yield was increased by Mo co- doping. The Mo copoped sample showed the highest light yield of 28000 photo/MeV, which is around 200% of light yield of the non co-doped crystal(fig.1). Absorption, emission spectra, light yield and scintillation decay time of the co-doped sample are comparable to the non-co-doped crystal. XPS and XANES were performed to discuss existance of Ce^{4+}.

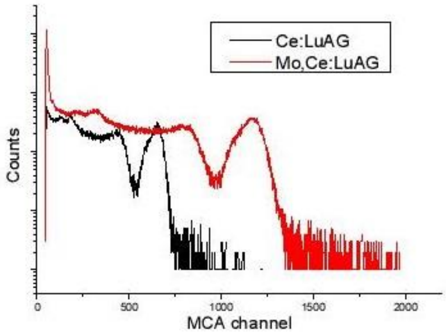

Fig.1 Energy spectra of Mo,Ce and Ce:LuAG exited by 663keV gamma-ray

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ALUMINUM-DOPED ZINC OXIDE THIN FILMS DEPOSITED BY ELECTROSPRAY METHOD

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Aluminum-doped ZnO (AZO) thin films are deposited by economically-versatile fabrication method of electrospraying onto three types of substrates – glass, silicon wafer and metal foil. Zinc acetate dehydrate dissolved in a mixture of deionized water, ethanol and acetic acid is used for deposition of undoped ZnO film. The influence of deposition parameters on structural, optical and morphological properties of ZnO films has already been revealed [1,2]. In this study, for Al-doping two precursors materials are chosen - aluminum chloride and aluminum nitrate. In order to obtain the best conditions for incorporating aluminum in the ZnO crystal structure two different doping approaches are used. The first method involves mixing the zinc and aluminum precursor solutions and spraying the mixture on the heated substrate. The second one includes simultaneous deposition from two separated emitters, one spraying the zinc solution and the other the doping solution thus enabling the synthesis of AZO films onto the substrate. The doping level is varied in the range 0-3 wt% and the concentration dependence of films properties is studied. The films structure and surface morphology are studied by X-ray diffraction and Scanning Electron Microscopy, respectively, while surface profile and roughness are inspected by Atomic Force Microscopy and optical profilometry. The composition, chemical and electronic state of the elements that exist within the deposited film's surface are revealed by the X-ray photoelectron spectroscopy. The optical properties are investigated by spectroscopic ellipsometry and photoluminescence measurements. The applicability of the studied films as transparent conductive electrodes is demonstrated by transmittance and sheet resistance measurements.

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Acknowledgement

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LUMINENSCENT DIAMOND PARTICLES WITH CONTROLLABLY EMBEDDED DOPANT ATOMS

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Luminenscent diamond particles with controllably embedded dopant atoms widely used as luminescent markers. Such particles have unsurpassed physical characteristics. Embedded atoms can form colour-centers with different luminescent wavelength. The choosing of dopant atoms for creating different colour-centers allows us to select the optimal optical characteristics. The effect of doping atoms on the crystal structure of diamond particles has an effect on the intensity of luminescence. Thus, the study of the diamond lattice structure is the key to obtaining diamond particles of the best optical quality.

The complex use of techniques of luminescent and Raman spectroscopy, EPR spectroscopy and HRTEM images and live time measurements give information about the effect of the diamond particle structure on its luminescence characteristics. In this work we presented studies of few different diamond particles synthesis:

- HPHT microdiamonds with embedded nitrogen atoms are demonstrate strong dependence of resonant enhancement of the NV^- photoluminescence (PL) with different concentration of the substitutional nitrogen atoms (NS). The EPR, Raman and luminescent spectroscopes, including time-resolved PL shows that of the NV^- center emission can be optimized by the appropriate choice of nitrogen doping concentration and energy of e-beam irradiation.[] There are competition between the increase of PL with increasing concentration of the NV^- centers, and nonradiative deactivation of these centers by defects induced by the dopant atoms in the diamond crystal lattice.
- Diamond particles with embedded of silica atoms are highly dependent of their diamond lattice structure. The same processes of competition between increasing of colour-centers amount as well as their luminescence and increasing of nonradiative defects lead to deactivation of these centers. This effect will be shown for diamond polycrystals produced by shock wave synthesis followed by grinding and separation into fractions of different polycrystal median sizes (25–1000 nm) [2] and technique of fabricate isolated diamond particles performed by microwave plasma-enhanced chemical vapour deposition (CVD) using silane as a source of impurity atoms. [3].

A serious dependence of optical properties and diamond lattice structure is shown for diamond particles with different controllably embedded atoms such as nitrogen and silica.

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INCORPORATION OF DEFECTS WITHIN Nb_2O_5 BRAGG STACK FOR OPTIMIZING ITS PROPERTIES AS A SENSOR FOR VOLATILE ORGANIC COMPOUNDS

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Brag stacks are structures of alternating layers of different materials that are engineered in such a way that upon interaction with light constructive interference occurs and part of light spectrum is completely reflected thus generating the so called reflectance band where the propagation of light is forbidden. The reflectance band is highly sensitive to any change in the optical parameters of the structure and that is why those structures could be used as an active media for external stimuli detection with optical read-out. If properly designed defects are introduced in those structures a very narrow transmittance band appears within the reflectance band having filtering capabilities. The position of this band depends on the position of the defect layer in the stack and a wavelength shift is observed when optical parameters of the defect layers change due to external stimuli.

In the present study we are presenting Bragg stacks of alternating dense and porous Nb_2O_5 thin films used as a medium for sensing of vapors of volatile organic compounds. Both types of thin films have been investigated by transmission electron microscopy. The optical parameters of the films have been determined by UV-VIS spectroscopy and nonlinear curve fitting method. The individual layers reaction towards different volatile organic compounds VOC's (for example chloroform, ethanol, methanol, acetone, etc) in terms of reflection change has been recorded. The amplification of the reaction due to incorporation of the layers in Bragg stack is presented. The position of the defect layer into the stack is initially optimized by computer modelling aiming at maximizing the sensitivity towards VOC's. Then defects are introduced in the structure of the Bragg stacks in order to investigate the role of their position within the structure on its optical response when exposed to vapors. Possible applications of those structures as optical sensors and filters in the visible light spectrum are demonstrated and discussed.

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ELECTRON TRAPS IN Ti-DOPED LUTETIUM OXIDE – A DFT PERSPECTIVE

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Cubic lutetium oxide, Lu_2O_3, space group Ia-3, is a promising matrix material for afterglow, persistence luminescence and permanent energy storage phosphors. The particular properties are tightly related to the nature of charge carrier traps in the materials – energy levels above valence band and below conduction band, capable of hole or electron trapping, respectively. In particular, Ti doping of Lu_2O_3 results in rather deep electron traps of 1.7-2.3 eV [1]. The topic has been intensively investigated using different thermoluminescence techniques. In this work, the matter is investigated using advanced all-electron density functional calculations.

In a unit cell of Lu_2O_3, several kinds of doping were modeled, namely: a $Ti^{3+/4+}$ ion in either of the two Lu sites, a $Ti^{3+/4+}$ ion accompanied with an interstitial O^{2-} in the nearest oxygen void, two Ti^{4+} ions with an O^{2-} in between, a Ti^{4+} ion in either of the two cation voids with two O^{2-} in the nearest oxygen voids. Oxidation state of the Ti dopant was controlled via total charge on the structure. The geometries of the structures were optimized using Quantum Espresso code, with either of Perdew-Zunger (PZ) LDA or Perdew-Burke-Ernzerhof (PBE) GGA density functionals and ultrasoft pseudopotentials from GBRV group (an unpublished Lu^{3+} potential with *4f* shell in-core was kindly provided by Kevin F. Garrity). Next, all-electron Elk code with RPP09 meta-GGA functional [2] for exchange and PZ correlation was used to calculate total energy and density of states of the structures.

The calculations showed presence of additional levels under conduction band corresponding to *d* orbitals of the Ti dopant. The states were either empty (Ti^{4+}) or filled (Ti^{3+}). The particular energies of the defect bands depend on the dopant site, oxidation state and presence of the interstitial oxygen. The corresponding electron trap depths are found in the 1-1.5 eV range, on the basis of both PZ and PBE results. However, according to RPP09/PZ calculations, the trap depths are as large as 2-2.5 eV, which agrees much better with the experimental data. Also, shallow traps (0.4-0.7 eV) are present along with the deeper ones (RPP09/PZ).

Electron trapping in Lu_2O_3:Ti can be attributed specifically to the dopant. Several traps of different depths can originate from the same doping site. The trap depths are sensitive to the dopant chemical environment, interstitial oxygen in particular. Clusters of two dopant ions with an interstitial oxygen exhibit more trap states per dopant atom. The study thus provides new insights in peculiarities of electron trap formation in Lu_2O_3, as well potential ways of tuning the traps (for instance, via enriching the sample with oxygen).

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IDENTIFYING THE FINGERPRINT OF OPTICALLY STIMULATED LUMINESCENCE BY EXCITATION LIGHT

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Optically stimulated luminescence (OSL) is a well-known phenomenon with important applications in e.g. medical imaging or geological and archeological dating. The luminescent materials used in those applications are first exposed to high energy radiation, which induces trapping in the material and allows to store energy or information. This information can be read out at a later time, ranging from hours up to years after exposure. This read-out is accomplished by illuminating the sample with radiation of lower energy, typically green, red or infrared light, which empties the traps, eventually leading to optically stimulated luminescence upon recombination at a luminescent center. However, the occurrence of OSL is not limited to the above-mentioned storage phosphors, but manifests itself in all materials in which trapping takes place.

A class of materials that are of special interest are afterglow phosphors. They are usually excited using blue or ultraviolet light and the thermal energy at room temperature suffices to induce detrapping which leads to delayed emission long after excitation has stopped. This property makes them perfectly suited for applications such as safety signage, bio-imaging or glow-in-the-dark road markings [1]. To improve the performance of these phosphors, the amount of energy that can be stored during excitation needs to be improved.

Recently it was shown that OSL during the excitation, induced by excitation light, plays an important role during the charging of the persistent phosphors and that it is an important limiting factor of their storage capacity [2,3]. Therefore it is important to identify how OSL influences several key phosphor properties, with the quantum efficiency being particularly interesting. It will be shown that in the case of $SrAl_2O_4$:Eu,Dy the internal and external quantum efficiency depend strongly on the excitation intensity. This intensity dependence allows to determine the importance of OSL by excitation light. Furthermore it provides valuable insight on why this effect plays such an important role and it allows to identify experimental approaches that will enable further improvement of persistent phosphors. Implications for the field of phosphor converted LEDs are discussed.

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MODULATION OF PHOTOCURRENT BY DUAL EXCITATION IN INDIVIDUAL GAN NANOWIRES

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Persistent photoconductivity effect with several thousands of seconds growth and decay times have been observed in GaN nanowires. This long response time, which is believed to be due to the entrapment of photo generated holes at the surface, is the reason for high photocurrent gain reported in this system. However, too slow a recombination is also not desirable from application perspective. It is thus important to address the central question of how to make the photoresponse of GaN nanowires faster. One interesting strategy will be to de-trap the photo-excited holes by exposing the wires to a sub-bandgap light in order to influence the photoresponse. It is noteworthy that such an investigation has hardly been carried out in GaN nanowires.

Here, we investigate the photo-response of vapor-liquid-solid (VLS) grown m-axial $[10\ \overline{10}]$ individual GaN nanowires of diameter ranging from 30 to 100 nm under joint illumination of above and sub-bandgap lights. When illuminated with above band gap light, these wires show persistent photoconductivity (PPC) effect with long build-up and decay times. The study reveals a quenching of photoconductivity (PC) upon illumination with an additional sub-bandgap light. PC recovers when the sub-bandgap illumination is withdrawn. Interestingly, both the quenching and the recovery have much faster time scales as compared to PC growth/decay times. This observation can lead to the application of these wires for infrared photodetection purpose. A rate equation model attributing PPC effect to the entrapment of photo-generated holes at the surface states and the PC quenching effect to the sub-bandgap light driven release of the holes from the trapped states has been proposed. The average height of the capture barrier has been found to be about 400 meV. The study also suggests that the capture barrier has a broad distribution with an upper cut-off energy of ~2 eV

OXYGEN-SENSITIVE LUMINESCENCE OF RARE EARTH IONS IN TiO_2 THIN FILMS

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During the last decade a number of metal oxide nanomaterials have been found possessing a gas sensitive photoluminescence (PL). In particular, the PL of both intrinsic defects [1] as well as Sm^{3+} impurity ions [2] in TiO_2 nanostructures were shown to be sensitive to oxygen content in the ambient. Due to a moderate band gap of TiO_2 (~3.2 eV), a near-UV light can efficiently excite even thin layers of the material. Moreover, such semiconductor material allows integration of optical and electrical sensing. Therefore, TiO_2 nanomaterials constitute a promising platform for novel gas sensor developments. Suitable deposition techniques are needed to obtain thin porous films doped with various activator ions.

Hereby we applied pulsed laser deposition (PLD) to obtain thin (70–80 nm) TiO_2 films containing either Sm or Nd impurity ions (1–2 at%). The films were deposited at room temperature in oxygen atmosphere (0.05 mbar) and thereafter annealed at 800 °C, resulting in anatase phase. It was possible to excite both Nd^{3+} and Sm^{3+} fluorescence through an energy transfer upon excitation of TiO_2 host by 355 nm laser beam.

The PL of both impurity ions systematically responded to oxygen content over a wide concentration range (Figure 1). The intensity of Sm^{3+} emission increased monotonically with increasing oxygen partial pressure. This was attributed to elimination of PL quenching defects through a redox process caused by adsorbed O_2 [2]. Nd^{3+} emission followed such trend in the region of low O_2 pressure, but at certain intermediate O_2 concentration the dependence became reversed. We consider this behavior as being due to a concurrent process, possibly connected to the excitation path of Nd^{3+}.

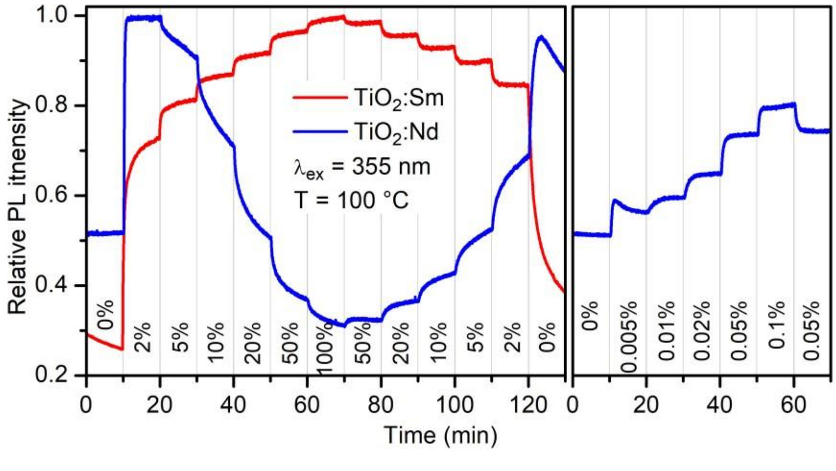

Figure 1: Development of Sm^{3+} and Nd^{3+} PL intensities with changing oxygen content in the flow of O_2/N_2 mixture at normal pressure (volume fraction of O_2 indicated).

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DEEP RED AND NEAR INFRARED PERSISTENT LUMINESCENCE IN RE^{3+} CO-DOPED $ZnGa_2O_4:Cr^{3+}$ GLASS CERAMICS

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With the aim of doing nano-probes for *in vivo* imaging, persistent luminescent materials take some advantages due to the absence of excitation light, limiting auto fluorescence. Several persistent luminescent materials have been designed to emit in one of the three partially transparent biological windows [1]. Owing to its persistent luminescence in the deep red range (696 nm), $ZnGa_2O_4:Cr^{3+}$ is a well-studied compound in view of this application. Glass ceramics (nanoparticles embedded in glass) elaboration remains a good way to obtain this compound at nano-metric scale [2], required for *in vivo* imaging applications. These materials possess efficient persistent properties [3]. Here we report a study on RE^{3+} co-doping in $ZnGa_2O_4:Cr^{3+}$ transparent glass ceramics with the aim to obtain persistent emissions at various wavelengths in the NIR range. The experimental results show that Yb^{3+} co-doped samples possess persistent luminescence emission in both the deep red range (Cr^{3+}) *i.e.* in the first biological window and the near infrared range (Yb^{3+}) *i.e.* in the second biological window. We also removed the nanoparticles from glass matrix by selective glass dissolution in reactive solution. This underlines the promising applications of such materials.

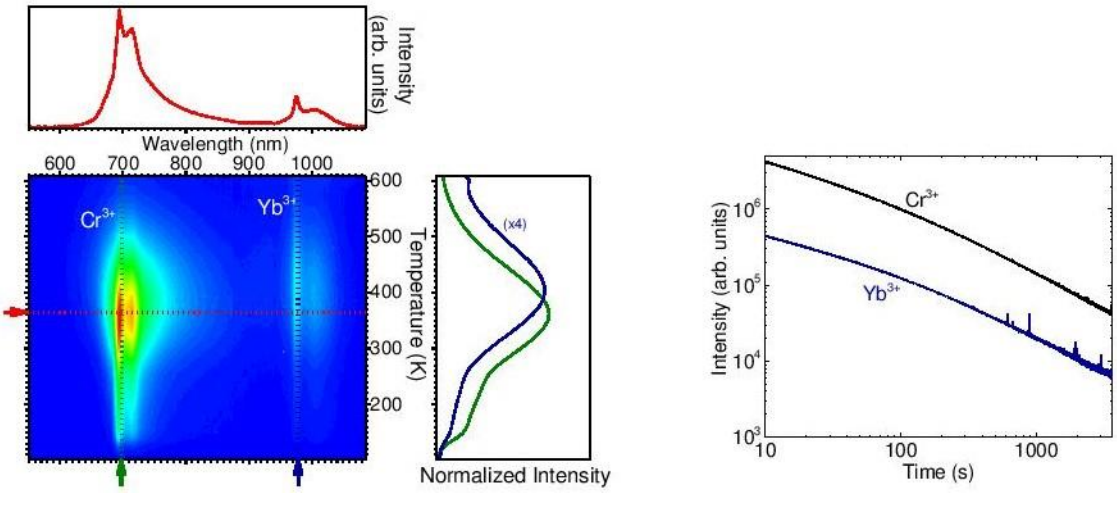

Figure 1. (left) 2D TL glow curve of ZnGa2O4:Cr^{3+},Yb^{3+} glass ceramics. (right) Afterglow decays of this sample monitoring Cr^{3+} and Yb^{3+} emissions at room temperature.

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THE CHALLENGE OF THE FABRICATION OF Y_6MoO_{12} CUBIC OPTICAL TRANSPARENT CERAMICS FROM NANO-CRYSTALS

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The main purpose of our research is to fabricate the first transparent optical ceramics based on rare-earth-doped cubic tungstates and molybdates. Up to now such ceramics were not reported but as they should benefit from mechanical, chemical and thermal resistance of these materials, they would be useful as laser materials, luminophores and scintillators. As we already succeeded to obtain the first translucent micro-ceramics from Yb^{3+}-doped La_2MoWO_9 [1-3] by using a very simple method (nano-powders were formed into tablets by pressing under pressure of 4 atm/5 min and sintered at 1200 °C/6 h under vacuum), we continue our analysis of cubic molybdates by selecting $Y_6MoO_{12,}$ another potential candidate to receive transparent ceramics. Previously, $Nd^{3+}/Eu^{3+}/Yb^{3+}$-doped Y_6MoO_{12} have already been studied by us in the form of nano- and micro-powders [4].

In this presentation we axamine the possibility to fabricate optical transparent ceramics on the base of un-doped nano-crystalline cubic Y_6MoO_{12} molybdate by using Spark Plasma Sintering (SPS) and Hot Isostatic Pressing (HIP) methods. To prepare ceramics the ultrafine nano-powders-with minimal thermal treatment were used. For all experiments the powders were prepared by combustion synthesis, which leads to very fine powders with nano-sized grains. As transparency is the goal, density of the ceramics must reach 99.99 % of theoretical value. As shown our studies, the application of the SPS method for Y_6MoO_{12} is quite complicated, because of the presence of metastable cubic phase and phase transformations (cubic-rhombohedral-cubic) during the thermal treatment under pressure and reductive atmosphere. Such ceramics showed decomposition of the phase and presence of oxygen vacancies what made black specimens. To apply HIP method, first it is necessary to get ceramics without open porosity (which is normally achieved with at least 94% theoretical density). As the densification by SPS is off the table for studied composition, the samples must be densified by natural sintering. The Thermomechanical Analysis (TMA) was made to determine the best sintering temperature. Nano-powders were shaped into pellets by uniaxial pressing followed by Cold Isostatic Pressing (CIP) and sintered in air atmosphere at 1550°C. The correlation between heating rate, mass loss and pellet density was found. The specimen with the best density and with closed porosity was choosen, but reductive atmosphere present in this method made the ceramics black. Performed experiments shown that more tests has to be performed to optimize the sintering process.

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UPCONVERSION FOR PHOTOCATALYSIS APPLICATIONS

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Photocatalysis is an efficient and simple way to drive a chemical reaction but it is generally limited by the necessity to use ultraviolet or deep blue light. In the recent years there has been strong efforts to modify catalysts materials so that their band to band absorption comes more to the visible part of the electromagnetic spectrum. This has led to the synthesis of the so- called black titanium oxide. An alternative option is to use infrared or visible light and through the use of upconverting materials to transfer the excitation to the photocatalytic material.

In the last years several groups have demonstrated that there could indeed be some transfer from upconverting materials to titania [1-5] leading to some increase in the photocatalytic efficiency. However this increase is still rather limited because of the low efficiency of the upconverting process in particular for generating UV photons equivalent excitation.

In order to optimize the transfer towards the photocatalyst it is important to optimize the doping geometry of the upconverting nanoparticles. To do so we developed a model of energy transfer of the excitation over long distances as shown on the figure below [6].

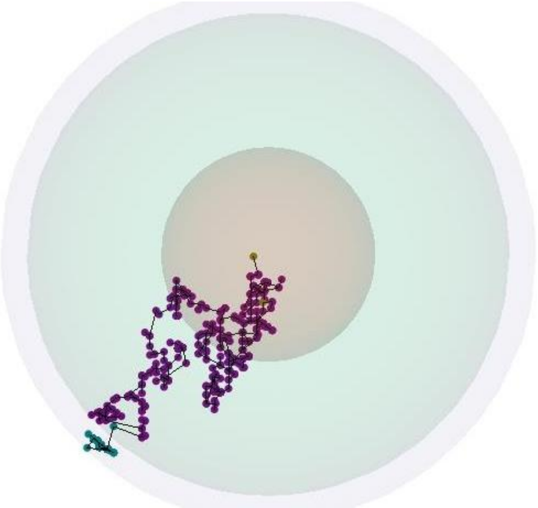

Figure 1 : projection of calculated tracks in a structure composed of a 4 nm radius core of $NaGdF_4$:Yb(50%)Tm(1%) surrounded by a first 5 nm thick shell of pure $NaGdF_4$ and a second 1 nm thick shell of $NaGdF_4$:Tb(15%). Only the ions participating to the track are shown, Tm^{3+} ions in yellow, Gd^{3+} ions in magenta and Tb^{3+} ions in cyan.

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COLLOIDAL CRYSTALS BASED PORTABLE CHROMATIC SENSOR FOR BUTANOL ISOMERS AND WATER MIXTURE DECTECTION

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In this work, we report on a structurally-colored composite colloidal crystal able to change its color in presence of different polar solvents such as butanol and to distinguish its isomers. Herein, polydimethylsiloxane (PDMS) infiltrated polystyrene opals are fabricated by means of a two steps approach and their final structure exhibits a green opalescence, the diffraction peak wavelength position changes as a function of the analytes spotted on the surface. In fact, the realized composites present a colorimetric variation in their response, since a remarkable red-shift of the diffraction peak is observed. An analytical model has been proposed and validated in order to assess the optical chromatic response, according to which the changing of the filling factor is the main element that produces the variation in the optical response. The selectivity, sensitivity and the reusability of the sensor have been investigated by monitoring the static reflectance spectra considering a mixture of 2- Methylpropan-2-ol (TerB) and water.

Dynamic reflection spectra (DRS) have been employed as an appropriate technique for the recognition of butanol isomers such as TerB, Butan-1-ol (NB) and Butan-2-ol (2B). The results demonstrate that the prepared photonic crystal sensing material and the interrogation approach used are a suitable tool for the development of low cost, portable sensors for homologues and isomers.

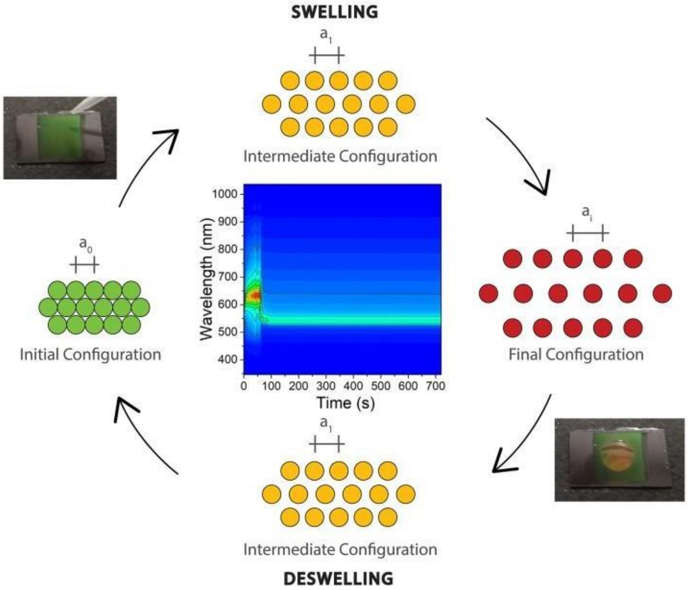

Figure: Sketch of the working principle of the chromatic sensor and typical DRS of 2-Methylpropan- 2-ol.

Acknowledgements

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SiO_2-SnO_2 GLASS-CERAMICS ACTIVATED BY RARE EARTH IONS FOR PHOTONICS

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Glass-ceramics are nanocomposite systems that exhibit specific morphologic, structural and spectroscopic properties allowing developing novel photonic devices, based on the enhancement of the luminescence, critical for integrated optics, quantum cutting, down-shifting, frequency converters, laser, detectors and light emitting systems.

Among diverse materials that could be used as nanocrystals to embed silica matrix, tin dioxide presents interesting characteristics. Tin dioxide has shown its outstanding properties for photonic applications, such as luminescence quenching reduction, wide transparent range from UV to NIR, luminescence sensitizing efficiency for rare earth (RE) ions and photorefractivity. Here we present sol-gel silica tin dioxide glass-ceramics system doped with rare earth ions. The energy transfer from the SnO_2 nanocrystals to the RE ions was proved by experiments and the results were clarified by the simulations on the structure and the bandstructure of studied system. The SiO_2-SnO_2 glass-ceramics in form of monoliths and planar waveguides have been fabricated and characterized for further processing into photonic devices.

This research activity is performed in the framework of the projects: COST MP1401 (2014 – 2018), Centro Fermi MiFo, ERANET-LAC FP7 Project RECOLA (2017-2019). L.T.N. Tran acknowledges the scholarship of the Ministry of Education and Training from Vietnam.

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ALD Al DOPED ZnO FILMS AS TRANSPARENT CONDUCTORS

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Transparent conductive films play an important role in optoelectronic devices such as thin film solar cells and light emitting diodes (LEDs), touch panel transparent contacts, static discharge dissipation, and IR windows. Most of these films are n-type wide band gap metal oxides like Sn-doped indium oxide (ITO). Films of Aluminum-doped Zinc Oxide, (AZO), are electrically conductive and have the property of high transmission in the visible region and acceptable transmission to IR wavelengths. AZO is a promising replacement transparent conducting oxide (TCO) for ITO for all corresponding applications [1].

In order to achieve high quality transparent and highly conductive AZO film, ALD is one of the best available deposition techniques. AZO films with different doping concentration are deposited using Beneq TFS-200 system in thermal mode from DEZ and TMA precursors. The electrical and optical properties of Aluminum-doped Zinc oxide films are investigated by sheet resistance measurements, spectrophotometry and spectroscopic ellipsometry, respectively. X-ray photoelectron spectroscopy (XPS) is used for measuring the elemental composition, chemical state and electronic state of the elements in AZO films.

AZO films with the best figures of merit, according to the measured optical and electrical properties, are implemented as transparent electrodes in liquid crystal display devices. The electro-optical modulation characteristics of these devices are measured and compared to those of devices using commercial ITO electrodes to prove the feasibility of AZO as an alternative low-cost and with high performance transparent conductor.

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OPTICAL PROPERTIES OF Dy^{3+}-BASED CRYSTALS FOR VISIBLE LASER APPLICATIONS

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Yellow-emitting lasers are of great interests in medical and scientific research fields. However, techniques to achieve yellow laser emission are to date limited. Frequency conversion of Nd^{3+}-doped gain media can provide laser emission in the yellow spectral range whereas the slope efficiencies are typically a few percent. Dy^{3+}-doped crystals have been considered as potential gain medium for high-efficiency yellow lasers owing to the largest branching ratio of the yellow emission band. In recent years, blue-diode-pumped Dy^{3+}-lasers based on oxide or fluoride crystals have been demonstrated, which give slope efficiencies more than 10% [1- 3]. This motivates us to study the spectroscopic properties of Dy^{3+}-doped crystals to evaluate their potential for visible laser applications.

Single crystals of Dy^{3+}-doped $CaYAlO_4$, $Ca_2Al_2SiO_7$, and $YCa_4O(BO_3)_3$ were grown in our laboratory [4]. Optical spectroscopic characterizations were concentrated on the optical transitions in the visible spectral region. Ground-state absorption spectra of these crystals show that the $^6H_{15/2}\rightarrow{}^4I_{15/2}$ transition at around 453 nm exhibits the largest transition cross- sections in the visible and matches the output wavelength of commercial blue laser diode pumps. The peak absorption cross-sections were measured to be 3.3×10^{-21} cm^2, 1.6×10^{-21} cm^2 and 1.8×10^{-21} cm^2 in Dy:$CaYAlO_4$, Dy:$Ca_2Al_2SiO_7$, and Dy:$YCa_4O(BO_3)_3$, respectively. These values are comparable to the reported Dy^{3+}-based gain materials. Furthermore, the broad spectral linewidth in Dy:$CaYAlO_4$ and Dy:$Ca_2Al_2SiO_7$ deriving from their disordered structure makes them superior for broadband LD pumping. The maximal emission cross- sections of the yellow $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition around 580 nm were found to be ca. 1.5×10^{-21} cm^2 in Dy:$Ca_2Al_2SiO_7$ and Dy:$YCa_4O(BO_3)_3$ while Dy:$CaYAlO_4$ gave a much high value of 4.0×10^{-21} cm^2. Nevertheless, emission cross-section of 2.7×10^{-21} cm^2 at 759 nm was observed in Dy:$YCa_4O(BO_3)_3$, which is the largest value among these materials. Fluorescence decay curves of the $^4F_{9/2}$ excited state were recorded. They exhibit a non-exponential decay behavior due to the cross-relaxation process. Judd-Ofelt calculations were performed to obtain the radiative lifetime. Dy:$CaYAlO_4$ yields the largest quantum efficiency of more than 50%. The Judd-Ofelt analysis also reveal that the $^6H_{15/2}\rightarrow{}^4I_{15/2}$ transition has a relatively large contribution from the magnetic dipole transition. This is proved by the significant anisotropy of magnetic dipole transition observed in the polarized absorption spectra.

In conclusion, Dy:$CaYAlO_4$ shows the best spectroscopic properties for yellow laser application. On the other hand, an exceptionally strong emission line at 759 nm was found in Dy:$YCa_4O(BO_3)_3$, which is interesting for laser operation as well.

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OPTIMIZING THE EXCTRACION EFFICIENCY OF EMISSION FROM SINGLE InAs/InP QUANTUM DOTS AT TELECOMMUNICATION WAVELENGTHS

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One of the main challenges in the development of efficient solid state quantum emitters suitable for long distance secure communication in fiber networks is brightness of the source limited mainly by the photon extraction efficiency. In case of standard homogeneous medium, the emission from nanostructures as epitaxial quantum dots is in principle isotropic, which for standard optical detection system means that the fraction of the collected signal is on a level of a few percent, at the best. The issue of small efficiency of photon extraction can be overcome by engineering nano or micro photonic structures, which can induce a directionality of emission due to cavity effects, i.e. by coupling with the cavity modes that leak out in a specific direction. At short wavelengths below 1 µm, many approaches have evolved allowing to increase this collection efficiency by more than an order of magnitude. However, the record ones could be achieved by using the coupling of the emitter to electromagnetic field of a high quality factor microcavity, which is a technologically challenging approach and requires a precise control and tunability of the relative quantum dot and cavity mode energies to get them into resonance very narrow spectrally resonance. The latter makes it rather inefficient in the sense of practical exploitation of naturally inhomogenous quantum dot systems whereas the former becomes even more difficult at longer wavelengths.

In this work, we discuss a spectrally broadband approach using the photonic environment in a form of simple mesa structure of cylindrical geometry. We model the material system of InAs on InP which is the most suitable for the telecommunication range, especially the 3rd low-loss transmission window at 1550 nm. We focus on optimizations leading to a collection of high fraction of dipole emission along the growth direction as used for common detection alignment, and we evaluate the extraction efficiency neglecting the Purcell effect due to low finesse of the considered cavity-like photonic structures.

We used finite-difference time-domain numerical calculations [1] to characterize the emission pattern from a dipole placed in cylindrical mesa structure made of InP or InGaAlAs matrix in dependence on mesa geometry, dipole position and numerical aperture of the collecting optics. We performed calculations for two cases, for pure InP substrate and after including an InP/AlGaInAs distributed Bragg reflector underneath the mesa structure. We demonstrated that extraction efficiencies of at least 12 % and 32 % are achievable, which is significantly beyond state-of-the-art in this spectral range and also exceeding those reported for InGaAs/GaAs structures [2]. We also address the robustness of the approach and low sensitivity of the extraction efficiency to particular geometrical parameters or especially the emission wavelength in the range of 1.3-1.55 µm at least.

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LEAD FREE NEW PEROVSKITES: BAND GAP ENGINEERING

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A key challenge in current photovoltaic arena is the design of lead-free new materials which can act as an absorber for solar cell as well as LED applications. $ABB'X_6$ is a family of newly discovered double perovskite systems which has elapsolite structure, where A=Cs, Rb, or Tl, $B=M^+$ monovalent cation and $B' =M^{3+}$ trivalent cation with high symmetric cubic kind of arrangements in the crystal structure. With A site being fixed as Cs, appropriate choice of B and B' cations along side X (the halogens; Cl, Br and I) allows one to realize a large variation in the physico-chemical properties of these new perovskites. For example, Cs_2AgBiX_6 (with a band gap of 2.2 eV) is considered the one of the most promising optoelectronic candidates given their Shockley-Quiesser limit, a theoretical maxima of photo-conversion efficiency (PCE) of 16.4%.

Synthesis of these compounds is not straight forward and remains an extremely challenging task. Recently, we found a novel room-temperature method for the synthesis of Cs_2BBiBr_6 (B = Ag, Na, K) double perovskites. Next, the fabrication task was extended to B site variation to silver, sodium and potassium. We aim to generalize this process to other compounds which can render a suitable band gap with high absorption coefficient. Additionally, we have prepared, under room temperature conditions only, Pb doped $Cs_2BB'X_6$ perovskite to tune the band gap to direct. We have kept the Pb concentration to the lowest possible limit. The idea of lead doping originates from the nature of Pb p-states, which usually occur at a lower energy (in the conduction band) and reduce the band gap as compared to those of the parent CS2BBiBr6. From our first principles calculation, Pb is also found to help in changing the band gap from indirect to direct in various double perovskites. The optical properties such as absorption coefficients and simulate efficiency also turn out to be promissing, and hence our choice.

Besides the currently explored platform to improve the absorption properties, based on A site substitution (organic methyl ammonium is popular choice to inorganic), we aim to develop original compound based on variations in B site sublattice, thus allowing to tune/enhance the optical absorption. Various elemental B-site substitution will be first checked by ab-initio calculations. Based on the calculated stability, band gap, optical transition probability and absorption properties, selected compounds will be chosen for further characterization.

LUMINESCENCE BLINKING BEYOND NANO-CONFINEMENT: THE CURIOUS CASE OF PEROVSKITE MICROCRYSTALS

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Temporally random, discrete photoluminescence (PL) intermittency between bright and dark intensity levels, designated blinking, has been long recognized to be characteristic of single quantum-emitters. Apart from molecules, a variety of quantum-confined semiconductor nanocrystals also exhibit photoinduced blinking, generally attributed to Auger ionization-recombination leading to charging-discharging of NCs, or to long-lived carrier trapping in surface traps. However, luminescence intermittency is seldom reported beyond nanoscale dimensions because (*i*) spatiotemporally uncorrelated emission intensity fluctuations average out over the ensemble, and (*ii*) contributions of surface-states in radiative-recombination processes are far less significant compared to that of the bulk. There are a few rare examples where multi-level intermittency is exhibited by spatially extended (~µm) yet nano-confined (1 or 2 dimensional) systems [1-3], however, such fluorescence blinking dynamics is almost overwhelmingly found to be spatially heterogeneous, *i.e.*, spatiotemporally uncorrelated.

Using real-time (25 Hz) fluorescence video microscopy under ambient conditions, we investigated various organo-metal (hybrid) halide perovskite microcrystals (MCs), some of which have been earlier shown to exhibit PL blinking in local nanodomains [4]. Here, we present a highly unusual phenomenon, where entire individual methylammonium (MA) lead bromide ($CH_3NH_3PbBr_3$) MCs, bulk polycrystalline materials (volume ~0.1-3 μm^3) with no dimensional confinement, undergo discrete and prominent intensity fluctuations between multiple levels on top of a slow (>sec) time-varying base [5]. Further, abrupt PL blinking is found to be spatially-synchronous across each MC, which is astonishing because this implies extremely long-range (>µm!) communication amongst majority of photogenerated carriers at distal locations in each crystal. Such remarkable long-range correlation in intra-crystal blinking is attributed to extensive delocalization of carrier wavefunctions, and is perhaps intricately related to high carrier diffusion propensities reported for hybrid halide perovskites. This intriguing observation is explained using a phenomenological model which invokes the formation and removal of few metastable non-radiative traps which act as quenchers. Highly mobile charge carriers anywhere in the crystal can recognize the presence of, and efficiently migrate to these quenching sites, leading to abrupt, albeit temporary, intensity fluctuations over entire individual MCs. While further investigations are necessary to indentify the exact nature of the metastable quenchers as well as understand the role of organic (MA) cations in concerted blinking o hybrid halide perovskites, our results hopefully, will stimulate theoreticians to ponder upon and elucidate alternate possible mechanism(s).

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SCINTILLATION AND OPTICAL PROPERTIES OF ORGANIC CRYSTAL SCINTILLATORS WITH A HIGH MELTING POINT FOR α-PARTICLES DETECTION

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ZnS:Ag has a high light output of ~198,000 ph/5.5 MeV (α) for alpha particles, while ZnS:Ag has a slow decay time of 1-10 μs [1,2]. Although organic scintillators have lower light output than ZnS:Ag, pulse-height of the direct signal from photo-detectors, like a photo-multiplier tube (PMT), can be higher than ZnS:Ag due to faster scintillation decays of ~ns, typically, for organic scintillators. Also, organic scintillators can detect alpha particles or neutrons with low gamma-ray background noise, because of the low atomic number and density than ZnS:Ag or other inorganic scintillation materials. On the other hand, conventional organic scintillators, such as trans-stilbene, have a low melting point (397 K: trans-stilbene), and alpha-ray measurement at over 370 K cannot be operated. Thus, in this paper, we investigated scintillation and optical properties of the novel organic scintillators with a higher melting point for alpha particles monitor in nuclear reactor plants.

Trans-stilbene, pure benzoic acid, 1,4-bis(2-methylstyryl) benzene (bis-MSB)-doped benzoic acid, and pure BisMSB crystals were grown by the self-seeding vertical Bridgman (SSVB) method using an enclosed chamber [3]. Here, the melting points of trans-stilbene, benzoic acid, and bis-MSB were 397, 395, and 454 K, respectively.

After cutting and polishing, pulse height spectra and scintillation decay curves for these sample excited by 5.5-MeV alpha rays from an ^{241}Am source were recorded with a PMT (R7600U-200, Hamamatsu Photonics). The bis-MSB crystal had the fastest decay time of ~4.2 ns and light output of ~6,700 ph/5.5 MeV(α). We also measured temperature dependence of photoluminescence intensity for the BisMSB crystal at between 298-398 K using the integrated sphere and the spectrophotometer (detail of the setup is described in [4]). The emission wavelength was 474 nm (excitation wavelength: 260 nm) originated from the π-π* transition and the luminescence intensity of bis-MSB was constant up to 398 K (Fig.1). Therefore, bis-MSB can be applied to detection of alpha particles which requires a high counting rate of up to 398 K.

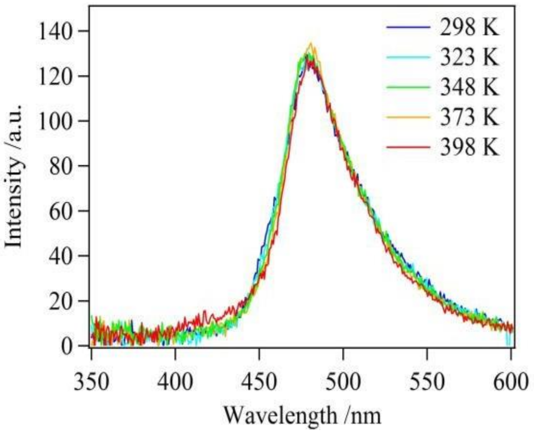

Fig. 1 Temperature dependence of photoluminescence intensity for bis-MSB crystal at between 298-398 K

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LUMINESCENT PROPERTIES OF ALUMINA CERAMICS DOPED WITH MANGANESE AND MAGNESIUM

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An experimental study of the optical properties of materials is important for understanding the structural state features and predicting the properties of new functional materials. The introduction of various dopants into the initial matrix of the material leads to a significant change in the luminescent properties that depend on the impurity concentration [1-2]. Oxide systems with various dopants currently have promising applications in the form of ceramics.

Alumina ceramics were manufactured with 2 hours sintering of compact at varying temperatures in vacuum (0.013 Pa) 1500-1700 ºC and in air 900-1500 ºC. Compacts were produced by cold static pressing under pressure 0.5-0.7 GPa from high purity (99.5 %) nanopowder α-Al_2O_3 and were impregnated in solutions of magnesium and manganese nitrates with concentration: 0.001-6.85 wt. % Mg and 0.001-18 wt. % Mn in solution.

Pulsed cathodoluminescence (PCL) was measured in the spectral region (350-770) nm by spectrometer "Klavi" at excitation of an electron beam with the pulse duration of 2 ns and the average energy of electron 130±10 keV. Photoluminescence (PL) measurements were carried out on the Perkin Elmer LS-55 luminescent spectrometer. Termoluminescence (TL) measurements were performed by the dosimetry system "Grey" in linear heating in range 300-670 K by photomultiplier HAMAMATSU Photonics (Japan) H10722.

PCL spectra of ceramics doped with both impurities have luminescent centers with the maximum at 420 nm (F-center of Al_2O_3) and with the maximum at 693 nm (R-line of Cr^{3+} impurity ions). A band peaked at 540 nm is associated with center of Mg impurity in ceramics doped manganese and a band peaked at 676 nm – doped centers of Mn. The PL spectra measured with different concentration of impurities were shown correlation with PCL spectra. It was shown that an increase in the concentration of dopant leads to an increase in the luminescence intensity of the emission band of the impurity and a decrease in the inner-alumina band, that is, there is a quenching of the luminescence in the 420 nm band. The TL peaks at 380 K and 580 K can be associated with complex aggregate centers as intrinsic defects obtained as a result of annealing and impurity centers. Both peaks depend on the temperature of the sample synthesis and on the concentration of dopant.

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OPTICAL PROPERIES OF Cr-DOPED β-Ga_2O_3 AS RED AND NEAR INFRA-RED EMISSION SCINTILLATORS

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Radiation therapy has been widely used to treat the tumor. However, it is said that some medical accident occur due to over dose [1]. Thus, real-time dose-monitoring system is expected to suppress the accident. Here, human body has an optical transparent area around near infra-red region (650 to 1200 nm), and using this "window", a novel real-time dosimeter system can be developed with infra-red emission scintillators; When X rays or other radiation particles for medical use generate the scintillation light in the infra-red scintillator, the luminosity or count rate of infra-red scintillation light can be read out of the patient. Since the dose is related to the luminosity or count rate, we can measure the dose with a real time. The previous study of near infrared scintillation materials has not been investigated well, and light outputs are not enough for the medical use. Since β-Ga2O3 (thin film) has smaller bandgap of approximately 4.9 eV [2] compared to the conventional oxide scintillation crystals (e.g. Lu_2SiO_5: ~6 eV, Al_2O_3: 8.8 eV), Cr^{3+}-doped β-Ga_2O_3 is expected to have good light output. Thus, we report the optical and scintillation properties for β-Ga_2O_3 materials.

Cr-doped and un-doped β-Ga_2O_3 crystals were grown by the floating zone method, and we confirmed the single crystal phase and compositions by powder X-ray diffraction analysis and with an electron-probe micro analyser, respectively. All samples had broad emission bands in the red and infra-red region when excited by both 450 nm photons and X rays which were associated with $^4T_2 \rightarrow A_2$ transitions.

Since Cr-doped sample have long decay times of over 10μs, single photon counting method to estimate the light output is hard. Comparison of the intensity of radio-luminescence spectra have large error to estimate the light output, because the intensity depends on X-ray source intensity and shape/size of the sample. X-ray source have fluctuations of the X-ray intensity (flux), especially Pyroelectric type. We have developed a novel evaluation-device consisting of a complementary metal oxide semiconductor (CMOS) camera and lenses; to obtain the image, size effect can be suppressed relatively, and we used radiation sources like an ^{241}Am source as an excitation source as a constant-flux radiation-emitter. Using this device, we found the light output of Cr: β-Ga_2O_3 had twice as large as that of Cr: α-Al_2O_3 [3] which is conventional red-scintillator. We show the above results, and discuss the feasibility for the medical use.

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DETERMINATION OF HIGH QUANTUM YIELDS IN RHODAMINE B-DOPED ORGANIC/SILICAMONOLITHIC XEROGELS

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The study of thermal and optical properties of modern materials based on laser dyes incorporated in inorganic and inorganic-organic hybrid hosts is an area of technological interest with applications in random lasers, solar concentrators, sensors, etc. [1],[2]. Research conducted over the last few decades has focused on new hybrid materials, as sol–gel-derived organic/silica. However, there are few reports in the literature about absolute quantum yield determination of luminescent dyes in solid matrix.

Rhodamine B (**RB**) doped hybrid organic/silica sols were prepared with 3-glycidoxypropyltrimethoxysilane (GPTS) and tetraethylorthosilicate (**TEOS**), with RB homogeneously dispersed [1]. The sol samples were dried and RB concentrations in the solid matrix (monolithic xerogel) were determined, ranging from ~ $(0.04 – 19.3)\times10^{-3}$ mol/L. Thermal Lens (**TL**) measurements were performed in the mode mismatched configuration with 543 nm excitation laser [3].

TL spectrometry, as well as all photothermal methods, relies in the measurement of the fraction of absorbed energy converted in heat, which in turn is proportional to quantum yield ($\boldsymbol{\eta}$). Figure 1 shows the results of η and the fraction of monomers (estimated from the emission spectra) for RB-doped GPTS/TEOS xerogel samples. Maximum quantum yield (η~ 91%) were obtained for concentration up to 0.2 mmol/L, them the yields decrease to η ~ 82 % for concentration up to 5mmol/L. The quantum yields decrease with concentration similarly to the monomers fraction. However, the η values of the dye dimmers are quite high indicating that the formation of non-fluorescent aggregates was prevented in this matrix.

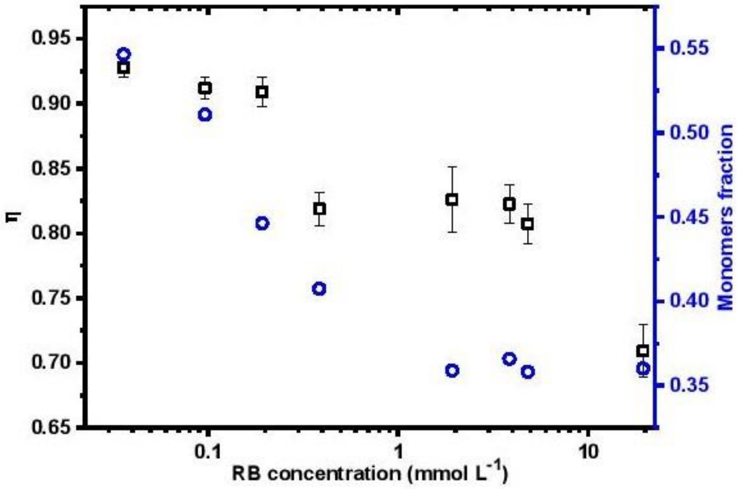

Figure 1. The $\eta$and monomer fraction data values for RB-doped GPTS/TEOS xerogel samples.

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NON-QUADRATIC RELATION BETWEEN INTRINSIC AND UPCONVERSION LUMINESCENCE

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Grant's rate-equation model [1] assumes that migration of excitation among neighboring ions is infinitely fast, establishing a "sea" of excitation. It implies that the rate R_{ETU} of an energy-transfer upconversion (ETU) processes involving two ions in the same level i scales quadratically with the level population density N_i, $R_{\mathrm{ETU}} \propto N_i^2$. More sophisticated models [2–5] imply somewhat more complex relationships. Nevertheless, all these models treat active ions spectroscopically equally, thereby assuming a homogeneous ion distribution, such that the upconversion luminescence follows a relationship with the intrinsic luminescence, as given by the model.

Here we demonstrate a fundamentally important spectroscopic effect that is directly related to the usually non-homogeneous distribution of ions in a host material. At reasonably low dopant concentrations some ions are isolated, hence do not participate in ETU, whereas other ions have neighbors and can, in principle, participate in ETU. The measured intrinsic luminescence is the sum of both classes of ions, whereas the upconversion luminescence is emitted only by ions from the second class. This de-correlates the two luminescences from each other, thereby leading to a fundamental deviation from the assumed law of upconversion (Fig. 1), e.g. the quadratic dependence mentioned above. Our theoretical considerations have been verified experimentally by measuring intrinsic infrared decay and yellow upconversion decay of Nd^{3+} ions in two host materials with various dopant concentrations and modelling the luminescence decays by a stochastic model for the ion distribution [6].

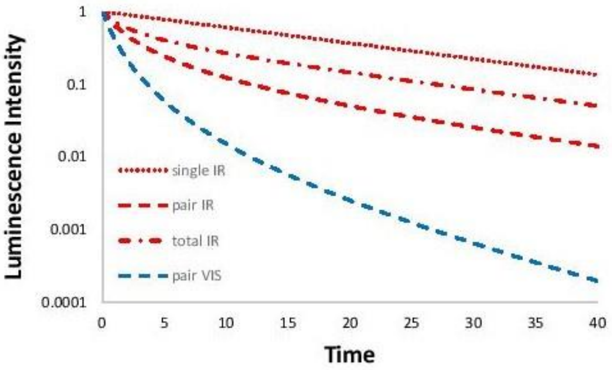

Fig. 1. Intrinsic infrared (red lines) and visible upconversion (blue line) luminescence decay. *Dotted red line*: intrinsic decay from single ions. *Dashed red line*: intrinsic decay from ions with neighbors. *Dashed-dotted red line*: total intrinsic decay when assuming 30% of single ions. *Dashed green line*: upconversion decay from ions with neighbors.

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Z-SCAN AND THERMAL MIRROR MEASUREMENTS IN Tb^{3+} DOPED ALUMINOSILICATE GLASSES

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Time-resolved Z-scan and Thermal Mirror measurements were performed using an cw Ar^+ laser at 488 nm, close to the resonance of $^7F_6 \rightarrow ^5D_4$ absorption, where $^7F_6$ is the ground state and $^5D_4$ is the first metastable state of Tb^{3+} (lifetime 1.9 ms). A strongly nonlinear dependence of the amplitude of the Z-scan signal with incident intensity (I) was observed and attributed to the high excited state absorption cross section, two order of magnitude higher than the ground sate one [1]. Consequently, the refractive index change (Δn) was expressed as a power series $\Delta n = n_2.I + n_4.I^2 + \ldots$ A similar strongly nonlinear behavior was observed in the photothermal signal (thermal mirror) and attributed to the heat released after excited state absorption (ESA) in resonant with the $4f \rightarrow 5d$ transitions of Tb^{3+} (~ 36.000 cm^{-1}) and the band gap of glass host matrix. Most of heat release is due to the energy transfer from the excited of Tb^{3+} ion to the host matrix. In the luminescence spectra, saturation of the green emission from $^5D_4$ level at relative low intensities (~ 2×10^4 W/cm^2). This behavior is also attributed to ESA process [2]. Moreover blue upconversion luminescence was observed from the $^5D_3$ level.

Excellent discrimination of electronic and thermal contributions of the measured refractive index changes (Δn) could be obtained by the combination of time-resolved Z-scan and Thermal Mirror techniques. The Z-scan signal is attributed to the electronic effect, caused by the polarizability difference, $\Delta\alpha_p$, between the excited (metastable) and ground states of Tb^{3+}, $^5D_4$ and $^7F_6$, respectively [2]. Therefore, n_2 is proportional to $\Delta\alpha_p$ and analogously, the real part of n_4 is related to $\Delta\alpha^*$, the polarizability difference between the second excited state ($^5D_3$) and the ground state. We obtained $\Delta\alpha_p \sim 7\times10^{-25}$ cm^3, this value is one order of magnitude larger thanobserved in other rare earth doped materials. Moreover $\Delta\alpha^* \sim 7\times10^{-24}$ cm^3 is one order of magnitude than $\Delta\alpha_p$.

The $\Delta\alpha_p$ and $\Delta\alpha^*$ decrease by one order of magnitude with the increase of Tb^{3+} concentration, from 1.9×10^{19} to 1.4×10^{21} cm^{-3}. It is remarkable the similarity between this behavior and the decrease of area in UV transition (277 nm) observed in the excitation spectra and, attributed to the $4f \rightarrow 5d$ transitions. Moreover, $\Delta\alpha_p$ and $\Delta\alpha^*$ decreases strongly with the increase of silica content in the glass matrix composition, which decreases the cut off absorption wavelength from 340 to 280 nm. All results indicate the high sensitivity of $\Delta\alpha_p$ and $\Delta\alpha^*$ to the crystal field, confirming their relation with the 5d levels which are not shielded.

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TRANSPARENT OPTICAL CERAMICS BASED ON RARE EARTH IONS- DOPED CUBIC TUNGSTATE/MOLYBDATE MATRICES: A CHALLENGE AND PROSPECTS FOR NEW EFFICIENT OPTICAL MATERIALS

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Surprisingly, today available rare earth (RE^{3+}) luminescent ions-doped cubic optical transparent ceramics used as laser sources or phosphors for lighting are limited to a very small number. The main objective of this project is to select carefully new RE^{3+} luminescent ions-doped tungstate/molybdate chemical compositions, fulfilling two conditions, cubic crystallographic system and size of the crystallites up to 100 nm, different of usual garnets, sesquioxides or fluorites, owing to their long longevity, low cost, and excellent chemical stability. The choice of RE^{3+} ions has been Nd^{3+} and Yb^{3+} for IR and visible lasers and Eu^{3+} for red phosphors. The host lattices, in which the substitution of optically un-active trivalent La^{3+} or Y^{3+} by RE^{3+} ions will take place have been preferred. For each composition, nano-powder materials are researched by various methods: Pechini, combustion, hydrothermal, methods and high-temperature solid state reaction [1-4].

The results on both synthesis and spectroscopic characterizations of Nd^{3+}, Eu^{3+} and Yb^{3+} -doped La_2MoWO_9, $La_2Mo_2O_9$ and Y_6MoO_{12} nano and micro-powder solid solutions will be presented. Our attention is now focused on both, the crystal growth by using the micro-pulling down method (µ-PD) and the fabrication of transparent ceramics by the fast SPS (Spark Plasma Sintering) and the slower but efficient HIP (Hot Isostatic Pressing) techniques.

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EFFECTS OF COHERENT RADIATION ON THE SPECTRAL AND LUMINESCENT CHARACTERISTICS OF WHEAT SEEDS

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In recent times, steadily growing interest to action of coherent radiation on plant organisms. Main interest in this problem is due to need to clarify the fundamental aspects of interaction with the biosystem, and applied tasks [1,2]. The interaction of coherent radiation with plant organisms leads to certain photobiological reactions. In this paper, we present the results of an investigation influence of coherent radiation on luminescence properties of wheat seeds.

Irradiation of wheat seeds with monochromatic radiation, the generation wavelength λgen = 650 nm., was performed using a continuous semiconductor laser. The desity of radiation power in working area is 2.3 mW. Exposure time 10-900 sec.

Registration of excitation and fluorescence spectra of the samples were performed by spectrometer SM2203 (Solar). The excitation and fluorescence spectra of wheat seeds were measured in holders for solid samples. Photoexcitation of luminescence of wheat seeds at a wavelength λ equal 440 nm. The luminescence spectrum of wheat seeds has a maximum of intensity at a wavelength λ_{max}= 505 nm., and half-width of spectrum $\Delta\lambda_{1/2}^{emiss} = 72nm.$

It is established, when photoexcitation the wheat seeds, observe increase the intensity of emission. Increases intensity of emission to some critical value (t=240s), and further increase irradiation time lead to decrease intensity of luminescence.

Kinetic characteristics of fluorescence were measured by the time-correlated photon counting method when the samples were excited by a diode laser (λ_{gen} = 488 nm, τ = 40 ps). Measurements have shown that the logarithmic curves for the decay of the luminescence of non-irradiated wheat seeds have a nonlinear dependence throughout the entire time range of the measurements. In this case, two linear sections with different luminescence lifetimes can be distinguished in the kinetics. The lifetimes of the excited states, obtained by approximating the damping curves by an exponential function, were τ_1 = 0.51 ns and τ_1 = 1.1 ns, respectively. The lifetime of the luminescence of wheat seeds after irradiation with coherent radiation varies with respect to the lifetime τ_{fl} without irradiation.

It is established, germination and grow energy of wheat seeds from duration time of irradiation has some extremum. The increase of germination of wheat seeds from duration time of irradiation. The duration time of irradiation begined with 30 s., and this indicator significantly changing. The maximum value of germination and energy of germination of wheat seeds reaches in a range of irradiation time 30, 160, 240 s. The germination of seeds increased to 12,0 % beside control sample (88,0 %) and amounted to 100,0 %.

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ALLOYED HALIDE DOUBLE PEROVSKITES AS NEXT PROMISING MATERIALS FOR SOLAR ABSORBERS

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Solar energy plays an integral role in supplementing the need of renewable energy. Silicon, in its various forms, covers almost 90% of today's commercial photovoltaic energy production. But manufacturing and installation processes for silicon devices are still quite expensive. As such, finding novel materials for solar cell applications is an elemental part of photovoltaics research. Hybrid Lead halide perovskites ($CH_3NH_3PbI_3$) are one of the well sought material in recent past. From 3.8% efficiency in 2009,[1] it has now reached an efficiency of 22.1% .[2] Yet, the main negative issues, i.e. stability in external environment and toxicity of Pb remain a concern. This led to a search for alternative materials. Double perovskite materials have gained some attentions recently, but most of these materials either have indirect band gap or direct but large optical band gap. So, the next possible direction is to find a way to either decrease the optically allowed band gaps or to engineer and acheive direct nature of band gap.

We propose a way to make indirect-direct band gap transition via orbital matching by small Pb^{+2} doping at both B and B' sites in Cs_2B(Cu, Ag, Au)B'(Sb,Bi,Sc,Y) X_6 (X=Cl,Br,I) double perovskites. This kind of doping has helped to change the topology of band structure triggering an optically allowed transition. It also reduces the band gap significantly, bringing it well in the visible region. Simulation reveals comparable/higher absorption coefficient and solar efficiency with respect to the state of the art photovoltaic absorber material $CH_3NH_3PbI_3$. Our experimentally measured properties for one of the material, $Cs_2(Ag_{0.75}Pb_{0.25})(Bi_{0.75}Pb_{0.25})Br_6$ agrees fairly well with the theoretical predictions. This material is shown to be even more stable than $CH_3NH_3PbI_3$, both under the humidity (~55%) and temperature (T=338 K). With better stability and optical properties, we propose these materials to be the next most promising material for solar absorber and help to significantly advance the field of photovoltaic research.[3](This work is recently accepted in Physical Review Materials)

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BULK CRYSTAL GROWTH OF Ce DOPED $Gd_3(Ga,Al)_5O_{12}$ SINGLE CRYSTAL FROM THE MELT IN THE COLD CRUCIBLE

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The GAGG:Ce scintillator - $Gd_3(Ga,Al)_5O_{12}$:Ce, was developed in 2011 [1], become well known to be attractive material for application in many fields such as nuclear science, industry, environmental monitoring, gamma ray astronomy, and medical imaging [2]. The scintillators are known to have high density (6.63 g/cm^3), good light output - between 40.000 and 55.000 ph/MeV - and fine energy resolution, even as good as 3.7% at 661.7 keV, [3].
Recently, it is found that the Mg^{2+} codoping in GAGG:Ce improve the light yield and acceleration of decay time [4]. This effect is starting to be understood [5,6]. In the discussion, fine discussion is carried out using small amount of co-doping, defects, charge valence. However, so far, all the crystals were grown in Ar or N_2 atmosphere and this atmosphere generate large amount of oxygen vacancy and Ga vacancy. The atmosphere is selected not for the nature of the GAGG, but for protecting the iridium crucible from oxidation.
In this study, iridium crucible was NOT used and GAGG:Ce were grown in AIR. Cold crucible pulling (CCP) method is used for the single crystal growth. This method is the fusion of skull method and Czochralski method. Higher frequency was used to heat the GAGG melt directly and crystal were pulling from the melt. In the presentation, detail of CCP method will be reported. The luminescence and scintillation properties of GAGG:Ce grown in air will be presented comparing the GAGG:Ce, GAGG:Ce,Mg grown in Ar or N_2 atmosphere.

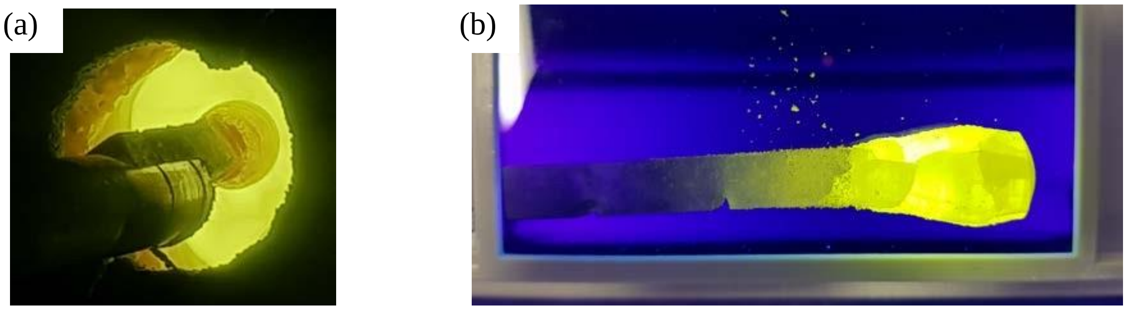

Fig. 1 (a) Photo of crystal growth with CCP method. (b) GAGG:Ce grown from the CCP method. Yellow emission is observed by UV exitation.

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FLUORESCENCE AND TIME DELAYED LASING DURING ONE LASER PULSE EXCITATION OF A MM-SIZED RH6G DYE DROPLET

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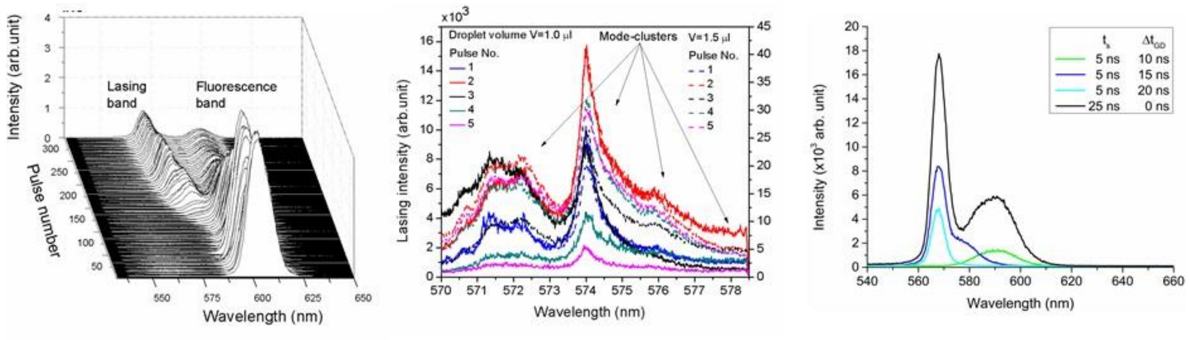
Fluorescence and lasing emissions that are produced separately in time during 532 nm excitation with single laser pulse of a water solution of Rhodamine 6G (Rh6G) presented as pendant microliter droplet is reported. Fluorescence amplification due to internal reflections in the droplet which behaves as an optical resonator leads to lasing emission [1-3], shifted towards blue [4] and evidenced by a measurable mode structure [5] (Fig 1). Measurements of temporal evolution of droplet's emission along a single pulse excitation were performed by varying the spectrograph signal acquisition gate time width, global or sampling, and gate delay with respect to the start of 25 ns full time width of the pumping pulse (Fig. 1c). The characteristics of both peaks depend on solution concentration, pumping energy and emission- sampling time with respect to pumping pulse.



(a) (b) (c)

Figure 1. Emission spectra of 1 µl pendant droplet containing 5x10^{-4} M Rh6G solution in water: (a) blue-shift of lasing peak during consecutive laser pulse excitation at 8 mJ energy [4]; (b) high- resolution spectra analysis of lasing peak at 18 mJ excitation energy [5]; and (c) fluorescence and time-delayed blue-shifted lasing emission during one laser pulse excitation at 18 mJ excitation energy. In (c) sampling spectra were obtained keeping the acquisition gate time width t_s= 5 ns and modifying gate delay Δt_{GD} in steps of 5 ns, and the global one keeping t_g= 25 ns and fixed Δt_{GD}= 0 ns; each spectrum is measured for a single droplet and laser pulse.

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Acknowledgements
The present research was supported by UEFISCDI through the projects PN-III-P2-2.1-PED-2016-0420, PN-III-P2-2.1-PED-2016-0446 and MCI by the Nucleu programme, project LAPLAS 5/2018.

DYE-SENSITIZED DOWNCONVERSION

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Downconversion, also known as quantum cutting, has attracted much attention due to the potential application in photovoltaic cells. The downconversion materials placed on the front surface of solar cell are able to harvest the far above-bandgap light and split a high-energy photon into two photons that can still be absorbed by the solar cells. This is an avenue to realize current (and thus efficiency) doubling for the high-energy (blue, UV) part of the solar spectrum.

Even though downconversion has been demonstrated for a variety of materials, downconversion materials are still far from practical application. Downconversion materials rely on lanthanide ions. Their low absorption cross sections result in low excitation efficiency and only a small fraction of the solar spectrum can be harvested. Therefore, enhancing the efficiency by means of broadband absorption by so-called sensitizers is crucial. An important class of sensitizers, organic dyes, has been extensively investigated in upconversion materials because of the 3-4 order of magnitude higher absorption cross section, but so far not for downconversion. In this work, we demonstrate dye-sensitized downconversion with a proof-of-concept experiment. Luminescence spectra and decay lifetime measurements show the occurrence of Förster resonance energy transfer from dye molecules absorbed on the surface of $NaYF_4$:Pr,Yb nanocrystals to Pr^{3+} in nanocrystals, followed by energy transfer to two neighboring Yb^{3+} ions with emission of two infrared photons. The $NaYF_4$:Pr,Yb nanocrystals have ~30 times stronger infrared emission intensity after dye-sensitization. The decrease in lifetime of the dye emission after coupled to the nanocrystal surface serves as evidence for energy transfer and can be used to quantitatively determine the efficiency of Förster resonance energy transfer. The present study demonstrates the feasibility of dye-sensitized downconversion and the strategy can be used to enhance the downconversion efficiency for a wide range of lanthanide doped materials.

TALBOT CARPETS BY ROGUE WAVES

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Rogue waves are giant nonlinear waves that randomly appear and disappear in oceans and optics. Talbot carpets are ordered recurrent images of linear light and plasma waves. We demonstrate how to produce Talbot carpets by rogue waves.

EFFICIENT ENERGY TRANSFER IN TRANSPARENT NANOSTRUCTURED RE^{3+} DOPED SOL-GEL SiO_2-LaF_3 GLASS-CERAMICS

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As it is known the luminescence efficiency of rare-earth (RE) doped materials strongly depends on their local environments, responsible for multi-phonon decay rates, population of metastable energy levels, energy transfer (ET) and cross-relaxation (CR) processes. In this sense the use of low phonon energy hosts are desirable to avoid quenching intermediate energy levels. Fluorides exhibit low phonon energies when compared with oxides, which considerably reduces multi-phonon transitions, and so increasing the lifetime of excited RE doping ions. However, RE ions exhibit lower Stark splitting, narrower excitation spectra and, consequently, a lower absorption from the ground to excited levels. Thus, fluorides hosts become suitable candidates for RE doping ions, since they favor long excited lifetimes and high absorption cross-sections.

Oxyfluoride nano-glass-ceramics (nGCs) present the excellent optical properties of fluorides with higher quantum efficiency, higher optical cross-section absorption, and good mechanical, electric, dielectric and magnetic properties than other reported hosts. The advantages of these materials are based on the incorporation of RE ions into fluoride nanocrystals, with smaller size than

We have successfully obtained, sol-gel derived nano-glass-ceramics containing undoped and Ce^{3+}, Gd^{3+}, Tb^{3+} and Eu^{3+} single or co-doped LaF_3 nanocrystals, after adequate heat treatment of precursor glasses. X-ray diffraction and high-resolution transmission electron microscope images confirmed the precipitation and distribution of nanocrystals, with controlled size dispersed, in an amorphous silica network. Characteristic UV and VIS emissions were obtained and modulated as a function of doping level, taking advantage of the involved energy transfer mechanisms. Results suggest these materials have potential applications as efficient UV to VIS converters.

THERMAL EFFECTS ON RAPID MICROWAVE SYNTHESIZED GREEN EMITTING Mn^{2+} DOPED $ZnAl_2O_4$ PHOSPHORS

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Green emitting $Zn_xMn_{(1-x)}Al_2O_4$ nanoparticles were synthesized for the first time through a microwave assisted method in just 10 minutes using metal organic precursors. Crystalline and phase-pure material with average crystallite size of ~5 nm was obtained in the as prepared form at a reaction temperature as low as 185 °C. The sample with $x = 0.005$ showed maximum photoluminescence (PL) emission intensity at 512 nm for a $\lambda_{ex} = 458$ nm and this was used to study the effects of annealing on the structural and optical properties of the material. Annealing in air until 1000 °C gradually increased the crystallite size to ~30 nm and also changed the colour tone of the material, attributing to the diffusion of Mn^{2+} into the host matrix. The emission spectra comprised of an intense green band centered at 512 nm, originating due to the $^4T_1 \rightarrow {}^6A_1$ spin allowed transitions of tetrahedral Mn^{2+}, the intensity of which increased with annealing temperature. Spectroscopic parameters such as the crystal field splitting parameter (Dq) and the Racah parameter B, calculated from the excitation spectra and the Tanabe-Sugano diagrams, confirmed the presence of Mn^{2+} in a weak tetrahedral symmetry. The novelty of this work lies in the simplicity and swiftness of the microwave assisted synthesis that can be extended to other ceramic phosphors suitable for display and W/LED applications.

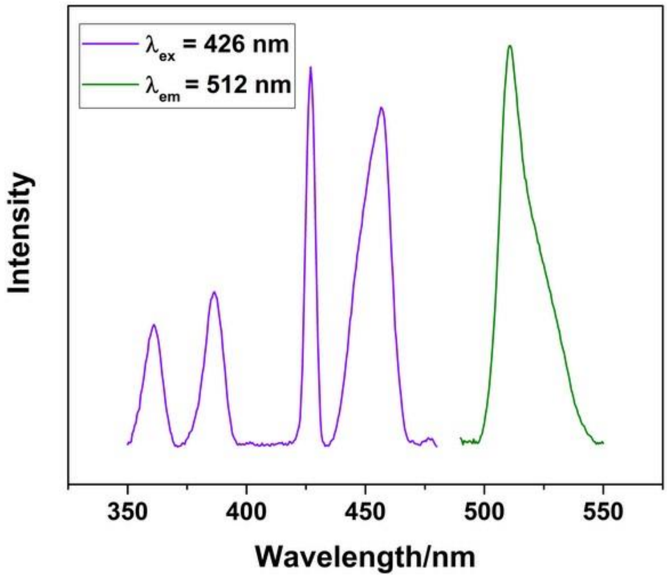

Fig. 1 PL excitation and emission spectra of $Zn_{0.995}Mn_{0.005}Al_2O_4$ nano powders annealed at 1000 °C for 2 h

INNOVATIVE BIOMATERIALS FOR APPLICATION IN PHOTONICS

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Limited mineral materials resources associated with their pollution problems push at present the interest of scientists onto biological materials which originate from renewable resources and are biodegradable. Among them the biopolymers like deoxyribonucleic acid (DNA) and collagen show very interesting properties as possible matrices for active molecules, being able to replace synthetic polymers [1] and bring more. These biopolymers are extracted from the waste of food processing industry and their sources are practically unlimited. However, their degradation time, if unprotected, is much faster than that of synthetic polymers in similar conditions.

On the other hand, the scientists turn also their attention to natural photosensitive materials, which can be extracted from flowers or fruits, like anthocyanines showing some interesting photosensitive properties for photonics applications.

In this presentation we will describe and discuss the results of our study on bio-active molecules present in the nature made materials like: green tea, sea buckthorn, marigold, cranberries and blueberries extracts. It is well known that they exhibit a significant antioxidant activity.

In this context, the deoxyribonucleic acid (DNA) and collagen were functionalized with vegetable extracts in aqueous solution. Bovine collagen is extracted from the skin of dead cows, sterilized and liquefied. The obtained material is soluble in water and form good optical quality thin films by spin coating and solution casting. The optical properties were characterized by UV –VIS spectroscopy [2, 3].

The nonlinear optical (NLO) properties of functionalized thin films were studied by the optical third harmonic generation (THG) technique at 1064.2 nm fundamental wavelength. The results of spectroscopic studies and THG measurements indicate that the studied complexes are promising material for biophotonics.

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WAVEGUIDE EVANESCENT FIELD MICROSCOPIES: WEFF AND WEFS MICROSCOPY

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Two evanescent field microscopy technologies based on slab waveguides with coupling gratings were developed: Waveguide Evanescent Field Fluorescence Microscopy (WEFF) and Waveguide Evanescent Field Scattering Microscopy (WEFS). The technologies are clearly described and discussed. The various advantages of the waveguide method in comparison to classical TIRF and TIR, e.g. possibility to determine quantitative data, are addressed. Various applications with biological and material science aspects for WEFF and WEFS microscopy are presented. With a two mode approach the location of a fluorescence dye above the waveguide surface can be determined allowing to create dye-distance maps. If the plasma membrane of a cell is stained, quantitative distance data on the cell's adhesions and the membrane bending between adhesions can be gained. WEFS microscopy can easily be applied for bacterial colony formation screening and for monitoring bacteria sterilization, e.g. by UV irradiation. An outlook into the newest developments for user friendliness and waveguide chip development for mass production are discussed.

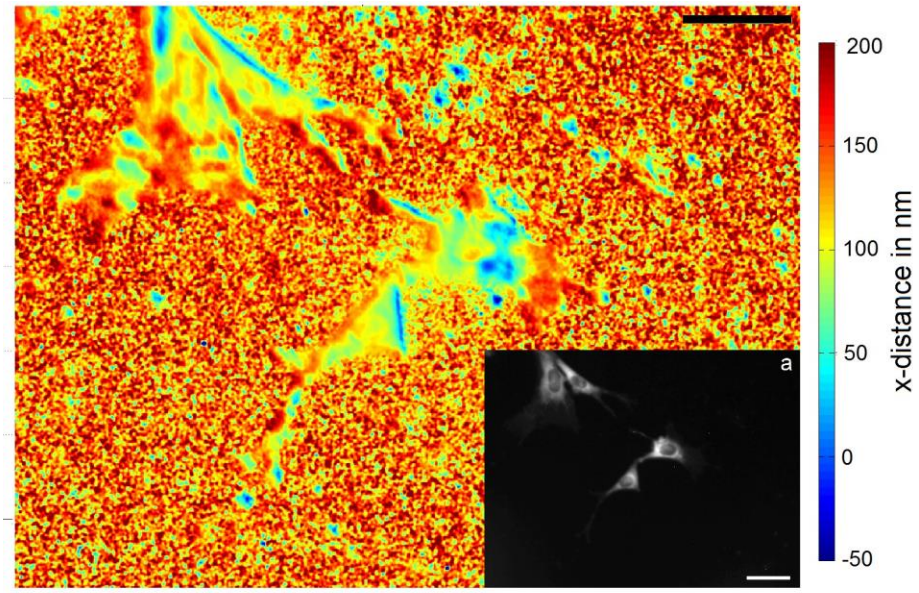

Fig. 1 False color representation of a dye distance map with four osteoblasts. The inset represents an overexposed WEFF image of the same field of view. Osteoblasts appear at dye/plasma membrane distances between ~ 75 to 110 nm. Dye locations very close to the surface, adhesion areas, are labeled blue. Both scale bars represent 50 μm. The color bar shows a range from - 50 nm to 200 nm. One pixel is equal to (0.266 μm)^2.

HUGE STABILITY ENHANCEMENT TO RADIATION OF Bi DOPED $MAPbI_3$ HYBRID PEROVSKITE

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The extraordinary efficiency values reached with MAPbI3 (MA: CH3-NH3) based photovoltaic cells has recently boosted the efforts in the search of new hybrid perovskite alternatives for photovoltaic energy production. These perovskites have in common a high sensitivity to ambient atmosphere (especially water and oxygen) and to visible irradiation that strongly handicaps their stability. Obtaining more stable compounds as well as understanding the complex behavior of the band-to band emission upon illumination and time are main concerns to be tackled. The photoluminescence behavior is strongly sensitive to different parameters, especially to the presence of defects and traps whose evolution with time is related to ion migration and perovskite transformations [1, 2].

In the present work, BiI_3 is introduced in the synthesis of the MAPbI3 films to stabilize the compound. Films with nominal Bi content up to 33% were obtained and studied by x-ray diffraction (XRD), profilometry, SEM, EDX, optical absorption and micro- photoluminescence (with 488 nm laser excitation).

The incorporation of Bi^{3+} in the perovskite lattice up to around 7 at% at the Pb^{2+} site, which corresponds to 33% nominal Bi introduced in the synthesis, is demonstrated by x-ray diffraction. Bi doping produces a reduction of the tetragonal lattice parameters and favors a higher density of the films. Moreover the reduction of the unit cell volume produces a small increase of the bandgap in contrast to previous reported results. A spurious $MA_3Bi_2I_9$ phase is detected for nominal Bi > ca. 15% while the usual spurious PbI_2 phase in undoped films is not detected for any Bi doping.

The red band-to-band transition (Pb 6p $\rightarrow$ I 5p) around 770 nm is totally quenched upon doping while a NIR emission at 1300 nm is detected. However, for high enough power densities the red emission band raises with time with a rate which is dependent on the power density and the Bi content. This emission is stable for extremely high power densities compared to undoped samples. Bismuth induced novel effects in terms of emission and transport properties will be discussed and a mechanism to explain the origin of this increased stability will be proposed.

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LUMINESCENT CARBON NANODOTS DIRECTLY GROWN ON Si-BASED SUBSTRATES BY CHEMICAL VAPOR DEPOSITION

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In this paper, we report on a novel approach in which carbon nanodots can be directly grown on Si-based substrates by chemical vapor deposition. It is clarified by combining Raman, Atomic Force Microscope (AFM), and X-ray photoelectron spectroscopy (XPS) measurements that the carbon nanodots with the controlled diameters are uniformly distributed on the substrates. Photoluminescence (PL) measurement reveal that the carbon nanodots feature a sharp blue light emission. The PL peak position is almost independent of the nanodot size. This suggests that the photoluminescence of carbon nanodots should not originate from quantum confinement effect but from the surface effect of nanodots. Our work provides a promising simple approach to obtain luminescent carbon nanodot for practical applications.

INSIGHT INTO THE UV-NIR ENERGY TRANSFER MECHANISM IN $YP_{0.95}V_{0.05}O_4$:Yb^{3+}

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Energy transfer (ET) process from the vanadate group to Yb^{3+} involves the conversion of ultraviolet (UV) to near-infrared (NIR) and has been reported in a variety of host lattices. However, the ET mechanism is still under debate. First downconversion via cooperative energy transfer was proposed, resulting in emission of two NIR photons for every absorbed UV photon. Later single-step ET was proposed involving a one-to-one photon downshifting process. Here, we report experiments on the ET mechanism between the vanadate group and Yb^{3+} in YPO_4. Luminescence spectra and decay curves of the vanadate emission as a function of Yb^{3+} concentration provide strong evidence for single step energy transfer between the vanadate group and nearest neighbor Yb^{3+} ions. Temperature dependent measurements and the characteristic behavior of the luminescence decay curves (Fig. 1(a)) reveals that the ET process proceeds via exchange interaction. With the help of vacuum referred binding energy (VRBE) scheme, we conclude that the exchange mediated ET occurs from the $^3T_{1,2}$ excited state of vanadate group to the Yb^{3+} $^2F_{5/2}$ state. Based on these findings, we construct a configurational coordinate model depicting the energy transfer process (Fig. 1(b)).

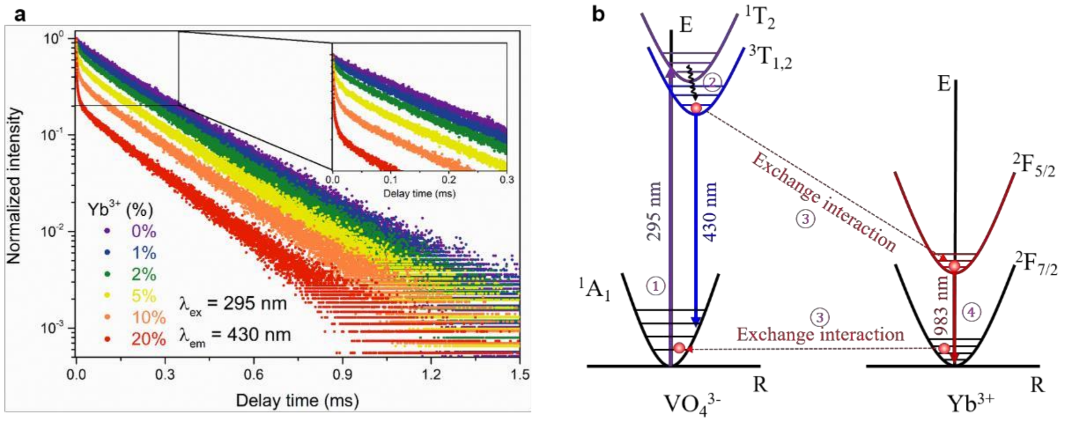

Fig. 1. (a) Luminescence decay curves of the vanadate emission in $Y(V,P)O_4$: x%Yb^{3+};
(b) A configurational coordinate model shows the energy transfer process via exchange interaction.

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DUAL MODE EMITTING Ho^{3+}/Yb^{3+} DOPED BaWO4 ENERGY HARVESTING MATERIAL FOR Si-SOLAR CELL APPLICATION

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Now a days, one of the most key issues to us is clean energy because of limited fossil fuel resources and enormous emission of greenhouse gas which is the main reason for global warming. It can be avoided using different kind of renewable energy sources for power generation. Photovoltaics (PV) is an advanced and well known technique that can directly convert solar energy into electrical energy. This technique can full fill our goal. Recently, silicon (Si) based soalr cells are dominating the power generation world. Though, it has some drawbacks in solar energy conversion efficiency. A huge purtution (70%) of solar spectrum loses by thermal and transmission losses due to the spectral mismatch between the solar cell response and solar spectrum. The efficiency of the solar cell can be increased by converting UV (250–400 nm) and NIR spectrum (800–1700 nm region) in to visible (500-750 nm) region which can be efficiently absorbed and appreciably convert in to electricity. Therefore, it is necessary to develop such material which can convert both UV and infrared region light in to visible region for efficient solar cell preparation. This purpose can be full filled by dual mode emitting phosphors. Rare earth doped down and up converting material can serve this purpose and avoid the energy harvesting problems in Si-Soalr cell. To achieve this goal, Ho^{3+}/Yb^{3+} doped BaWO4 phosphor was developed by using high temperature solid state reaction method. The crystal phase has been identified by using X-ray diffraction measurement. Crystal parameters have been calculated using Rietveld refinement method. The prepared material has been excited by both UV and NIR light source. Ho^{3+}/Yb^{3+} doped BaWO4 phosphor efficiently convert the UV and NIR light in to visible region. The conversion efficiency also calculated. Thus, the material efficiently behaves as a dual mode emitting phosphor. This technique can open a new dimension on energy harvesting for Si-solar cell.

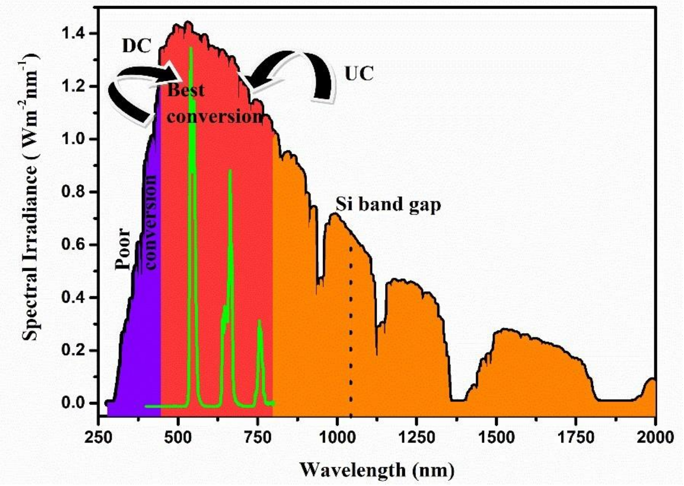

Fig: Dual mode emission of Ho^{3+}/Yb^{3+} doped BaWO4 phosphor

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SOFT CHEMICAL SYNTHESIS OF COMPLEX FLUORIDE NANOPARTICLES FOR WARM wLEDS

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Fabrication of warm white light-emitting diodes (wLEDs) with a high color-rendering index is considered to be a very important task from practical point of view. Currently commercial approach for production of wLEDs is based on addition of Eu^{2+}-doped red emitting complex nitrides [1]. Mn^{4+}-doped complex fluorides present promising and cheaper alternative for these materials, exhibiting strong narrow-line red luminescence in the desired region and having better chemical stability. The aim of the present work was to develop an approach to the synthesis of micro- and nanocrystalline powders of compounds of hexafluoride family A_2BF_6 (A = Na, K; B = Si, Ti) and $Na_3Al_2Li_3F_{12}$ garnet phase, both pure and doped with Mn^{4+}. In order to control morphology and preserve dispersibility of final particles we used soft chemical routes for their synthesis.

A_2BF_6 phases are probably the most popular fluoride hosts for Mn^{4+} ions. Nevertheless, vast majority of existing publications explore only one synthetic route of these phases. In this method preliminary synthesized particles of A_2MnF_6 are added to forming A_2BF_6 phase during its precipitation in water solution at room temperature. This leads to rather inhomogeneous distribution of dopant. Also low synthetic temperature results in high concentration of defects in the crystal structure of product. To overcome these drawbacks, we developed a new microwave-hydrothermal synthesis method for compounds of this family. It is based on treatment of gels, precipitated from true solution, which ensures better homogeneity of dopant distribution and a high degree of crystallinity.

Cryolithionite phase ($Na_3Li_3Al_2F_{12}$) is of significant interest as a member of the only family of inorganic complex fluorides with garnet structure. Unlike hexafluorides, where the anionic sublattice is built up of MF_6^{2-} structural units or other complex groups, in this compound it consists of single fluorine ions, while all metal ions occupy cationic positions.

We developed a new method for synthesis of microcrystalline A_2BF_6 and nanocrystalline cryolithionite powders. Cryolithionite nanoparticles show a high degree of crystallinity, almost dissagregated with sizes around 40-80 nm and, therefore, are suitable for microLEDs. Mn^{4+}-doped A_2BF_6 and $Na_3Li_3Al_2F_{12}$ particles exhibit photo- and cathodoluminescence in the range of 620-630 nm, which is optimal for red phosphors in warm wLEDs.

This work is supported by Estonian CoE TK141 "Advanced materials and high-technology devices for sustainable energetics, sensorics and nanoelectronics" and "NANOLED“ project funded by by the Estonian Research Council, the Russian Foundation for Basic Research (grant 16-52-76028 ERA_a) and BMBF (Germany) within the ERA.NET.Rus + programme.

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ULTRAFAST-LASER ERASING OF LASER-WRITTEN CRYSTALLINE TRACKS IN OXIDE GLASSES

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One of the promising methods of ultrafast-laser micromodification of dielectrics is space-selective crystallization of glasses providing growth of continuous crystalline architectures with functional properties in the glass bulk [1,2]. Optimization of laser treatment parameters and beam shaping enabled writing of nonlinear-optical $LaBGeO_5$ crystal-in-glass waveguides in lanthanum borogermanate (LBG) glass [3,4]. Very recently, we have suggested a technique of erasing a crystal-in-glass track in LBG glass by remelting the crystal with a high repetition rate femtosecond laser beam moving in a helical path along the track at a speed much higher than a maximal growing speed of a crystalline track [5]. We have also demonstrated re- writing the erased part of the crystalline track restoring its continuity that can be used for healing occasional cracks in crystal-in-glass tracks.

In the present study, besides $LaBGeO_5$, we applied this technique to other nonlinear optical phases including fresnoite $BaTi_2Si_2O_8$ and $LiNbO_3$ crystalline tracks laser-written, respectively, in $40BaO$-$20TiO_2$-$40SiO_2$ (BTS) and $33Li_2O$-$33Nb_2O_5$-$34SiO_2$ (mol.%) (LNS) glasses. Experiments on space-selective crystallization and further remelting of the crystalline tracks were performed using PHAROS SP laser emitting 180 fs pulses at pulse repetition rate of 200 kHz. The pulse energy used for remelting was close to that inducing crystalline track growth at low laser beam scanning speed (below 50 µm/s)

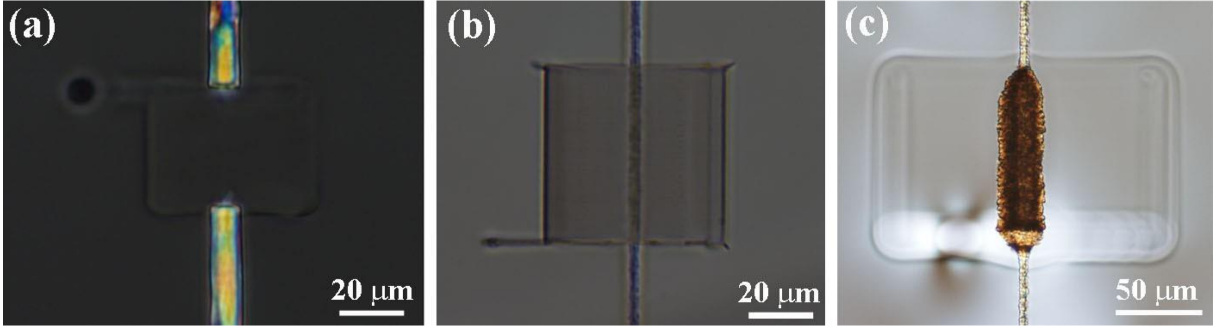

Figure 1: Cross-polarized optical images of remelted sections of crystalline tracks in LBG (a) and BTS(b) glasses, and a recrystallized track in LNS glass (c).

We have revealed that crystalline tracks consisting of $LaBGeO_5$ and $BaTi_2Si_2O_8$ phases corresponding to glass-forming compositions could be amorphised by the femtosecond beam (Fig. 1(a,b))., whereas remelting of a $LiNbO_3$ crystalline track was always followed by intensive recrystallization of $LiNbO_3$, showing that microdomains with non-glass-forming composition persisted after its laser-induced remelting (Fig. 1(c)).

This work was supported by the Russian Science Foundation (grant 17-73-20324).

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SURFACE PLASMON POLARITONS IN STRUCTURE OF GRAPHENE-ANTIFERROMAGNETIC (α-Fe_2O_3)

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Most of the magnetic materials are multicomponent systems. In the spectrum of its own magnetic oscillations of such systems, besides the usual acoustic modes, exchange modes are presented, which frequencies are comparable with the energy of exchanges fluctuations and lie in the infrared and visible spectral ranges. Exchange modes are electroactive. An example of such magnets can be an antiferromagnet α-Fe_2O_3. Nowadays, in plasmonics great researchers attention is paid to investigation of graphene-based nanostructures and perspectives of its applications in data processing and storage devices Research of nanostructures based on graphene and antiferromagnetic material will provide new opportunities for the management of their properties in the infrared and visible regions of the spectrum [1].

In this paper, the existence of a surface plasmon polaritons (SPPs) in the vacuum-graphene-antiferromagnet structure. In this paper, the conditions for the existence of SPPs are given. The dependence of the refractive index and attenuation coefficients on the magnitude of the external magnetic field and frequency is modeled. Three different geometries were investigated: ($\gamma \parallel Z$, $\beta \parallel Y$, $\vec{H} \parallel Z$), ($\gamma \parallel Y$, $\beta \parallel Z$, $\vec{H} \parallel Z$) и ($\gamma \parallel Y$, $\beta \parallel X$, $\vec{H} \parallel Z$). In this formulation, γ is the attenuation coefficient, β is the propagation constant.

In this work, the SPP propagation at the vacuum-graphene-antiferromagnet boundary was studied, the spectrum of these waves was investigated as a function of the magnitude of the external magnetic field and frequency. As an example of antiferromagnet α-Fe_2O_3 was considered. Its dielectric constant is a tensor and was taken from [2]. We also obtained dispersion equations for SPPs in the case of different geometries. The SPPs spectrum, propagation constants and attenuation coefficients are calculated. Conditions for the propagation of TE and TM modes are obtained. TM-modes are propagated at all frequencies. TE-modes propagate in a narrow range of frequencies and chemical potential values. We calculated eff:ective magnetic fields (the inverse Faraday effect) induced by SPPs in antiferromagnetic and dielectric layers.

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STUDY OF HYDROXYL GROUPS ABSORPTION IN TELLURITE GLASSES FOR FIBER OPTICS

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Tellurite glasses have high transparency in the near and mid-IR range and solubility of rare earths oxides, good crystallization stability, suitable viscosity and mechanical properties allow to produce high quality optical fibers [1,2]. Tellurite glasses, synthesized by conventional method from a mixture of oxides in a crucible at a relatively low temperature of 750-850 °C, usually contain impurity of hydroxyl groups with absorption bands near ~1.5, 2.3, 3-3.3 and 4.4 µm. The position, intensity and width of the bands depend on the OH concentration and glass composition. However, the use of purified oxygen inside a sealed reactor allows to minimize the concentration, and consequently the absorption of hydroxyl groups [2,3]. An important problem is not only to obtain glasses with a minimum hydroxyl groups content, but also the development of techniques for their determination and processing, especially at an extremely low level.

In this work, the absorption of hydroxyl groups in tellurite glasses and their effect on optical loss in fibers in the near and mid-IR spectral regions were studied.

Zinc and tungstate-tellurite glasses, including rare earths doped, with low hydroxyl groups content were synthesized in a sealed silica glass reactor in a stream of purified oxygen. To obtain the most dry samples, a small fluoride content was introduced into the initial batch. The samples with a higher hydroxyl groups concentration were also obtained using an oxygen flow with an increased water vapor content. Step-index optical fibers were produced from the glasses.

The glasses samples of different lengths were studied by the method of Fourier transform infrared spectroscopy, volume and surface absorption of hydroxyl groups at the band maximum near 3 µm were calculated using the Beer-Lambert-Bouguer law. The volume hydroxyl groups absorption in glass samples was as low as 0.001-0.003 cm^{-1} in the best samples. The hydroxyl groups concentrations were calculated using molar extinction coefficients. Optical losses in the fibers were measured by the cut-back method using immersion with an indium-gallium alloy, the minimal optical loss was at the level of several tenths dB/m in the mid-IR, reaching 2-3 dB/m at the peak of hydroxyl groups band near 3 µm. The work was supported by the Presidium of the Russian Academy of Sciences (basic research program № 32).

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OPTICAL PROPERTIES OF Er:Gd CODOPED CERIA NANOPARTICLE-POLYMER COMPOSITE THIN FILMS FOR WAVEGUIDE APPLICATIONS

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Over the last two decades, cerium oxide (ceria) as a host material has been investigated for various technological applications such as an electrolyte material of solid oxide cell fuel [1], electrochromic [2], up-conversion for bioimaging [3], solid state lasers, 3-dimensional displays [4], and photonics [5] when it is doped with luminescent lanthanides. However, some of other potential applications of this new host material could be optical sensing, optical waveguide amplifiers, and lasers in the visible and near-infrared (NIR) for optical communication, which have not been exploited yet. The attractive properties of doped ceria nanoparticles are low phonon energy (470 cm $^{-1}$), high refractive index (n=2.0 – 2.2), high transparency in the visible and NIR region, quick expedient transformation of the oxidation state of cerium between Ce(III) and Ce(IV), and high thermal stability. Furthermore, the absence of electrons in the CeO$_2$ 4*f* shells because of the charge transfer from O^{2-} to Ce^{4+} could be beneficial for an efficient photoluminescence (PL) host material in the NIR. The visible and NIR photoluminescence in ceria lattice doped with rare earth ions. While rare earth ions doped polymer materials have been studied extensively for their potential use in integrated optical amplifiers and lasers. However, the main technical challenges associated with this is the relatively poor performance of the rare earth conjugated complexes in polymer due to PL quenching comparing to inorganic glasses and crystals. Therefore a new strategy of incorporating rare earths in polymers through the dispersion of rare earth doped nanoparticles in polymer thin films is actively under research [6]. The physical and optical properties of the particles are important for this approach to be successful.In this paper we report the use of Er, Gd co-doped ceria (CeO2) nanoparticles (EGC) synthesis and their dispersion in siloxane polymer. The siloxane polymer-nanocomposite is then formed into thin films on silica substrate using spin coating technique. The surface morphology, and the compositional and structural characteristics of EGC and the nanoparticles-polymer thin films on silica substrate are investigated using scanning and transmission electron microscopy (SEM and TEM), TEM- energy- dispersive X-ray spectrometry, X-ray diffraction (XRD), and Raman spectroscopy. The excitation of Er^{3+} ions photoluminescence (PL) and lifetime measurements at 1534 nm using a 980 nm laser diode excitation exhibit strong PL signal and long lifetime for both bare nanoparticles and nanoparticle- polymer composite thin film on silica substrate. The properties of inorganic nanoparticles-polymer composite achieved open up a new opportunities for optical sensing and optical waveguide amplifier/laser devices engineering on polymer platform.

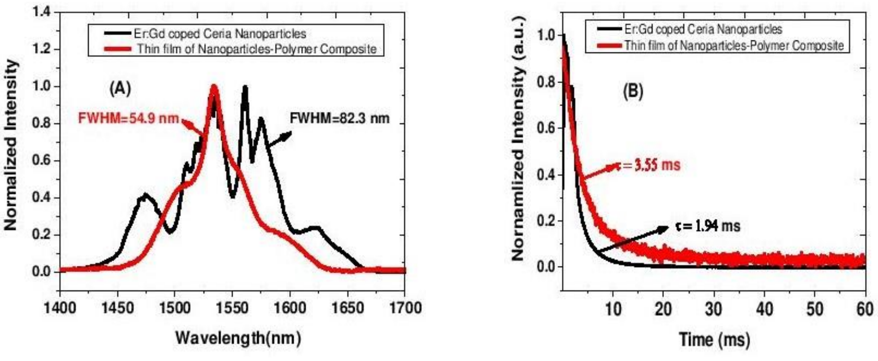

Fig 1. (A) Photoluminescence spectra of the 1.5 µm Er3+: ^{4}I13/2 – ^{4}I15/2 transition for Er:Gd co-doped Ceria nanoparticles and nanoparticle-polymer composite thin film on silica substrate and (B) Corresponding lifetimes.

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DESIGN AND OPTIMIZATION OF ABSORBER SECTION FOR MODE-LOCKED INTERBAND CASCADE LASERS

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Recently, a dual-comb spectroscopy has been brought to the mid-infrared spectral region by means of an actively mode-locked quantum cascade laser (QCL) [1], allowing for broadband field measurements with resolution of 0.0027 cm^{-1} around 7 µm. Although QCLs have become standard semiconductor laser sources in the mid-infrared above 4 µm the possibility of passive mode locked operation in the saturable absorber scheme is questionable due to the very short upper state lifetime [2]. In contrast, interband cascade lasers (ICLs) might be considered as an alternative since they exhibit relatively long (nanoseconds) upper state lifetime [3], operate in continuous wave mode up to 7 µm at temperatures above ambient and have much lower threshold current densities than QCLs, and still produce cw output power exceeding 500 mW. Thus, mode-locked ICLs would open a pathway for compact and low- power consuming optical sensing systems capable of detecting multiple transitions over a wide spectral range with high spectral resolution.

Hereby we present design and experimental verification of ICLs' absorber section for passive mode-lock operation in the fast saturable absorber scheme. In order to reduce upper-state lifetime in the absorber section two different approaches were studied based on band structure engineering and ion implantation. Both approaches assume employing fast saturable absorber (τ_a) scheme [4] with recovery time significantly faster than the pulse duration (τ_g), $\tau_a << \tau_g$. To realize that the semiconductor laser is divided into two parts with a common bottom contact. As a result two sections are present, the gain and absorber, and both might be biased individually. The former approach relies on the impact of external electric field on the oscillator strength (OS) of optical transitions. Since the assumption is to have significantly larger optical transition rates in the absorber section than in the gain section, the aim is to probe an active region design with large difference between the OS under the reversed bias (the respective carrier lifetimes are inversely proportional to the OS). Two designs based on asymmetric type II quantum wells will be compared. The first studied design utilizes a standard W-shaped band alignment, whereas the second one benefits from a triple quantum well design. In the latter approach the impact of the ion implantation on the ground optical transition will be studied. Three structures with different energy of the implanting ions will be compered from the point of view of the oscillator strength.

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TUNING PERSISTENT LUMINESCENCE PROPERTIES IN $Sr_{1-x/2}Al_{2-x}Si_xO_4$:$Eu^{2+}$,$Dy^{3+}$ TRANSPARENT CERAMICS

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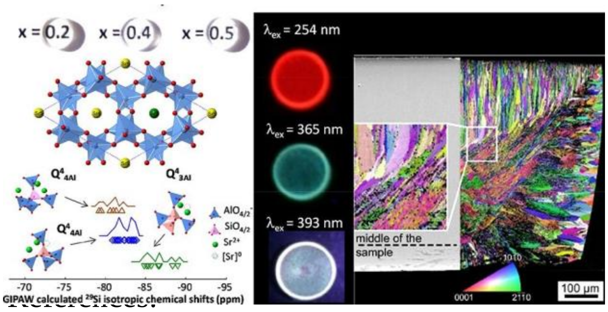
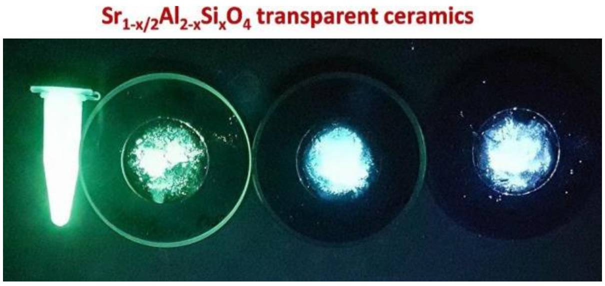
Transparent ceramics are an emerging class of photonic quality materials competing with single crystal technology for a diverse range of applications. They offer several advantages, particularly in the fabrication of complex shapes and large-scale industrial production, and enable greater and more homogenous doping of optically active ions than is possible in single crystals. However, up to date, only a limited number of cubic or nanocrystalline transparent polycrystalline ceramics requiring complex and expensive synthetic approaches has been reported.

Our recent work shows the possibility to elaborate innovative transparent ceramics by full and congruent crystallization from glass. This was demonstrated in the case of several new compositions showing transparency both in the visible and infra-red ranges.[1-3] Lately, we have focused our work on the development of hexagonal $Sr_{1-x/2}Al_{2-x}Si_xO_4$ transparent ceramics[4-6] which demonstrate tunable photoluminescence and afterglow emission when doped by Eu^{2+} and Dy^{3+}. The emission color can be tuned from green to white/blue when the silicon content is increased (see figure below for $0 \leq x \leq 0.6$ compositions).





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LOW VALENT URANIUM

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In contrast to the 4f elements, i.e. the lanthanides, the analogous 5f metals display a significantly larger range of oxidation states, at least with respect to the early elements in the row like uranium, neptunium, and plutonium. Of these latter elements uranium is certainly the best investigated because its radioactivity is low and it can be handled in an ordinary lab. Uranium exhibits the oxidation state +VI as the most common one, usually stamped by the appearance of the uranyl cation $[UO_2]^{2+}$. However, with respect to the properties the lower oxidation states are of interest because of the partially filled f orbitals of U^{5+} (f^1), U^{4+} (f^2), U^{3+} (f^3), and U^{4+} (f^4). It would be of interest to compare these configurations with their well known congeners within the lanthanide series. For this purpose we have started to prepare uranium compounds with different anionic ligands and we tried to address different oxidation states for the same ligands.[1-3]. The ligands are electronically innocents, e.g. simple halides, oxides, or oxoanions (Fig. 1). In this contribution we will discuss how the different compounds can be prepared and how their spectroscopic properties differ from those of related lanthanide compounds. Up to now we have investigated especially the halides of uranium, e.g. UCl_4 and UI_3, for spectroscopic measurements doped into appropriate host lattices ($ZrCl_4$, LaI_3). Furthermore, a number of oxoanionic compounds could be gained, for example the sulfate $U(SO_4)_2$ (Fig. 1) and two modification of the methanesulfonate $U(CH_3SO_3)_4$. These are the first non-solvated species with these anions known so far.

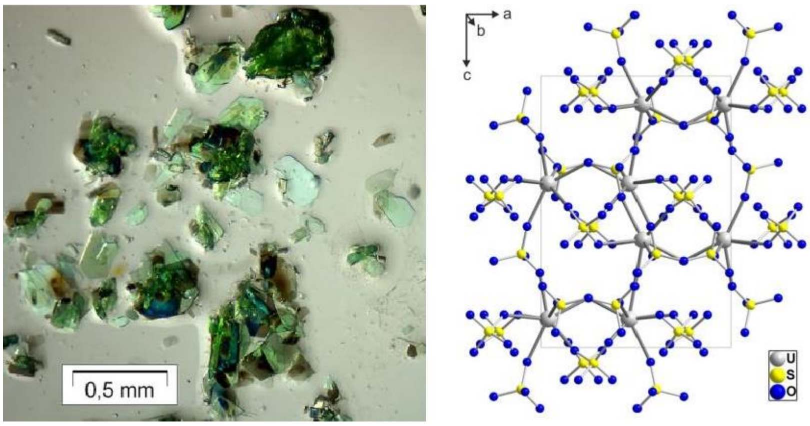

Fig. 1 Single crystals and crystal structure of $U(SO_4)_2$

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ROS GENERATION AND ANTIBACTERIAL PROPERTIES OF GO-ZrPc COMPOSITES

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The graphene family materials have been recently recognized as worthy of attention antimicrobial agents. To strengthen and broaden their mode of action against bacteria, various composites are tested. Proper composition and additional external stimuli, such as light, may result in high activity against multidrug resistant pathogens.

Novel composite materials based on graphite oxide (GO), silver nanoparticles (Ag), and different zirconium(IV) phthalocyanine complexes (ZrPc) are presented. Their optical properties (absorption and photoluminescence spectra) are examined. Optical techniques are used to show generation of reactive oxygen species (ROS). The activity of composites at ambient condition is compared with that under near infrared radiation. The antimicrobial properties are shown as well. The results show that ROS are generated by composites with ZrPc during irradiation. For selected strains, the antibacterial activity of tested materials was increasing in the following order: GO, rGO/Ag, GO/ZrPc, and rGO/Ag/ZrPc. The usefulness of these materials in antimicrobial photodynamic therapy, for example, in the case of wound infection or endodontic treatment, are discussed.

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VISIBLE LIGHT ABSORPTION OF SURFACE-MODIFIED WIDE BAND-GAP OXIDES: A COMPARATIVE DFT AND EXPERIMENTAL STUDY

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Surface modification of wide band-gap oxides such as TiO_2, CeO_2 and Al_2O_3, prepared using various synthetic routes (colloidal, sol-gel, *etc.*) with small colorless organic molecules, induces interfacial charge transfer (ICT) complex formation and the appearance of absorption in the visible spectral region. Comprehensive microstructural characterization of synthesized materials involving transmission electron microscopy, X-ray diffraction analysis, and nitrogen adsorption– desorption isotherms was performed. The attachment of catecholate-type of ligands (catechol, caffeic acid, gallic acid, dopamine and 2,3-dihydroxy naphthalene) and salicylate-type of ligands (salicylic acid and 5-amino salicylic acid) to the surface of wide band gap oxides leads to the formation of colored powders and activates their absorption in visible-light spectral region. The density functional theory (DFT) calculations with periodic boundary conditions were performed in order to estimate the energy gaps of various inorganic/organic hybrids. The calculated values compare well with the experimental data. The photo-degradation of different organic dyes and hydrogen production was used to test photocatalytic performance of synthetized hybrids.

SLOW SWITCHING DYNAMICS OF FLUORESCENCE INTENSITY FROM COOPERATIVE ENSEMBLE OF QUANTUM EMITTERS IN A DIELECTRIC HOST MATERIAL

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We propose a theoretical description of switching between distinct fluorescence regimes produced by a collective ensemble of emitters in a dielectric matrix. The intensity switching patterns correspond to the experimentally observed spontaneous transitions between one "dim" and several "bright" fluorescence regimes of an ensemble of color centers in a diamond microcrystal irradiated by a continuous wave laser light. Transitions are characterized by pronounced dynamics of growth and decrease in the intensity of the fluorescent signal on the seconds time-scale. The theory explaining the observed emitting regimes and transitions is based on the possibility for a cooperative ensemble of emitting centers inside a dielectric microcrystal to show intrinsic cooperative optical multistability. It is shown that the Maxwell-Bloch type equations describing such a system, in the presence of a considerable inhomogeneity of the ensemble and large values of the phase relaxation rate, retain the possibility of having several stable steady state solutions that form a multistable optical response for certain combinations of the pump power and concentration of the emitters. Alternative reasons for such a behavior are discussed.

ELECTROMAGNETIC MODELING OF THE LIGHT INTERACTIONS WITH ACTIVE LUMINESCENT MATERIALS

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The electromagnetic interaction of light with optical gain material is of great interest especially in the context of active luminescent devices. To understand the microscopic details of luminescent action in order to optimize the device designs, accurate simulations of the electromagnetic interaction with the active luminescent medium are required.

Thus, we here develop and report an auxiliary differential equation Finite-Difference Time-Domain (ADE-FDTD) computational model for understanding and simulating the underlying dynamics of population densities in optical gain medium. This model is based on a semi-classical quantum system of 6 discrete energy-levels, and the electron transitions between these quantized energy levels are governed by coupled differential rate equations and the Pauli Exclusion Principle. Each level-pair is simulated in this model by defining a macroscopic polarization vector and solving the quantum-mechanics-corrected polarization equation along with the classical Maxwell's equations.

Such a semi-classical approach allows efficient simulations without the need of a full quantum-mechanics calculation. By advancing into a more sophisticated 6-level quantum system, more realistic and physically meaningful simulations can thus be expected in comparison with the previously-reported 4-level algorithm [1]. This model is then utilized to model the lasing characteristics of a Distributed Bragg Reflector, a microdisk laser, and a Quantum Dot (QD) emitter embedded in photonic crystal micro cavity. The simulated results agree well with lasing theory. The technical details and numerical results are to be covered and discussed during the presentation.

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DESIGN OF CHIRAL LANTHANIDE HELICATES AND TETRAHEDRAL CAGES WITH CHIRAL OPTICAL PROPERTIES

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“Supramolecular diastereoselective phenomanence” to engineer high order chiral self-assembly architectures is an important area of research especially in the design and development of chiral functional materials for applications such as for catalysis and sensing functions. This has been especially hard in the case with lanthanide ions due to the issues of variable coordination number, kinetic lability and poor stereochemical preference of the lanthanide ions.

In our study of the formation of lanthanide tetrametallic supramolecular tetrahedral cages, we discovered that significant diastereoselectivity (only ΔΔΔΔ– or ΛΛΛΛ–τwisted conformation was observed with NMR) can be easily broken to significantly less diastereoselectivity (ΔΔΔΔ– and ΛΛΛΛ–twisted conformation) by slight alterations of (a) position or (b) steric bulkiness of point chirality at the ligands.

The self-assembly of europium (Eu) tetrametallic tetrahedral cages from three closely related chiral ligands based on the same diagonal 2,6-diaminoanthraquinone linked bis(pyridine-2,6-dicarboxamide) moieties is demonstrated to show very different supramolecular formation phenomenon. One ligand exhibits a high diastereoselective assembly of homochiral (either ΔΔΔΔ or ΛΛΛΛ) Eu tetrahedral cages where as two other ligands, with two different approaches of loosened point chirality, leads to a significant break down of the diastereoselectivity to generate a mixture of (ΔΔΔΔ and ΛΛΛΛ) isomers in ~ 1:1.06 to 1:1.20 ratios. Highly emissive (quantum yields: 16 to 19%) with strong circularly polarized luminescence (|glum|: up to 0.22) are also observed for the first time with these tetrahedral cages. In further studies it is also identified in an unprecedented case, to correlate the nonlinear enhancement of the chiroptical response to a nonlinearity dependence on point chirality.

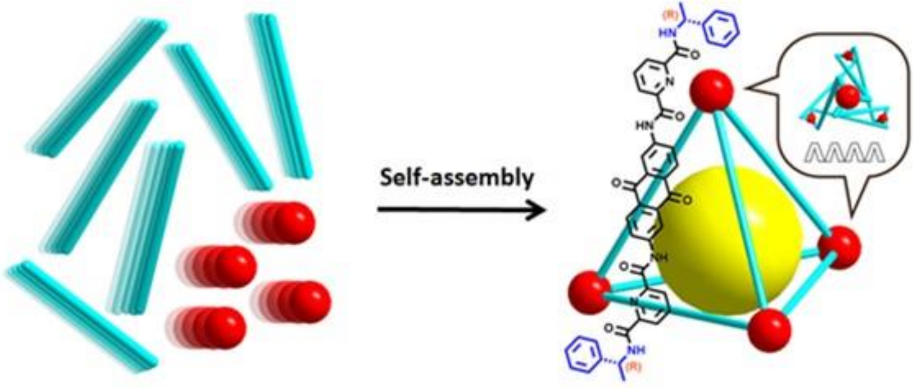

Figure 1. Schematic diagram showing the self-assembly formation of the Eu tetrahedral cages

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STRONG TiO2 SENSITIZATION OF Tb^{3+} BY PREVENTING Ti-Tb CHARGE TRANSFER QUENCHING IN SUBNANOMETER MULTILAYER STRUCTURES

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In many luminescent materials, strong absorption is desired. One of the stronger absorption mechanisms in oxide hosts are oxygen-to-metal charge transfer in d^0-transition metal oxides. Strongly absorbing materials with high luminescence efficiencies have been developed based on hosts such as $CaTiO_3$, YVO_4 and $CaWO_4$. Unfortunately, they cannot be combined with Ce^{3+}, Pr^{3+} or Tb^{3+}. These ions will participate in Ln^{3+}-to-metal intervalence charge transfer (IVCT), which is at lower energies than the host absorption and will often strongly or fully quench the emission [1]. Thus, even though TiO_2:Eu^{3+} is well known [2], reports of TiO_2:Tb^{3+} is scarce and emission is often due to secondary phases containing Tb^{3+}.

We have obtained strong TiO_2 sensitization of Tb^{3+} using a sub-nanometer Al_2O_3 layers between TiO_2 and Tb_2O_3 layers in repeating multilayer films by atomic layer deposition (ALD). ALD give us control individual layer thicknesses as thin as 0.4 nm [3], allowing us to design multilayer structures that allows FRET from sensitizer (TiO_2) to activator (Tb^{3+}) while preventing the very short range IMCT quenching. Allowing and preventing different types of transfers is controlled by the number of Al_2O_3 ALD-cycles in the repeating – TiO_2 – Al_2O_3 – Tb_2O_3 – Al_2O_3 – multilayer structure. This approach also allows us to design the sensitizer and emissive layers independently, for example utilizing quantum confinement effects and the reduced concentration quenching in 2D layers.

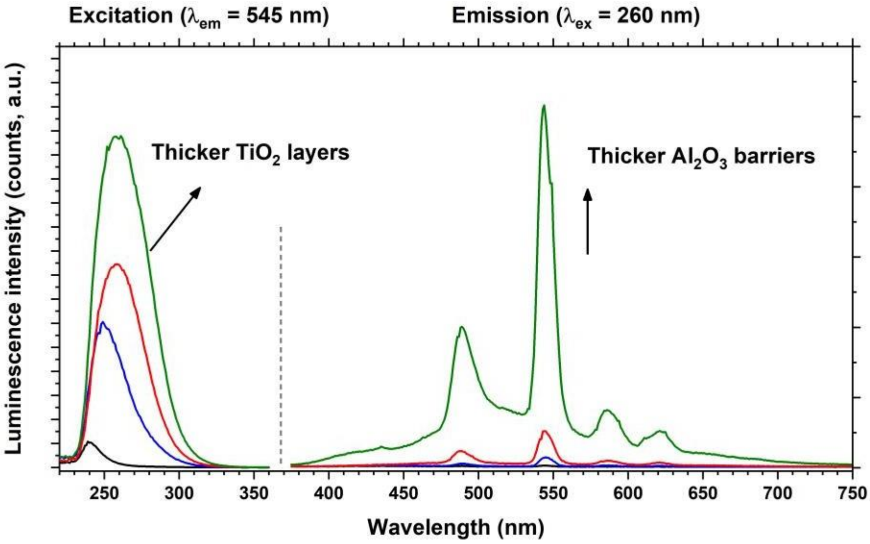

Figure 1: (left) The TiO_2 absorption redshifts and efficiency increases with TiO_2 layer thickness, and (right) Tb^{3+} emission jumps once the Al2O3 layer is sufficiently thick to prevent IMCT.

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NEAR-INRARED LUMINESCENSCE OF Nd ACTIVATED ANATASE NANOPARTICLES

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Pure phase crystalline anatase TiO_2 nanopowders doped with rare earth (RE^{3+}) into titanium (Ti^{4+}) sites is a challenge that could be overcome by optimizing synthesis method. The hydrolytic sol-gel method was found to be an adequate procedure for the successful synthesis [1–3]. To obtain Near-infrared luminescence of toxicology safe material, we doped anatase nanoparticle with neodymium ions. The effect of Nd^{3+} doping into anatase TiO_2 nanoparticles was studied by X-ray powder diffraction, transmission electron microscopy, Raman, UV-Visible, and photoluminescence spectroscopy.

For the TiO_2:1 at.% Nd^{3+} sample crystallite size was determined to be around 7 nm. The powders were made of agglomerates of nanoparticles of spheroidal shape with diameters of around 10 nm. There was no precipitation or enrichment present; all the elements (Ti, O, and Nd) were equally distributed. Results of diffuse reflectance measurements performed on the nanoparticles revealed strong absorption of UV light (< 400 nm) which is a typical optical feature of anatase TiO_2 (band gap of 3.2 eV), along with the Absorptions in the spectral region of 450–950 nm originating from *f-f* electronic transitions of Nd^{3+} dopant ions. Numerous assigned absorption bands presented in the figure correspond to excitation bands, giving multiple possible excitation energies for photoluminescence. When excited with 752 nm, after nonradiative deexcitation from $^2S_{3/2}$ to $^4F_{3/2}$ exited level, radiative transfers to $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ ground energy levels are detected as Near-Infrared luminescence in the 850–1450 nm spectral region.

Because Nd^{3+} *f-f* transitions can produce both, excitation and emission, within the first biological window (700–980 nm) where the transparency of living tissues is high, a potential of Nd^{3+} doped material could be significant for deep-tissue luminescence imaging and temperature sensing [4].

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LUMINESCENCE OF RE^{3+}-DOPED $GdVO_4$ THIN FILMS GROWN BY PULSED LASER DEPOSITION

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This report focuses on fabrication, characterization and fundamental optical properties of Eu^{3+} and Sm^{3+}-doped $GdVO_4$ luminescent thin films. Thin films' structure, morphology and photoluminescent properties were investigated and discussed in detail to propose the use of RE-doped $GdVO_4$ thin films for multifunctional applications.

Thin films were deposited by pulsed laser deposition technique (PLD) on transparent quartz and sapphire substrates, as well as on non-transparent thermally grown SiO_2 substrates. Structure of the thin films characterized by X-ray diffraction (XRD) showed that independent of the substrate type, highly crystalline films were formed. The diffuse reflectance spectra of representative thin films deposited on quartz substrates used to estimate energy band gap revealed values in agreement with published results for $GdVO_4$. Photoluminescent (PL) spectra show reddish-orange emission in the Sm^{3+} doped samples and red emission in Eu^{3+} doped ones. In order to investigate influence of morphology on the luminescent properties of the films plots of integrated PL intensity and roughness of the films as a function of substrate were presented. Plots show that PL intensity depends on the surface morphology and is higher with higher roughness of the phosphor films.

In conclusion, independent of the substrate type: quartz, thermally grown SiO_2 or sapphire, RE-doped $GdVO_4$ thin films show crystalline morphology, good photoluminescent properties and adhesion to the substrate surface. This proposes $GdVO_4$ as a promising multifunctional material giving him potential for a wide range of applications. A set of different experiments is underway in our two labs.

LASER-HEATED PEDESTAL GROWTH AND OPTICAL PROPERTIES OF 50at%Ho^{3+} - DOPED YAG

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We have succeed to grown by Laser-Heated Pedestal Growth (LHPG) technique, The 50 at % Ho^{3+} doped $Y_3Al_5O_3$ (YAG) single crystals, with High-quality in the shape of 7-10 cm in length and with diameters of 1 mm , The pulling rates of this crystal were between 0.1 and 1 mm /mn, their extremely high melting point is of around 1965°C.
Fibers obtained of YAG:Ho^{3+} (50 at %) are yellow colored in the sun light, but they are pink in the local light (Fig.1), all fibers are transparent and free of inclusions, or cracks Spectroscopic investigations of Holmium 50% doped fibers are given, the radio-luminescence spectra recorded in the U.V, visible and IR domains, corresponding to the $^5G_4 \rightarrow {}^5I_8$ (360nm) , $^5G_5 \rightarrow {}^5I_8$ (411nm), $^5F_4 \rightarrow {}^5I_8$ (490nm), $^5S_2 \rightarrow {}^5I_8$ (550nm), $^5F_5 \rightarrow {}^5I_8$ (658nm), $^5I_4 \rightarrow {}^5I_8$ (757nm) and $^5G_4 \rightarrow {}^5I_8$ (360nm) transitions (see Fig .1), Raman diffusion and Micro Raman Fischer in YAG:Ho^{3+} (50 at %) single crystal are given for the different modes excited at 633nm and 785 nm .

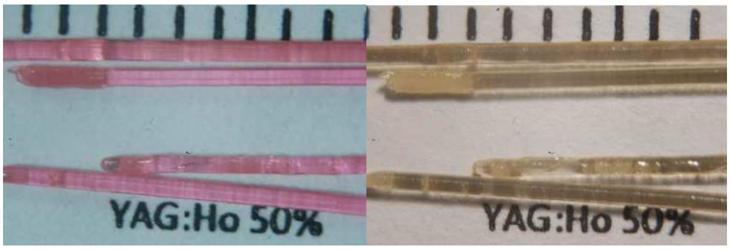

Fig.1 Fibers of 50 at % (Ho^{3+}) - doped YAG grown by LHPG technique

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AROMATIC ABSORPTION AND FLUORIDE HOST EMISSION IN MULTILAYER ORGANIC-INORGANIC NANOCOMPOSITES BY ATOMIC LAYER DEPOSITION

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We have recently shown that it is possible to design multilayer structures with individual layer thicknesses as thin as 0.4 nm by atomic layer deposition (ALD) [1]. Using the exceptional chemical flexibility of ALD we have recently expanded this work to combine two very differently material classes, organic molecules and crystalline fluorides, in multilayer thin films structures. This approach successfully combines the absorption strength of the organic molecule and the luminescence properties of the fluoride host, utilizing the best of both material classes. The samples consist of repeating multilayers of an aromatic acid and TbF3 with a second lanthanide dopant. The acid effectively donates energy to Tb^{3+} or Eu^{3+} which emits light, or to the TbF3 layer which acts as a bridge by allowing the energy to migrate from Tb^{3+} to Tb^{3+}, leading the energy into the low phonon energy bulk of the fluoride layer. Once inside the fluoride layer, away from high energy organic vibrations, the energy can be donated to a third specie. This is exemplified in the 4 samples in Figure 1, where all emissions stem from aromatic excitation. Sm^{3+} is easily quenched by organic vibrations, but in this organic-inorganic nano-composite we are able to obtain strong Sm^{3+} emission. In addition, we obtain orange fluoride-like ${}^5D_0 \rightarrow {}^7F_1$ Eu^{3+} emission in the nano-composite while directly sensitizing Eu^{3+} with aromatic acids give red ${}^5D_0 \rightarrow {}^7F_2$ emission. This shows that by our ALD approach, we can tune the absorption of the organic part and emission in the inorganic part completely independently by using an appropriate energy bridge.

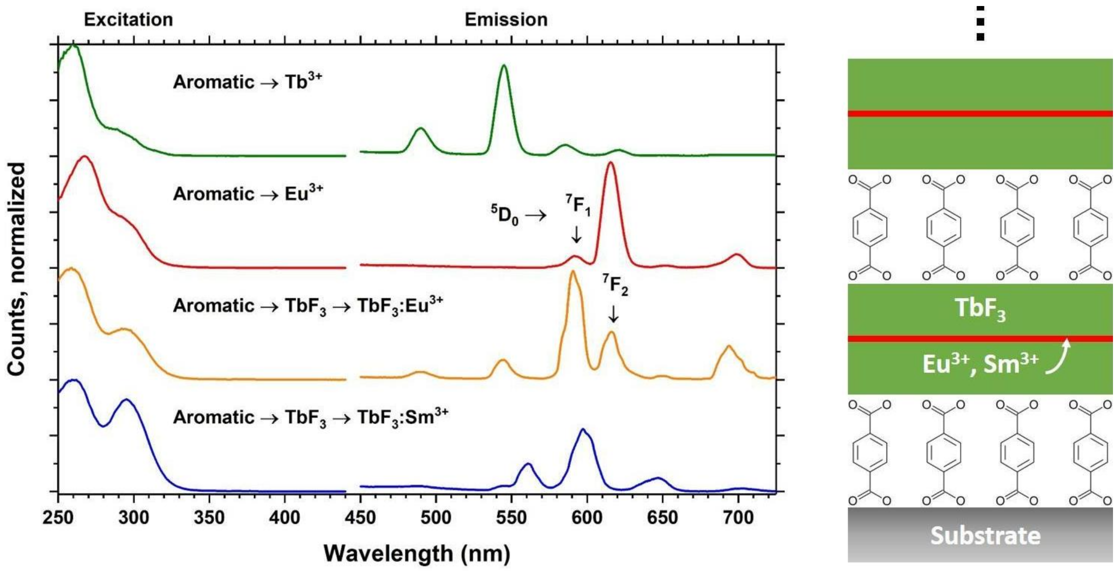

Figure 1: Excitation through aromatic acid gives fluoride-like emission of Eu^{3+} and Sm^{3+} in these organic-inorganic multilayer nano-composite films.

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DECIPHERING ORGANIC LUMINOPHORES EMBEDDED IN RIGID MATRICES USING TIME-RESOLVED SPECTROSCOPY

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Wet-chemically synthesized inorganic solid-state materials often exhibit luminescence behavior.[1,2] We recently showed that the amorphous yttrium-aluminum-borates (a-YAB) obtained by sol-gel and Pechini methods exhibit organic impurities, responsible for their intense visible photoluminescence and phosphorescence afterglow.[3,4] The heterogeneity of impurity organic compounds combined with difficulties in their intact extraction from solid inorganic host matrix limits the extraction based chemical analysis for luminophore identification.[5] Here, we propose a photo-physical route based on time-resolved triplet-state spectroscopy to construct the electronic structures of the trapped unknown luminophores, which successfully illustrates the luminescence properties of a-YAB powders in thorough detail and provides important insights intrinsic to the luminophores' nature. The experimental results help in identifying the luminophores trapped in rigid matrices by analyzing the electronic structures of known luminophores as well as comparing with the theoretically calculated electronic structures of probable candidates.

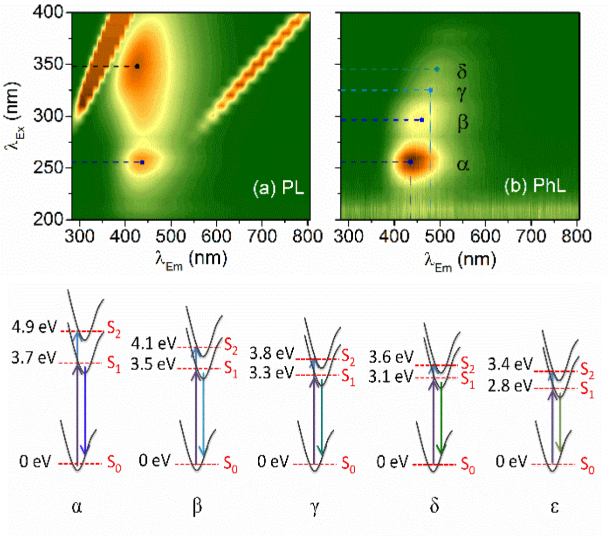

Figure 1. Steady-state (a) and time-resolved (b) luminescence contour maps of a-YAB powder. In (a), the diagonal features are excitation pump signals. In time-resolved plot (b), data represent the phosphorescence signals at 1 s after ceasing the excitation. The allowed electronic transitions and energy levels of few emitting centers in a-YAB powders are also presented.

The authors acknowledge the ANR LuminoPhor-LED project (ANR-14-CE05-0033) and colleagues from Univ. Grenoble Alpes, CEA, CNRS, INAC, SyMMES, F-38000 Grenoble, France and Inst NEEL, F-38042 Grenoble, France

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Tm^{3+}, Er^{3+} DOPED TELLURITE GLASS OPTICAL FIBERS FOR 2.3, 2.8 μm LASERS

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Mid-IR laser sources have a number of interesting applications in various fields of science, technology, environmental monitoring and medicine. The 2-3 μm spectral range is particularly attractive due to a very high absorption of hydroxyl groups. Tellurite glasses are considered as a promising active medium for bulk and fiber mid-IR lasers, they possess phonon spectrum intermediate between those of fused silica and fluoride glasses. Possibility of producing optical fibers with low optical loss up to 3-3.5 μm, the efficient luminescence of rare earths ions and high nonlinear optical properties have been already demonstrated [1,2,3]. However the application of tellurite glasses is currently limited to high optical loss in routine samples related primarily to the presence of 3d-transition metals and hydroxyl groups impurities. The following rare-earth ions optical transitions seem the most attractive within the range between 2 and 3 μm: Tm^{3+} ($^3H_4$ - $^3H_5$, λ~2.3 microns), Er^{3+} ($^4I_{11/2}$ - $^4I_{13/2}$, λ~2.8 μm). High-purity glasses of various Tm_2O_3 or Er_2O_3 concentrations, double-layer preforms and step-index optical fibers consisted of REI-doped glass core and undoped cladding were prepared using the original techniques [4,5]. The absorption and emission characteristics of the fibers were investigated depending on the excitation power and the length of the fiber. From the optical loss measurements by the cut-back technique optical losses in the fibers at the lasing wavelengths 2.3 and 2.8 μm do not exceed 1 dB/m.

The emission characteristics of the low optical loss Er^{3+} and Tm^{3+} doped optical fibers were studied in the bands at ~1.5, 2.8 μm under 0.975 μm pumping and in the band at ~2.3 μm while excited at 0.808 μm, respectively, depending on the pumping power and the length of the fiber. The results of the study showed that Er^{3+} and Tm^{3+} activated tellurite glass fibers are of considerable interest for laser generation at ~2.3 and ~2.8 μm.

The investigation was supported by Russian Science Foundation (grant 17-12-01324).

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CHARACTERIZATION OF THE PROPERTIES AND MICROSTRUCTURE OF AZOPOLYMER THIN FILMS FOR OPTICAL RECORDING

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Azopolymers prepared in the form of thin films are a promising candidate as a medium for optical recording due to their photoanisotropic optical properties. Their applicability for optical recording depends on the thermophysical and mechanical properties, as well as on the quality of the prepared films, i.e. roughness of the surface, uniformity of the thickness and smoothness of the layers formed. In the present study, azopolymer thin films are prepared by spin-coating on glass substrates. The glass transition temperatures are determined by differential scanning calorimetry (DSC) and vary from 35 to 106°C. The mechanical properties are crucial for the application especially when the use of a flexible substrate is envisaged, thus the following mechanical characteristics are determined by depth sensing indentation measurement (DSI): Indentation elastic modulus; Dynamic hardness and Martens hardness giving information about the material's response to total deformation; Indentation hardness which serves as a measure for the resistance to permanent deformation, etc. The surface topography of the azopolymers is studied by atomic force microscopy (AFM) and it reveals small deviations from the uniform thickness of about 40-50 nm for films with thickness of 2,1 µm which is less than 3 %. Hence, we can conclude that the proposed azopolymer thin films are suitable as materials for optical recording as far as their thermophysical and mechanical characteristics and surface quality are concerned.

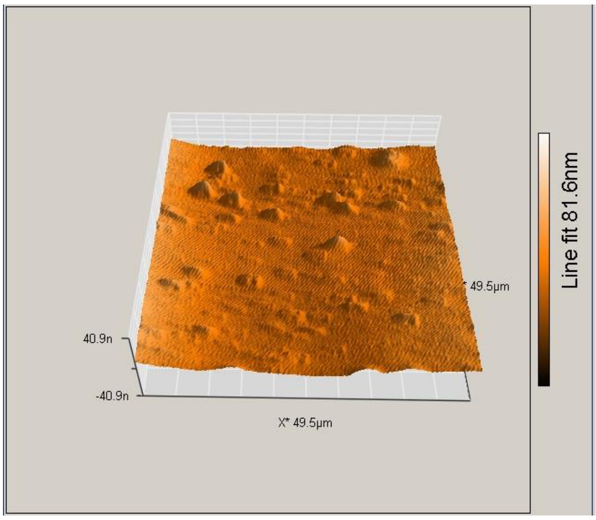

Figure 1. AFM - surface topography of a poly [1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1, 2- ethanediyl, sodium salt thin film.

Acknowledgements: This work is financially supported by contract DN08/13 with the Bulgarian National Scientific Fund.

IMPROVED OPTICAL ACTIVITY IN NANOCOMPOSITE FILMS OF NEWLY SYNTHESIZED AZO-DIIMIDES IN POLYIMIDE MATRIX

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Nanocomposite films of three newly synthesized perylene azo-diimide dyes were prepared by vapour deposition in polyimide matrix and characterized in order to examine their optical properties. The photoinduced birefringence measurements on the nanocomposite films under irradiation with polarized light at a wavelength of 355 nm, 442 nm and 532 nm have shown very good results compared to those obtained for the thin films of the single dyes. Generally, the major problem by using photoswitchable compounds as optical storage media is the lack of efficient switching processes in solid state due to hindered π-π stacking of the chromophores. For this reason we tried to improve the photoresponsiveness of the synthesized azo-diimide dyes using the “host-guest” nanocomposite system obtained by incorporation of the dyes into polyimide matrix. The evaporation process was carried out through vapour deposition from three sources, where the starting precursors for the polyimide matrix were ODA (4, 4’oxydianiline) and PMDA (pyromellitic dianhydride) as well as the azo-diimide dyes as a “guest” at two concentrations 5 and 10 wt %. The solid state imidization reaction to polyimide was performed by thermal treatment of the nanocomposite layers at 250 ^{0} C for 2 h. Write-erase profiles of optical inducing and deleting of linear birefringence in the prepared nanocomposite films have been also presented and discussed.

This work was financial supported by the Bulgarian National Scientific Fund Project ДН 18/5 of the Ministry of Education and Science.

THERMOLUMINECENCE AND HIGH-RESOLUTION LUMINESCENCE SPECTROSCOPY OF $LaPO_4:Eu^{3+}$ NANOPARTICLES

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Nanoparticles (5 nm) and nanorods (2 nm ×15 nm and 4 nm × 20 nm) of pure monoclinic monazite $LaPO_4:Eu^{3+}$ were successfully obtained by reverse micelle and co-precipitation techniques. [1] Effects of the particle size and surface defects on the luminescence intensity and shapes of emission lines were analyzed via high-resolution spectroscopy under ultraviolet laser (266 nm) and X-rays excitation (measured at 10K).

All synthesized samples showed similar spectral features with characteristic Eu^{3+} ions emission bands: $^5D_0\rightarrow{}^7F_0$ centered at 578.4 nm, most dominant magnetic-dipole transition $^5D_0\rightarrow{}^7F_1$ at 588–595 nm, electric-dipole transition $^5D_0\rightarrow{}^7F_2$ at 611.5–620.5 nm, $^5D_0\rightarrow{}^7F_3$ at (648–652 nm) and $^5D_0\rightarrow{}^7F_4$ at (684–702.5 nm). The quantity and intensity of Stark's components are maximal in case of 5 nm nanospheres. Additionally, the photoluminescence spectra of all samples irradiated with X-rays exhibited creation of stable defects, change of luminescence intensity and spectral distribution.

Moreover, the thermally stimulated luminescence (TSL) was recorded for the most intense peak at 611.5 nm. Two prominent and well resolved glow peaks at 58.7K and 172.3K were displayed for 5 nm-nanoparticles, while low-intensity glow-peaks at 212.1K and 212.2K were displayed in X-rays irradiated nanorods (Fig. 1). The TSL glow peak intensity is found to be enhanced in the case of heat-treated sample (in comparation with as-prepared samples). These TLS glows can be attributed to free and bound electrons and holes or to recombination of electrons of ionized oxygen vacancies with photo generated holes. It was shown that the Eu^{3+} doping creates traps in all $LaPO_4:Eu^{3+}$ samples. The values of activation energy of the traps involved in emission revealed that a considerable amount of re-trapping of electrons from deep to upper shallow trapes take place in all samples by stimulation due to thermal energy.

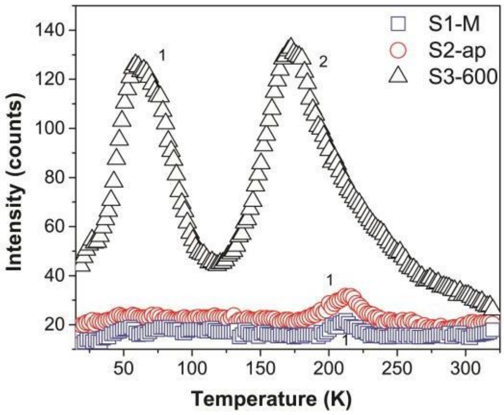

Figure 1. X-ray induced TLS spectra of $LaPO_4:Eu^{3+}$ samples

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DOWNCONVERSION AND UPCONVERSION PROCESSES EXAMINED IN $Gd_3Ga_3Al_2O_{12}$:Ln^{3+} (Ln^{3+}=Tm^{3+}, Er^{3+}, Ho^{3+}, Pr^{3+}) AND Yb^{3+} CO-DOPED SINGLE CRYSTALS

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Photovoltaic technologies require application of innovative optical materials which are able to divide effectively UV-Vis excitation into NIR photons. To increase the conversion efficiency of sunlight to electricity in the applicable solar cells, the reliable modification of solar spectrum is justifiable. The novel garnet optical systems may have potential applications in adjusting the solar spectrum to improve the effectiveness of silicon solar cells. Accordingly, a series of $Gd_3Ga_3Al_2O_{12}$:Yb^{3+}, Ln^{3+} (Ln^{3+} = Tm, Er, Ho, Pr) single crystals have been grown by the Czochralski method. The excitation spectra, emission spectra and luminescent excited state lifetimes have been analyzed in details to investigate the ability of these optical systems to effective down-conversion of UV-Vis excitation into Vis-NIR emission. The likely mechanisms of the luminescence phenomena and excited state relaxation ways were studied. Furthermore, the effect of the ytterbium doping concentration on the visible and NIR emissions as well as decay lifetimes was investigated.

The oxide crystals co-doped with ytterbium ions as a sensitizer can convert short NIR radiation into visible/ultraviolet light via energy transfer between lanthanide ions as well. Consequently, up-conversion processes were detected after 808 nm and 975 nm diode laser excitation in novel GGAG: Tm, Yb optical systems doped with various concentration of optically active ions. When 975 nm excitation was applied, the luminescence related to $^3H_4$- $^3H_6$ and $^1G_4$-$^3H_6$ transitions of Tm^{3+} has been observed. On the other hand visible up- converted emission was not detected for Tm^{3+} singly-doped GGAG crystals excited at 808 nm but this phenomena occurs for Tm^{3+},Yb^{3+} co-doped samples corroborating efficient Tm□Yb energy transfer. Up-conversion phenomena has been examined as a function of Tm^{3+} and Yb^{3+} concentration. The excitation power dependence of the integrated emission intensity and relaxation dynamic of the relevant excited states study were utilized to characterize mechanism of the observed phenomena. It was found based on detailed optical investigation that no resonance conditions are fulfilled for Tm□Yb energy transfer and consequently these processes have to be assisted by phonon emission.

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GAMMA-RAYS INDUCED COLOR CENTERS IN Pb^{2+} DOPED CaF_2

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Pure CaF_2 is transparent from ultra-violet to far infrared region; if chemical impurities are incorporated, even in parts-per-million, and the crystals are subjected to X, γ or neutron irradiation, absorption bands in the normally transparent spectral region appear due to the formation of radiation-induced color centers [1, 2, 3].

The purpose of this paper is to investigate the influence of small amount of Pb impurity on the optical properties of the γ-irradiated CaF_2 crystals. In spite of the fact that the addition of PbF_2 (~ 4%) in the CaF_2 melt is used as scavenger in the crystal growth process, sometimes a trace of Pb^{2+} are found in the obtained crystals.

Pure and PbF_2 doped CaF_2 crystals have been obtained using the conventional Bridgman technique [4]. The samples were irradiated at room temperature with γ rays from a ^{60}Co source. Optical absorption (OA) spectra were recorded before and after irradiation. OA spectra of γ irradiated PbF_2:CaF_2 crystal are characterized by two broad peaks centered on 400 nm and 730 nm. Our OA spectra differ from those reported by others [1, 2, 3] due to presence of the Pb^{2+} ions. The additional absorption spectra ($AA=\alpha-\alpha_0$, where α and α_0 are the absorption coefficient after and before γ-irradiation) were calculated to analyze the effect of irradiation (Fig. 1). The two broad peaks were decomposed by Gaussian multi-peak fit in order to identify the main absorption bands and to see the influence of the γ-dose on the created color centers (Fig.2). The optical properties of the γ-irradiated CaF_2 crystals are significantly affected by the presence of trace quantities (at the 40 ppm level) of lead ions.

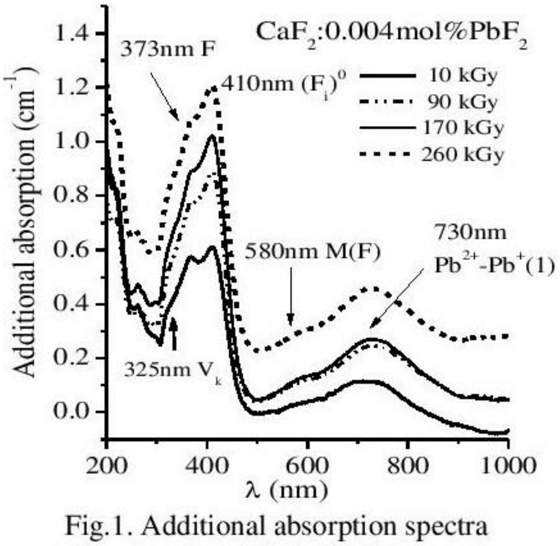

Fig.1. Additional absorption spectra of γ – irradiated CaF_2 (PbF_2) crystal.

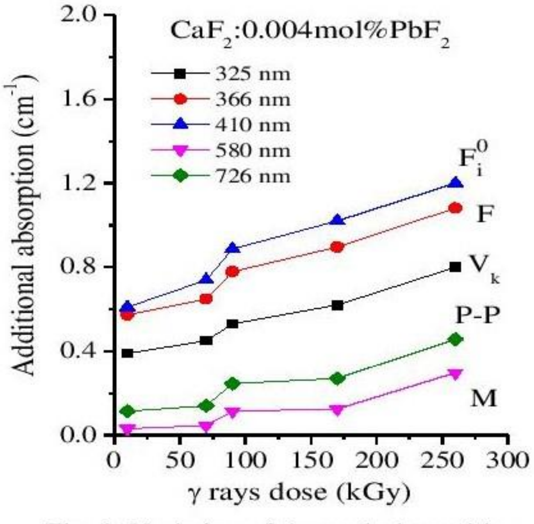

Fig. 2. Variation of the peaks intensities on the γ– rays dose.

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INFLUENCE OF ALKALI METALS ON SPECTRAL-LUMINESCENT PROPERTIES OF CHLORIDE PHOTO-THERMO-REFRACTIVE GLASSES

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Photo-thermo-refractive (PTR) glasses are sodium-zinc-aluminosilicate glasses containing components (Ce, Sb and Ag) being electrons donor and accepters and halogens (Br, F) involved in a crystalline phase formation [1]. After the UV irradiation and heat treatment (HT) a PTR glasses refractive index changes due to a photo-thermo-induced crystallisation. Because of this phenomenon, PTR glasses are widely used for a volume Bragg gratings recording to create on their basis lasers line-narrowing filters [2], spectral beam combiners [3], etc.

In this work, spectral-luminescent properties of chloride PTR glasses containing different alkali ions were studied.

PTR glasses based on Na_2O-ZnO-Al_2O_3-SiO_2-R_2O (where R=Li, Na, K, Rb, Cs) system were synthesised. The R_2O concentration was 50% of the total Na_2O+R_2O content that remains constant and equals 15 mol. %. The glass synthesis was conducted at a temperature of 1510°C in air atmosphere using quartz crucibles and a platinum stirrer. Glass transition temperatures (T_g) were measured with a differential scanning calorimeter. The samples were irradiated by a UV mercury lamp and heat treated in a gradient furnace at temperatures below and above the glass transition temperature. The HT duration for all samples varied from 1 to 10 h. The absorption spectra were measured within a wavelength range of 200–800 nm at all experimental stages. The luminescence spectra and absolute photoluminescence quantum yield (QY) were measured using a multichannel detector with an integrating sphere under excitation at a wavelength of 360 nm.

The studied glasses T_g increases with an alkaline ion atomic number growth from 450°C to 530°C. The absorption spectra of all virgin PTR glasses are similar to each other; therefore, the alkaline ions replacement does not change their spectral properties. After UV irradiation an increase in the absorption in the 350-550 nm range is observed in all glasses due to a neutral silver molecular clusters (SMCs) Ag_n formation. The subsequent HT at temperatures below T_g leads to an increase in the neutral SMCs number that have luminescence in the visible and near-IR ranges. The highest QY of 30% was observed for a PTR glass with Na^+ ions. The HT at temperature of 50°C below T_g results in a silver nanoparticles formation with a plasmon absorption band at 410 nm, however, the duration of such HT strongly depends on an alkaline ion. The UV irradiation and HT at temperatures above T_g cause a growth of silver nanoparticles without shell in all glasses.

As a result, spectral-luminescent properties of chloride PTR glasses containing different alkali ions were studied. The glass with SMCs can be successfully use as a down-converter for solar cells and phosphor for white LEDs.

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COMPOSITE COUNTER ELECTRODE PREPARED USING GRAPHENE AND INDIUM SULFIDE FOR PT-FREE DYE-SENSITIZED SOLAR CELLS

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As the dye-sensitized solar cell (DSSC) process is simple, flexible, and environment friendly, substantial research has been devoted to DSSCs in recent years. Platinum (Pt) is currently still the most extensively used counter electrode (CE) for DSSCs. However, Pt is one of the most expensive materials among DSSCs. It can be decomposed by the I^-/ I_3^- redox pair into PtI_4, which may give rise to the problems of cell performance, long-term stability and commercialization. Therefore, much effort has been paid to explore the low-cost alternatives for Pt CE. Many alternatives have been proposed as substitutes for the conventional Pt CE, such as carbon materials [1], conductive polymers [2], and metal sulfides [3]. Among the metal sulfides, there are only few studies on the effects of indium sulfide (In_2S_3) as the CE material for DSSCs. A composite material of ultra-long (up to 10 μm) In_2S_3 nanotubes grown on a graphene (GP) substrate [4] or a hybrid structure decorated with gold (Au) particles on the surface of carbon (C) covered In_2S_3 flower-like structures [5] has been used as a DSSC CE. These CEs are found to have excellent electrocatalytic activity for the reduction of iodide (I^-/ I_3^-) and have a very high power conversion efficiency. In this study, we instead introduce the GP/ In_2S_3 composite material formed by simply mixing different amounts of GP and In_2S_3 nanopowders as a CE catalyst in the Pt-free DSSC system. The preparation of the DSSC, except for CE, is referred to a typical DSSC. To fabricate CE, the multilayered GP nanopowder and the In_2S_3 nanopowder were mixed together according to 1 to 10 wt% to from an active material. Then, 80 wt% active materials, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) were dissolved in N-Methyl-2-pyrrolidone (NMP) and stirred for 12h in preparation of the paste for CE. Next, the prepared paste was applied on the fluorine doped tin oxide (FTO) glass substrate using the doctor blade method. Finally, the electrode was heated and dried in an oven for 30 min at 450 °C. Active material, In_2S_3 and Pt were also used as CEs for comparison. It was found that, after the GP content is optimized (5 wt%), the conversion efficiency of the DSSC with GP/ In_2S_3 CE under 100 mW/cm^2 AM1.5 illumination can reach 5.63%, which is comparable to that of a traditional Pt CE based DSSC (5.66%). Adding an adequate amount of GP in In_2S_3 may improve significantly the electrocatalytic activity of CE because of the large active surface area due to the lamellar structures of In_2S_3 and GP as well as their synergistic catalytic effect. The actual physical mechanism of GP/In_2S_3 composite material CE still requires confirmation by further analysis. However, the GP/ In_2S_3 CE, with its significant optical properties, has a great potential to be a low-cost alternative for the Pt CE in high performance DSSCs.

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SYNTHESIS AND CATHODOLUMINESCENT PROPERTIES OF $MgAl_2O_4$ CERAMICS DOPED WITH RARE EARTH IONS PRODUCED BY SPARK PLASMA SINTERING TECHNIQUE

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The modern development of optical materials is impossible without the development of optical materials of a new generation. Therefore, the creation of new optical materials is an important, relevant and strategic objective of an optical instrument and optical material science. Great interest for the modern element base of photonics, represent transparent ceramic materials [1]. This is explained a better technological performance of transparent ceramics compared with single crystals and transparent glass.

Spinel oxides find many applications as magnetic, electric, ceramic, catalysis and optical materials. $MgAl_2O_4$ (MAS) has received a great deal of attention as a technologically important material because of its mechanical strength, chemical inertness, wide band gap (6.8eV), relatively low density, high melting point (2105 °C), high thermal shock resistance, low thermal expansion coefficient, resistance to neutron irradiation and low dielectric loss [2]. MAS can be doped with rare earth ions with sharply differing charge states to achieve high luminescence efficiency [3, 4]. Nevertheless, the luminescent properties are greatly dependent on the amount of dopant and their surroundings.

In this work, we investigated the optical and cathodoluminescent properties of undoped MAS and single doped with Eu, Ce, Dy, Tb ceramics. The polycrystalline MAS spinel from nanopowder was consolidated by the spark plasma sintering (SPS) technique using the installation SPS-515S (Syntex Inc., Japan). SPS conditions were as following: sintering temperature T=1300 °C, vacuum $P=10^{-3}$ Pa, the pressure of 72 MPa, the heating rate of 5 °C/min. The duration of heating was 10 minutes. The diameter of pellets sintered in the graphite die was 20 mm.

A complex characterization of the crystalline and defect structure of the ceramic by XRD was carried out. Absorption, excitation, luminescence spectra were studied.

Optical properties of sintered ceramics have been studied by the double-beam spectrophotometers LOMO SF-256 UVI and SF-256 BIK in the spectral range of 200 – 1100 nm and 1100 – 2500 nm, respectively.

The integrated cathodoluminescence spectra and decay kinetics were investigated with the pulsed optical spectrometer based on a high-current electron accelerator GIN- 600 (E_{ex}=0.25 MeV, FWHM=15 ns, W=23 mJ/cm^2) and AvaSpec-2048 fiber spectrometer.

The luminescence decay kinetics of synthesized spinel ceramics in nano- and millisecond time range were investigated in detail. Nature of luminescent centers and mechanisms of luminescence are discussed.

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PHOTO - AND CATHODOLUMINESCENCE OF INDUSTRIAL YAG:Ce PHOSPHORS IN UV SPECTRAL REGION

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The spectral-kinetic characteristics of photoluminescence (PL) and cathodoluminescence (CL) of the group of industrial phosphors based on YAG: Ce were investigated in the 250−600 nm spectral region. Phosphors: MG-397, L-2083 and AWS-5, YAG (01−06) and SDL (2700, 3500, 4000) were selected for research.

Excitation spectra of the phosphors (PP) emission were investigated in region of 210−290 nm. CL of PP was excited by flux of 250 MeV electrons at 300 K.

The PL spectra of all the investigated PP consist of UV bands at 312, 380, 417 nm and a working band in the region 520−560 nm, which spectral position and intensity are determined by PP prehistory. In PL spectra of different PP both the position of UV emission bands and their FMHM are close, but the relationship between the intensities of these bands depends on the PP prehistory. The relationships between the intensities of the UV emission bands and the band in the range 520−560 nm are also different.

Type of excitation spectrum (number of bands and the ratio between them) of the emission in UV region depends on the PP prehistory.

The positions of the bands in CL spectra are the same as in PL spectra, but bands have sharply differing half-widths. For example, FMHMs of the band about 380 nm are equal to 0.43 and 0.10 eV in the PL and CL spectra of MG-397 phosphor, respectively. Moreover, in the CL spectra of the PP the intensities of the UV bands are much less than that for working band in region of 520−560 nm whereas in PL spectra, the band intensities in the UV and visible regions are commensurable.

It has been established that the efficiency of UV emission, the relationship between the intensities of the bands in the visible and UV spectral regions are not directly related to the elemental composition of YAG phosphors and depend on the technological conditions of the synthesis. It follows that the characteristics of PL and CL in the UV region be used to identify phosphors.

It is assumed that nanodefects (complex defects from matrix ions, activators, intrinsic lattice defects to compensate for charge and elastic stresses) are formed in the PP during the synthesis [1, 2]. The centers of the emission are seen as elements of nanodefect structure. Nano defects can be viewed as a new phase in the matrix structure with its own spatial and energy structure.

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CARBAZOLYL-CONTAINING IMIDES AS EMITTERS WITH THROUGH-SPACE CHARGE-TRANSFER: SYNTHESIS AND PROPERTIES

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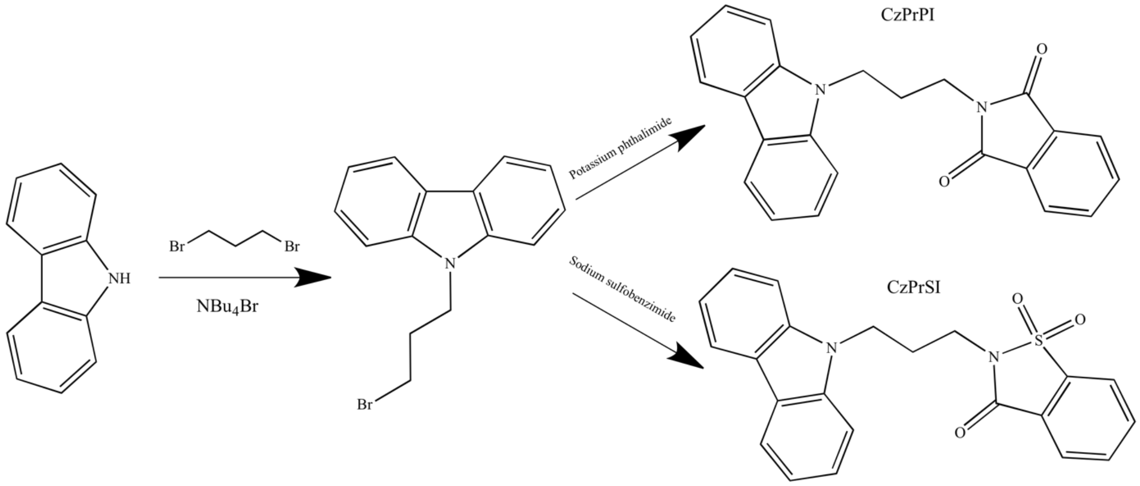
Organic light-emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) attract extensive interest as alternative for phosphorescent and fluorescent OLEDs due to metal-free structure, flexibility and effectiveness [1]. TADF is provided by reverse intersystem crossing of excitons from the triplet excited state (T_1) to the singlet charge- transfer state (S_1) and is achievable if energy gap between S_1 and T_1 is low [2]. Synthesis of novel materials which potentially can demonstrate TADF remains important target of researchers.



Scheme 1: Synthesis of CzPrPI and CzPrSI

The aim of this work was to synthesize low-molar-mass donor-acceptor materials with through-space charge transfer and as a result with small energy gap between the charge- transfer singlet and excited triplet states applying inexpensive materials and simple synthetic pathways. Exciplex forming materials CzPrPI and CzPrSI were obtained by two-step synthesis using nucleophilic substitution reaction. Structures of the compounds were confirmed by ^{1}H and ^{13}C NMR spectrometries. Photophysical and electrochemical properties of the compounds were examined. CzPrPI and CzPrSI demonstrate green and sky-blue emission in solid state with maximum photoluminescence intensity wavelengths of 503 nm and 487 nm respectively with photoluminescence quantum yield up to 20%.

Acknowledgement

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DERIVATIVES OF 9, 9-DIMETHYL-9, 10-DIHYDROACRIDINE AND PERFLUORO BIPHENYL AS EMITTERS SHOWING THERMALLY ACTIVATED DELAYED FLUORESCENCE

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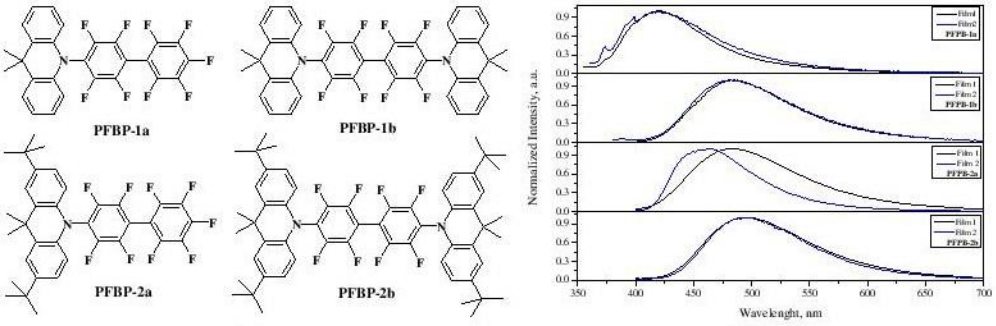
The recent introduction of thermally activated delayed fluorescence (TADF) emitters is widely considered as an important breakthrough for the development of high efficiency organic light-emitting devices (OLEDs) [1]. Efficient TADF light-emitting materials have to meet the following requirements: high photoluminescence quantum yield (PLQY), small energy difference ($\Delta E_{ST(LE)}$) between the local exciton triplet and singlet intramolecular charge-transfer states [2]. The aim of our work was to design and synthesize derivatives of 9,9-dimethyl-9,10-dihydroacridine (DMAC) and perfluoro biphenyl (PFBP) exhibiting efficient TADF (Figure 1a).



(a) *(b)*

Figure 1. Chemical structures *(a)* and PL curves of solid films *(b)* for PFBP derivatives

Derivatives of DMAC and PFBP were synthesized in one-step *via* catalyst-free aromatic nucleophilic substitution reaction. Thermal stability of the compounds was estimated by TGA and morphological transitions were studied by DSC. The temperatures of 5% weight loss were found to range from 205 to 317 □C. Compounds PFBP-1b and PFBP-2a showed glass forming temperatures at 64 and 120 □C respectively. Photophysical, electrochemical, electron photoemission and time-of-light properties of PFBP derivatives were investigated. TADF effect of the target compounds was studied by luminescence spectrometry including time- resolved one at room and low temperatures. For all synthesized compounds ΔE_{ST} values were found to be close to 0. The obtained derivatives demonstrate sky-blue and blue emission in solid state with maximum fluorescence intensity wavelengths ranging from 418 to 494 nm (Figure 1b). Two polymorphic modifications emitting different colour with PLQYs of 43 and 61% of non-doped films were detected for compound PFBP-2a. The maximum external quantum efficiency of 15.9 % was achieved for the best fabricated device.

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SILVER ION EXCHANGE IN PHOTO-THERMO-REFRACTIVE GLASS MATRIX: PROPERTIES AND APPLICATIONS

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Ion exchange (IE) in glass is well known for decades as a versatile tool for glass strengthening, fabrication of optical waveguides, and growth of silver nanoparticles. However, systematic studies of influence glass composition or dopants on spectral and optical properties of silver ion-exchanged layers absent. Photo-thermo-refractive (PTR) glass is a photosensitive medium used for Bragg gratings recording. PTR glass is a sodium-zinc- aluminosilicate one doped with cerium, antimony, and bromine. In this work influence of the dopants on the spectral and optical features of silver introduced by Na^+-Ag^+ IE was studied.

Glasses based on the Na_2O–Al_2O_3–ZnO–SiO_2–F system doped with different concentration of Sb_2O_3, CeO_2, and NaBr were synthesized. The samples were immersed in a bath with melt of nitrate mixture $5AgNO_3/95NaNO_3$ (mol. %) at 320°C for 1min-21h. The ion-exchanged samples were further heat-treated at temperatures in the range of 350-500°C for 1-24h.

Na^+-Ag^+ IE and subsequent heat treatment of PTR matrix-based (with no dopants) glass in air at 350-500 °C result in growth of SERS-active silver nanoisland film on the glass surface, while in the ion-exchanged layers silver remains in the ionic form. The film can be removed mechanically and restored by heat treatment for several times.

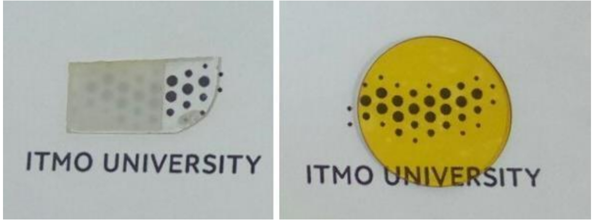

Figure 1. Daylight photo of the PTR matrix-based glass (left) and BK-7 Schott glass (right) after Na^+-Ag^+ IE and heat treatment. Silver nanoisland film on the PTR glass surface is partially removed.

Antimony and cerium are polyvalent ions that can exist in a glass matrix in different forms (Sb^{3+}, Sb^{5+}, Ce^{3+}, Ce^{4+}) and play a role of electrons donor for silver ions. Thus, subnanosized luminescent silver clusters with quantum yield up to 60% or plasmonic silver nanoparticles can be formed in ion-exchanged layers of Sb- and/or Ce-doped PTR glasses. Such glasses can find applications as a phosphors for white LEDs and spectral converters for solar cells.

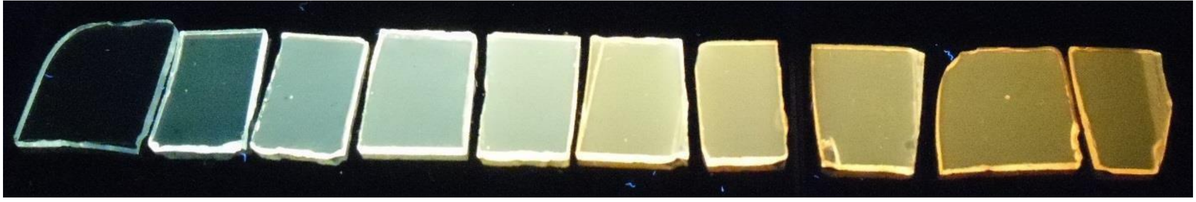

Figure 2. Photo of the ion-exchanged and heat-treated Sb-doped PTR glass samples under UV light (the IE duration increases from left to right).

Silver IE and subsequent heat treatment of Br-doped PTR glass at temperatures above the glass transition one lead to growth of silver bromide nanocrystals. Glasses with AgBr nanocrystals possess photo- and thermochromic properties and can be used for information recording and temperature measurements.

Thus, PTR glass is an attractive matrix for growth of functional silver nanostructures (silver clusters, silver nanoparticles, and silver bromide nanocrystals) for various photonic applications including lighting, sensorics, and plasmonics.

INCORPORATION OF EXCIPLEX-FORMING MATERIALS INTO ELECTROLUMINESCENT DEVICES BASED ON NON-DOPED FLUORESCENT EMITTERS EXHIBITING AGGREGATION INDUCED EMISSION ENHANCEMENT

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Organic dyes exhibiting aggregation induced emission enhancement (AIEE), which allows to mitigate or totally to overcome solid state fluorescence quenching, are established as efficient emitters for non-doped organic light emitting diodes (OLEDs) [1]. However, caused by the spin statistics, 5% limit of external quantum efficiency (EQE) can not be overcame for non- doped singlet emission based devices even having perfect AIEE-active fluorescent emitters with PLQYs of 100%.

In this study, to overcome the spin statistic limit for non-doped fluorescent OLEDs, we propose to incorporate interface exciplexes exhibiting thermally activated delayed fluorescence (TADF) to light-emitting layers of non-doped organic electroluminescent devices based on fluorescent emitters exhibiting AIEE. In the frame of this study, two derivatives of tetrafluorophenylcarbazole and tri/tetraphenylethylene displaying aggregation- induced emission enhancement were synthesized and investigated, by theoretical and experimental tools. The synthesized compounds exhibit efficient emission in solid state with fluorescence intensity maxima at 511 and 502 nm and photoluminescence quantum yields of 57% and 27%. The compounds were found to be capable to form glasses with glass transition temperatures of 80 and 112 ºC. They exhibited high thermal stabilities, with 5% weight loss temperatures exceeding 300 ºC. Ionization potentials for solid-state samples estimated by photoelectron emission spectrometry were found to be of 5.83eV and 5.87 eV. The compounds exhibited well-balanced hole and electron mobilities exceeding 10^{-3} cm^2/V·s at an electric field higher than $3 \cdot 10^5$ V/cm. The newly synthesized derivatives were used for non- doped organic light-emitting layers of electroluminescent devices which exhibited good performance as for fluorescent OLEDs. The fabricated devices were further modified placing the layers 3-bis(9-carbazolyl)benzene (mCP) and 2,4,6-tris[3-(diphenylphosphinyl)phenyl]- 1,3,5-triazine (PO-T2T) between two layers of non-doped light emitting layers. Note, that a solid-state mixture of PO-T2T and mCP is characterized by exciplex emission of TADF nature [2]. As a result, both singlet and triplet excitones can be harvested at the mCP/PO-T2T interface in the modified devices due to TADF of the interface exciplex mCP/PO-T2T. Therefore, the modified devices were characterized by higher efficiencies rieching 2.4 % in comparison to those (1.7%) of the initial devices.

Acknowledgements
This work was supported by Research Council of Lithuania (Project “OWEX” No S-MIP-17-101).

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AN ELECTROPLEX-FORMING DERIVATIVE BASED ON 1,8-NAPHTHALIMIDE AND PERYNYL AS THE HOST FOR RED PHOLEDS

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Organic light emitting diodes (OLEDs) technology is considered to be promising for the next generation flat and flexible panel displays and solid state lighting. Harvesting of both singlet and triplet excitons for emission is important to improve performance of devices.[1] Application of phosphorescent organic light emitting diodes (PhOLED) theoretically allows to reach 100% of internal quantum efficiency.[2]

Recently, electrically induced complexes (electroplexes) between excited state of a donor and the ground state of an acceptor have become a matter of a great interest. The electroplex host is found to induce light emission through an energy transfer process rather than charge trapping, and enables to dramatically improve lifetime of red, yellow, green, and blue PhOLEDs. Furthermore, the electroplex host is found to perform much longer lifetime than a common exciplex host.[3] Therefore, there is an increasing interest in developing of a host material as the single material electroplex host for efficient PhOLEDs.

In this work, we report on the synthesis and investigation of new compound containing 1,8-naphthalimide and pyrene moieties. Derivative was designed as bipolar charge transport host material for emitting layers of OLEDs. Red PhOLEDs were fabricated using a Ir(piq)2(acac) doped with the studied derivative for light-emitting layers with the different dopant concentrations. In addition, we fabricated and studied devices with a non-doped emitting layers to reveal electroplex forming abilities of the compound.

Ionization potential of the compound established by electron photoemission technique in air was found to be 5.93 eV. Electron and hole mobilities of 10^{-4} cm2 $V^{-1}\cdot s^{-1}$ were recorded for 4-(1-pyrenyl)-N-(2-ethylhexyl)-1,8-naphthalimide at an electric field of 3.5×10^{5} V/cm. Efficient energy transfer from electroplex-forming host to phosphorescent emitter was proved for the host:guest system ImPy:Ir(piq)2-(acac) resulting in pure emission of Ir(piq)2-(acac) in PhOLEDs. ImPy:Ir(piq)2-(acac)-based PhOLEDs demonstrated the highest maximum current, power, and external quantum efficiencies of 10.8 cd/A, 7 lm/W, and 13.6%, respectively.

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PHOTOLUMINESCENCE AND SCINTILLATION PROPERTIES OF Pr-DOPED $Ca_2Al_2SiO_7$ SINGLE CRYSTALS

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Scintillators convert ionizing radiation into a large number of low energy photons. The materials have been widely used in various field such as medical imaging, security, well-logging and astrophysics. In common scintillation mechanism, via interactions between incident ionizing radiations and materials, a large number of secondary electrons are generated in the host matrix, and then some of them are transferred to luminescence centers to emit light (or called scintillation photons) due to recombination of electrons and holes. Over the past decades, various different scintillation materials have been developed because required scintillation properties are different for each application.

We have focused on $Ca_2Al_2SiO_7$ (CASM) which is one of melilite compounds and has a high chemical stability and non-hygroscopicity [1, 2]. In our previous work, Ce-doped CASM single crystals were investigated as a scintillator [2], and the scintillation light yield was found to be 16,000 ph/MeV under γ-ray irradiation. Therefore, CASM is considered to be a promising candidate host for scintillator. In this work, to extend the research, CASM single crystals doped with Pr showing emissions due to 5d-4f and 4f-4f transitions of Pr^{3+} were synthesized by the floating zone method. We evaluated photoluminescence and scintillation properties of Pr-doped CASM single crystals. The properties of Pr-doped CASM have not been reported as far as we are aware.

The X-ray induced scintillation spectra are shown in Fig.1. The Pr-doped CASM single crystals show with several peaks around 300,400 and 500-700 nm, and these emission origins are due to the 5d-4f transitions of Pr^{3+}, an intrinsic luminescence and 4f-4f transitions of Pr^{3+}, respectively. Pulse height spectra upon ^{241}Am 5.5 MeV α-rays excitation of Pr-doped CASM single crystals are presented in Fig.2. The light yields of 0.3, 1.0 and 3.0% Pr-doped CASM single crystals show 140, 430 and 790 ph/ 5.5 MeV-α, respectively. In this presentation, we also report photoluminescence and afterglow properties.

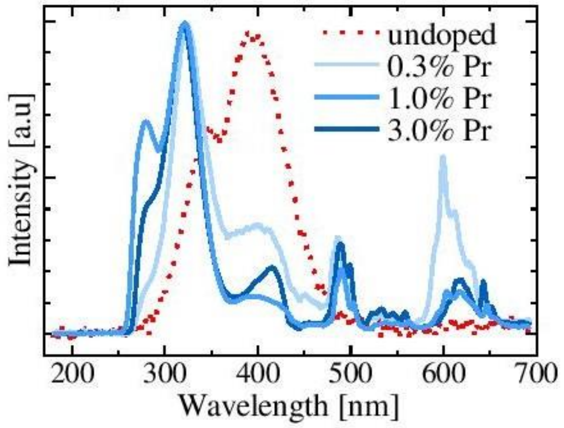

Figure 1. X-ray induced scintillation spectra

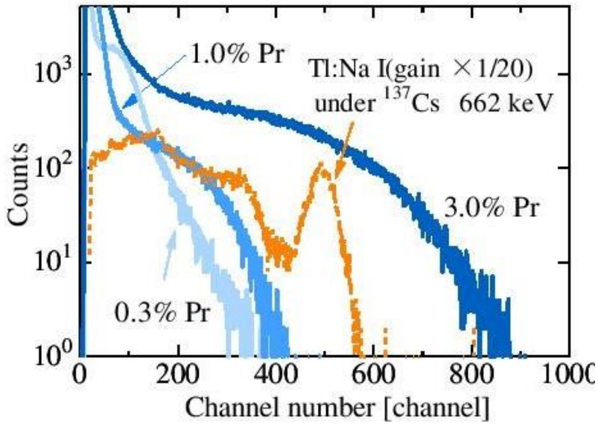

Fig.2. Pulse height spectra under ^{241}Am α-ray.

References:

[1] V. C. Teixeria, et al, Opt. Mat. 36 (2014) 1580-1590.
[2] T. Ogawa, et al., J. Lumin. 196 (2018) 270-274.

PHOTOLUMINESCENCE AND SCINTILLATION PROPERTIES OF Eu- AND Ce-DOPED $Ca_2MgSi_2O_7$ CRYSTALS

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Scintillators are phosphors that convert high energy ionizing radiation to a large number of low energy photons such as UV, visible and near-infrared light. The scintillators have been used in various fields including medical, security and astrophysics. Important properties for scintillators are high light yield, density, effective atomic number and short decay time. In reality, there is no ideal scintillator which fulfills all the properties required for all the applications, and many researchers have continued to pay an effort to develop new materials for scintillator applications.

Melilite compounds have chemical stability and non-hygroscopic nature, which are preferable properties for scintillators. Rare-earth-doped $Ca_2MgSi_2O_7$ (CMSM) have been studied for persistent luminescence materials [1, 2]. On the other hand, CMSM has not been studied for scintillator yet, and there is a large room for study in this point. In this work, we synthesized CMSM single crystals doped with 1% Eu and 1% Ce by the floating zone method since intense light emission can be expected by 5d - 4f transition of Eu^{2+} and Ce^{3+}. After the synthesis, we evaluated scintillation properties of Eu- and Ce-doped CMSM.

Fig. 1 shows X-ray induced scintillation spectra of Eu- and Ce-doped samples. Eu- and Ce-doped samples show a broad emission around 550 and 400 nm, and these origins are due to 5d-4f transitions of Eu^{2+} and Ce^{3+}, respectively. Fig.2. shows X-ray induced scintillation decay time profiles of Eu- and Ce-doped CMSM samples. The decay time constants of Eu-doped sample are 120 and 356 ns. The first component (120 ns) is due to the 5d-4f transitions of Eu^{2+}, and the second conponent (356 ns) would be due to the host. The decay time constants of Ce-doped sample are 41 and 326 ns. The first component (41 ns) is due to the 5d-4f transitions of Ce^{3+}, and the second component (326 ns) also would be due to the host. As the proof of the origin of second component, the decay time of the second conponent in these samples are close in spite of different dopant ions. In this presentation, we also report photoluminescence, thermoluminescence and afterglow properties.

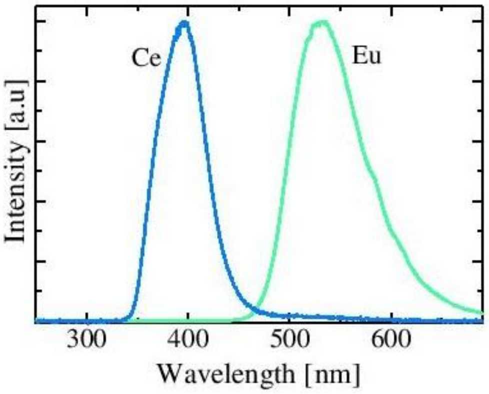

Figure 1. X-ray induced scintillation spectra.

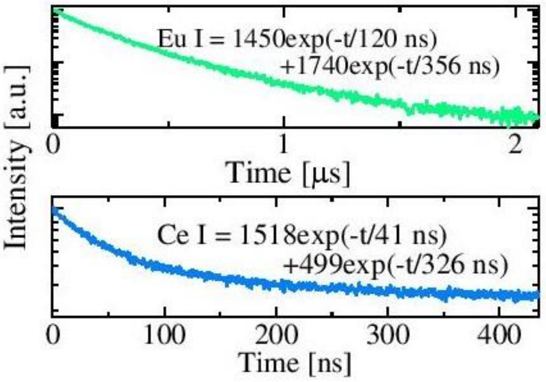

Fig.2. X-ray induced scintillation decay time profiles.

References:

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[2] I. P. Sahu, et al., Res. Chem. Intermed. 41 (2015) 6649-6664.

SCINTILLATION PROPERTIES OF Ce-DOPED $Yb_3Al_5O_{12}$ SINGLE CRYSTALS

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Scintillators are a type of phosphors which convert high energy photons or particles to low energy photons with the energy of typically a few eV. They have been applied in various fields of industries and basic science such as security, medical imaging, and particle physics. Important properties of scintillators are light yield, decay time and cross-section to the target radiation. In recent years, rare-earth-doped garnet-type single crystals ($RE_3Al_5O_{12}$) have attracted much attention as a candidate of host materials of scintillators. In our group, we prepared Pr doped $Yb_3Al_5O_{12}$ single crystal in the previous study and evaluated scintillation characteristic [1]. As a result, luminescence due to charge transfer transition of Yb^{3+} and a high speed intrinsic luminescence derived from a garnet structure were confirmed, but luminescence by the 5d-4f transition of Pr^{3+} could not be confirmed. In order to expand our research target, in this study, $(Ce_xYb_{1-x})_3Al_5O_{12}$ ($x = 0, 0.001, 0.005, 0.01, 0.02$) single crystals were prepared by the Floating Zone method. Structural properties of the samples and scintillation characteristics were evaluated.

The scintillation spectra under X-ray excitation are shown in Fig.1. Scintillation was observed from all samples, and the wavelengths were around 300-600 nm. The peak between 300-350 nm is considered to be the emission from the host. The scintillation decay curve can be approximated by two components, and scintillation decay time constants are 1 ns and 9-10 ns. Since the component with a short decay time constants agreed with the result in the previous study [2], the origin of luminescence is considered to be charge transfer transition of Yb^{3+}. Also, as for the long component, since it is reported that the decay time constant due to the garnet structure of $Lu_3Al_5O_{12}$ is 20-30 ns [3], we considered that the luminescence derived from a garnet structure is observed in a relatively high-speed form. The pulse height spectra are shown in Fig.2. We observed full energy deposited peak for all the samples under 5.5 MeV α-rays irradiation. Among them, non-doped sample showed the highest scintillation light yield. In this presentation, we will report more detailed scintillation characteristics in each sample.

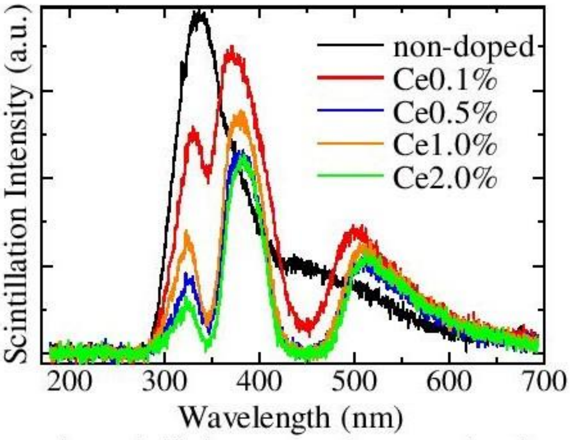

Fig.1 Scintillation spectra of 0-2% Ce-doped $Yb_3Al_5O_{12}$ under X-ray exposure.

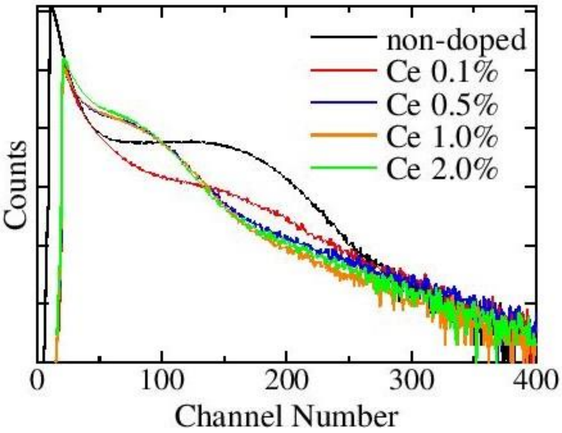

Fig. 2 Pulse height spectra of 0-2% Ce-doped $Yb_3Al_5O_{12}$ under ^{241}Am α-ray excitation.

References:
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SCINTILLATION PROPERTIES OF Ce-DOPED $Er_3Al_5O_{12}$ SINGLE CRYSTALS SYNTHESIZED BY THE FLOATING ZONE METHOD

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Scintillators are phosphor materials that emit light under irradiation of radiation and are applied to radiation detectors for medical and security applications. Characteristics required for ideal scintillators are high light yield and short fluorescence lifetime, and development of scintillator materials with better properties is vigorously carried out [1]. In recent years, rare earth element doped garnet structure ($A_3B_5O_{12}$) has attracted attention as a scintillator material with high light yield [2]. Among them, Ce and Er co-doped $Y_3Al_5O_{12}$ exhibited a high light yield due to interactions of Ce and Er [3]. Although studies using Ce and Er as additives can show good scintillation responses as described above, the scintillation characteristics of containing Ce or Er as a host material are unknown. Therefore, in this study, $(Ce_xEr_{1-x})_3Al_5O_{12}$ (x = 0, 0.001, 0.005, 0.01, 0.02) single crystals were prepared by the Floating Zone method. Structural properties of the sample and scintillation characteristics were evaluated.

The crystal structure of the samples prepared by the Floating Zone method was measured by powder XRD analysis. As a result, it was found that all the samples were obtained in a single phase. The scintillation spectra in the visible region under X-ray irradiation are shown in Fig.1. Scintillation was observed from all samples, and the wavelengths were around 420 nm and 520 nm. These luminescence at the same peak wavelength were detected even in non-doped sample, and we considered that luminescence of Ce^{3+} is not the main cause. Luminescence of Er^{3+} 4f-4f transition caused by $Er_3Al_5O_{12}$ host material is dominant. Scintillation spectra in near infrared (NIR) wavelength are shown in Fig.2. Scintillation was observed from all samples, and the emission wavelength was around 1000 nm. The luminescence origin of these peaks are 4f-4f transition of Er^{3+}. In addition, scintillation decay time was 550-700 μs derived from the 4f-4f transition of Er^{3+} both visible and NIR wavelength regions. In this presentation, we will report more detailed scintillation characteristics in each sample.

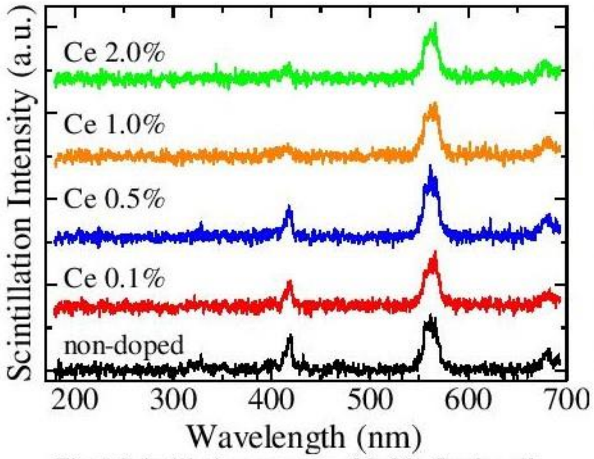

Fig.1 Scintillation spectra of 0-2% Ce-doped $Er_3Al_5O_{12}$ under X-ray exposure in visible region.

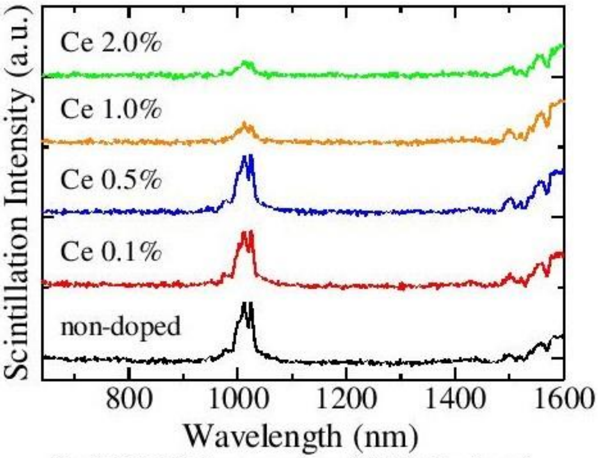

Fig.2 Scintillation spectra of 0-2% Ce-doped $Er_3Al_5O_{12}$ under X-ray exposure in NIR region.

References:

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SPECTROSCOPIC PROPERTIES OF NEW SOLID STATE SOLUTION $Gd_3Ga_3Al_2O_{12}$: Ln (Ln = Ce, Sm, Eu, Tb, Dy) GARNETS

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$Gd_3Ga_3Al_2O_{12}$ (GGAG) single crystals belong to garnet group and crystallize in the cubic crystal structure with space group *Ia-3d* (Z = 8). Gd^{3+} ions enter dodecahedral positions, surrounded by 8 oxygens (positions *24c* in Wyckoff notation) while Ga^{3+} and Al^{3+} occupy tetrahedral (*24d*) and octahedral (*16a*) positions surrounded by 4 and 6 oxygen ions, respectively. It has been found that active dopant can be situated in other than typical Gd^{3+} sites in this solid solution host. The starting formula was $Gd_{2.98}Al_{2.008}Ga_{3.012}O_{12}$ due to segregation of elements in final crystal, and stoichiometric in the case of nanopowder and nanoceramic. It has been found that (GGAG:Ce) crystals characterized by a high light output close to 50000 ph/MeV and a fast decay time of ∼50 ns belong to the most important discoveries that have entered the scintillator market in the current decade [1,2] and continuously attract a lot of attention [3,4].

In this presentation we describe and discuss spectroscopic properties of Sm, Eu, Tb, Dy doped in this material. It was shown that active ion can occupy at least three different local positions. Due to solid state solution nature, the absorption and emission bands of dopants are broader than for analogical $Gd_3Ga_5O_{12}$ garnet. The integrated sphere measurements returns high efficiency of energy conversion of excitation radiation to visible luminescence. Interesting properties was found for nano-powders and nano-ceramics. The lifetime and luminescence branching ratio depend strongly on the size of grains. The used pressure in the process of production of nanoceramics can induced strong movement of $4f^N – 4f^{N-1}5d$ bands. The new positions of d-levels are permanent and depends only on used pressure and temperature of calcination.

Possessing these properties the material can be proposed as a new candidate in solid state LED phosphors.

Acknowledgements

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NANOPOROUS SILICON / NANOMESH ALUMINUM LIGHT EMITTING SCHOTTKI STRUCTURE FOR ADVANCED MICROLED DISPLAYS

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Nanoporous silicon - nanomesh aluminum light emitting structure for high efficient CMOS compatible microLED displays system is discussing.

These displays can be incorporated in a low cost high quality augmented - reality or virtual-reality product instead of wide spread Liquid Crystal – on - Silicon, QLED or OLED-on- Silicon versions.

In general, this microLED display includes a matrix of a very fast electroluminescent nanoporous Si / nanostructured Al Schottki structures fabricated onto a silicon wafer using standard CMOS technology. The light emission in visible spectral range is evident.

The resolution of a microLED imaging system can be very high due to small pixel size (in the range of 1, 0 μm). Moreover, the electro optic response (switch on – switch off times) of a light emitting pixel is fast enough to address a large number of pixels in an independent manner using passive addressing technique.

In this paper we will concentrate on the usage of novel technologies to fabricate nanostructured materials with unique features for high efficient EL- and conductive transparent layers [1, 2]. Possible areas of application in low cost high performance augmented - or virtual-reality optical devices will be also discussed.

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SUPPRESSION OF METAL-TO-METAL CHARGE TRANSFER QUENCHING IN Ce^{3+} AND Eu^{3+} COMPRISING GARNETS BY CORE-SHELL STRUCTURE

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Phosphor converted LEDs (pcLEDs) dominate general and domestic lighting in the meantime. Currently, the broad-band emitter (Sr, Ca) $AlSiN_3:Eu^{2+}$ is widely applied as red emitting component. However, its luminescence spills over into the NIR region, decreasing the luminous efficacy. Line emitters such as Mn^{4+} or Eu^{3+} offer a much higher luminous efficacy and research activity in the field of alternative red emitting phosphors is high. Unfortunately, Eu^{3+} has low absorption coefficients in the visible spectral region and it is therefore not applicable for use in pcLEDs. Usually in such a case, sensitizers are used. However, the widely used sensitizer Ce^{3+} cannot be readily combined with Eu^{3+} as a metal-to-metal charge transfer (MMCT) quenches the luminescence. This problem can be overcome to some extent by utilizing Gd^{3+} or Tb^{3+} as an intermediary, as has been shown by Blasse and Setlur [1, 2]. However, this approach suffers from the low Eu^{3+} concentrations of 0.5-2% required to suppress the MMCT. Gui et al. prepared $NaYF_4$:Ce, Tb, Eu core-shell particles to separate Eu^{3+} in the core from Ce^{3+} in the shell [3]. Using a core-shell structure the concentration of Eu^{3+} can be much higher without causing MMCT quenching. However, while the synthesis of fluoride core-shell particles is easier than that of more complex oxides, Ce^{3+} absorption is in the UV-C region in such hosts. Therefore, this phosphor cannot be employed for application in pcLEDs. We chose $Tb_3Al_5O_{12}$ (TAG) as the material for core and shell as it combines a high Tb^{3+} concentration with absorption of Ce^{3+} in the blue spectral region. The external quantum efficiency and quenching temperature of the TAG:Ce^{3+}@TAG:Eu^{3+} particles are nearly the same as those of the TAG: Ce^{3+} reference. Thus, the MMCT quenching has been suppressed while maintaining a high Eu^{3+} concentration of 10%. These results show that the core-shell approach enables the use of Ce^{3+} as a sensitizer for Eu^{3+}, which in turn allows the application of Eu^{3+} phosphors in warm-white pcLEDs with high luminous efficacy (LE) and color rendering (CRI).

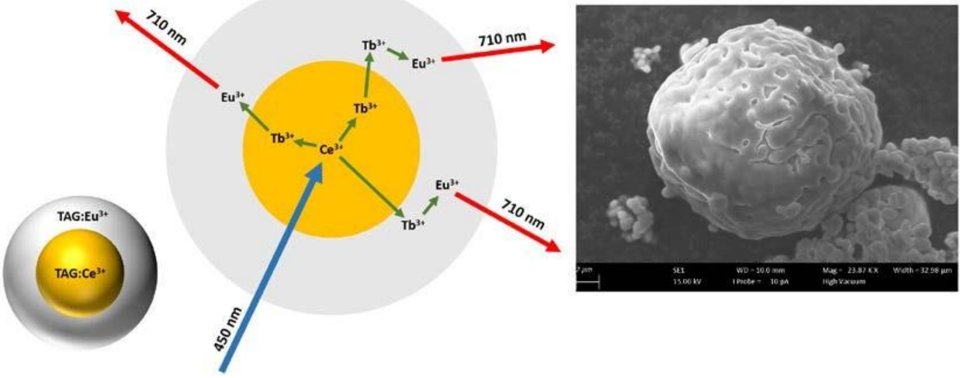

Figure. 1: Schematic structure of a core-shell particle and illustration of the luminescence process (left) and a SEM image of a core-shell TAG:Ce^{3+}@TAG:Eu^{3+} particle (right).

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LUMINESCENT AND LASER PROPERTIES OF CAG DOPED BY Tm^{3+} AND Ho^{3+}

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I. Introduction. Glasses based on CaO-Al_2O_3 system (calcium aluminate glasses, CAGs) are relatively new materials that have already found their place in optical industry. Their attractive features are high infrared transmittance (up to 5÷6 μm) combined with excellent mechanical properties and thermal conductivity (exceeding those of fused silica) and excellent moisture resistance. In contrast to silica, these glasses can easily include up to 3÷5% mole of lanthanide oxides. Here we demonstrate the luminescent and laser properties of activated CAGs in the spectral range where these glasses seem the most competitive - 2÷2.5 μm. Two lanthanide ions – Tm^{3+} and Ho^{3+}have optical transitions in this range.

II. Glass samples fabrication**.** The developed laboratory procedure of CAG synthesis differed from the methods used elsewhere. The main feature of this procedure is the use of inductively heated vitreous carbon crucibles. Dry rarefied nitrogen atmosphere has made it possible to obtain glass samples with OH-groups absorption at ~3 μm less than 0.005 cm^{-1}.

III. Spectral peculiarities of Tm^{3+} and Ho^{3+} in CAG. The emission spectra presented in Fig.1 were measured using laser diode excitation at 800 nm (for Tm) and 668 nm (for Ho). In comparison to other oxide or fluoride glasses, the presented spectra look rather unusual due to enhanced width and red shift, especially for Tm^{3+} $^3F_5$-$^3H_6$ transition, that extends up to ~2.4 μm and overlaps with ~2.3 μm $^3H_4$ – $^3H_5$ transition. Thus, the total tuning range of Tm-doped CAG laser can extend from ~1.9 to ~2.4 μm that is hardly possible in any other type of glass.

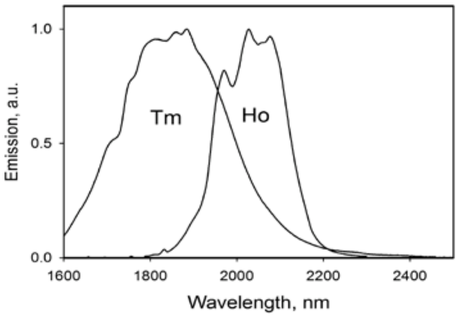

Figure 1 Emission spectra of Tm^{3+} ang Ho^{3+} in CAG.

The measurements of luminescent lifetimes of metastable manifolds $^3H_4$ (220μs), $^3F_5$(2500μs) Tm3+ and $^5I_7$(10000μs) Ho3+ in CAG have showed that they are an order of magnitude longer in CAG then in silica, enabling to create low-threshold lasers.

IV. Bulk CAG lasing demonstration. A 30 mm long flat-parallel polished CAG sample doped with 10^20 cm-3 Tm3+ was pumped by a pulsed ruby laser (incident pump pulse energy up to 0.7 J). In case of ~0.5% outcoupling cascade lasing at 2300 and 2100 nm was observed.

The investigation was supported by RFBR grant 17-02-00369.

COMPARISON OF SPECTROSCOPIC PROPERTIES OF LASER INDUCED ANTI-STOKES WHITE EMISSION OBSERVED FROM Sr_2CeO_4 OBTAINED BY CITRIC GEL AND SOLVOTHERMAL METHODS

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Strontium cerium oxide was prepared first time almost twenty years ago using combinatorial method [1]. This material has been extensively investigated by researchers due to its unique spectroscopic properties such as high emission efficiency, high absorption cross section and good thermal and mechanical stability. Here we report for the first time results considering broadband anti-Stokes white emission observed from Sr_2CeO_4 prepared using solvothermal method. Moreover we will compare them with results obtained for Sr_2CeO_4 synthesized by citric gel route. For each of proposed techniques the impact of average grain sizes of strontium cerium oxide on intensity of white emission was determined. The spectroscopic measurements of anti-Stokes white emission were carried out in reduced pressure conditions upon focused infrared laser diodes excitation as a function of excitation power density and ambient pressure. Furthermore the luminescence kinetics of Sr_2CeO_4 were determined by measurements of decays and rise times of emission. It was found that both power and pressure dependences exhibit threshold behavior typical for photon avalanche effect. The mechanism responsible for generation of white light from strontium cerium oxide will be discussed.

Acknowledgements
The authors would like to acknowledge NCS project for financial support (Grant No. NCN-2016/21/N/ST5/03072).

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ITO-FREE CONDUCTIVE TRANSPARENT NANOSTRUCTURED FILMS

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Generally, both photovoltaic and biophotonic devices working with ITO conductive transparent layers which have high optical transmittance (in the range of 80-85%) and sheet resistance as low as less than 1 Ohm/sq. But they also have some important drawbacks dealing with the unpredictable cost of Indium on the world market and their stability issues when using flexible templates [1].

In the presentation we will discuss the possible alternative approach to fabricate cheap nanostructured transparent conductive aluminum films onto a glass or a flexible substrate via simple anodizing process. The anodizing parameters are changed in the final stage of the process, which allows to open transparent windows and leave a nanomesh structure from the rest of aluminum [2].

In the nanostructured aluminum film transparent and conductive functions are separated in space, but this feature doesn't come out due to a sub wavelength size of the nanomesh pitch. It allows to overcome some fundamental limitations, which are specific to ITO or ultrathin metal films, where conductive electrons works as electric charge carriers and light absorbers simultaneously [3].

We have shown the possibility of manufacturing the structure of a solar cell, combining such advantages as simplicity of design and technology and low production cost. The solar cell based on a Schottky diode with an nanostructured aluminum electrode operates on the basis of the principle of direct conversion of solar energy into electrical and can be used as an autonomous low-power source.

On a substrate of single crystal silicon of n^+-type conductivity with an epitaxial layer of n- type of conductivity with resistance of 0.29-0.34 Ohm·cm an aluminum film of 0.5 μm is sputtered by a magnetron sputtering. Subsequently, the substrate was ground to a predetermined thickness. On the reverse side, metallization (titanium, nickel, silver) was formed by magnetron sputtering.

So, the proposed approach based on the simple and low cost technology can be real alternative to ITO – or ZhO films in photovoltaic or biophotonic applications.

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ENHANCED LUMINESCENCE OF $SrSi_2N_2O_2:Eu^{2+}$ PHOSPHOR AS A RESULT OF SYNTHESIS PARAMETER CONTROL

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Synthesis of $Sr_{0,96}Eu_{0,04}Si_2O_2N_2$ phosphor via one-step solid state reaction in a nitrogen flow in a graphite furnace could be influenced by some silicon losses in the form of $SiO_{(g)}$ in the presence of $CO_{(g)}$ resulting from $SrCO_3$ decomposition. The aim of the studies was to compare optical properties of the resultant phosphor if silicon losses were prevented by increased nitrogen pressure (Gas Pressure Sintering) or via addition of AlF_3 flux. It was expected that Al^{3+} could substitute Si^{4+} compensating expected silicon and nitrogen losses. The results of chemical analysis by XRF showed the expected changes in Sr and Si content but the XRD analysis showed some non-resolved peaks in the specimens derived from AlF_3 enriched composition apart from the presence of a triclinic $Sr_{1.02}Si_2O_2N_2$ phase. Significant differences in the excitation and emission range, quantum efficiency (QE) and luminous efficacy were identified in the tested specimens. The most considerable improvement of QE and thermal quenching was found in the pressure assisted derived specimens while substantial reduction of those properties was observed in AlF_3 modified phosphors if compared to the reference material. Discussion of the obtained results is provided.

HOLMIUM DOPED BARIUM GALLO-GERMANATE GLASSES FOR NEAR-INFRARED LUMINESCENCE AT 2000 nm

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Among the variety of inorganic glass-host matrices, germanate based glasses are becoming more interesting and attractive class of amorphous materials for photonics devices. Germanate based glasses doped with rare earth ions have demonstrated a strong potentiality towards the development of fiber amplifier and near-infrared solid-state laser. Barium gallo-germanate glasses belonging to wide family of low-phonon germanate amorphous host matrices are also attractive for optical applications. The previously published works are well demonstrated that barium gallo-germanate glasses doped with Tm^{3+} [1], Pr^{3+} [2] and Er^{3+} [3] are promising for broadband near-infrared luminescence.

The intention of our work was to synthesize rare earth doped barium gallo-germanate glasses and to characterize their near-infrared luminescence properties. Rare earths as the optically active ions were limited to trivalent Ho^{3+} emitting near-infrared radiation at about 2000 nm. NIR luminescence band located at 2000 nm corresponds to $^5I_7$ to $^5I_8$ transition of Ho^{3+} [4]. Several spectroscopic parameters for $^5I_7$ to $^5I_8$ near-infrared transition of Ho^{3+} ions in barium gallo-germanate glass were determined. The peak stimulated emission cross-section equal to $0.35x10^{20}cm^2$ is quite well consistent with value ($\lambda_{em} = 0.31x10^{20}cm^2$) obtained for $^5I_7$ to $^5I_8$ NIR transition of Ho^{3+} ions in lead silicate glass [5]. Our further investigations indicate that the luminescence lifetime $^5I_7$ (Ho^{3+}) is close to 3.58 ms and its experimental value strongly influenced on activator concentration. These aspects are presented and discussed in details.

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LUMINESCENT PROPERTIES OF YSZ CERAMICS DOPED WITH EUROPIUM IONS PRODUCED BY SPARK PLASMA SINTERING TECHNIQUE

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Optical properties of ceramic materials depend on the grain size, the size of residual pores, and the presence of defects [1]. In order to obtain ceramic materials with desired optical properties, a careful selection of the powder processing and sintering methods should be made. Among numerous manufacturing methods of high-quality ceramics, a promising method is dry compaction of nanopowders by the spark plasma sintering (SPS) technique.

Zirconia (ZrO_2) stabilized in the cubic structure is a promising photonic material owing to it is high mechanical strength, record high refractive index, low optical losses and high chemical/photochemical stability [2]. The luminescence of ZrO_2 doped with rare earth ions has been studied by a number of researchers [3, 4]. The cationic species added to ZrO_2 for tetragonal and cubic phase stabilization (Y) could affect the luminescence of rare earth ions. The rare earth ions substitutes Zr^{4+} ions in ZrO_2 and since the rare earth ion is inovalent (the charge state 2+ or 3+), the oxygen vacancy is involved for charge compensation.

In this work, we investigated the optical and luminescent properties of undoped yttrium stabilized zirconia (YSZ) ceramics and doped with Eu ceramics. The polycrystalline YSZ ceramics from nanopowder was consolidated by SPS technique using the installation SPS- 515S (Syntex Inc., Japan). SPS conditions were as following: sintering temperature T=1300 ^{o}C, vacuum P=10^{-3} Pa, the pressure of 140 MPa, the heating rate of 8°C/min. The duration of heating was 10 minutes. The diameter of pellets sintered in the graphite die was 14 mm.

Optical properties of sintered ceramics have been studied by the double-beam spectrophotometers LOMO SF-256 UVI and SF-256 BIK in the spectral range of 200 – 1100 nm and 1100 – 2500 nm, respectively. Photoluminescence spectra at room temperature were recorded with a fluorescence spectrophotometer (Agilent CaryEclipse) using a 150 W xenon lamp. The integrated cathodoluminescence spectra and decay kinetics were investigated with the pulsed optical spectrometer based on a high-current electron accelerator GIN- 600 (E_{ex}=0.25 MeV, FWHM=15 ns, W=23 mJ/cm^2) and AvaSpec-2048 fiber spectrometer.

A complex characterization of the crystalline and defect structure of the ceramic by XRD was carried out. Absorption, excitation, luminescence spectra were studied

The luminescence decay kinetics of synthesized YSZ ceramics were investigated. Nature of luminescent centers and mechanisms of luminescence are discussed.

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RADIOUMINESCENCE OF ERBIUM-DOPED YAG AND SPINEL CRYSTALS

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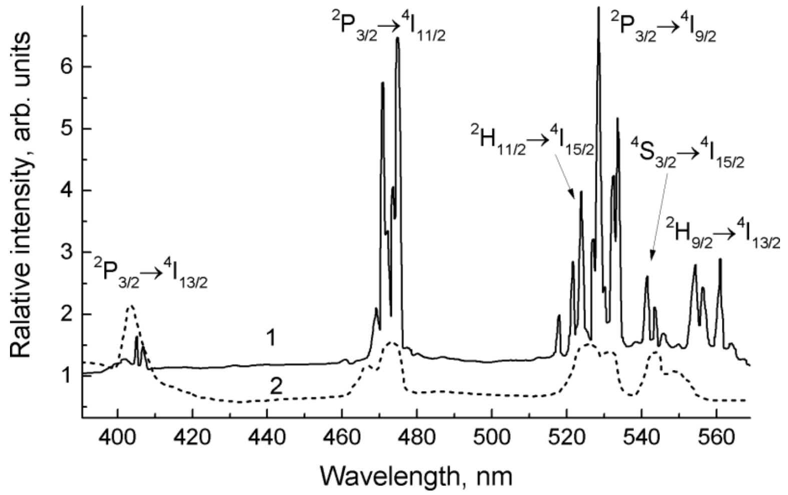
The comparative radio-luminescence (RL) spectra in the visible range of magnesium aluminates spinel (MAS) and yttrium aluminates garnet crystals (YAG) doped with erbium ions were investigated. The MAS of the non-stoichiometric composition $MgO\cdot 2.0Al_2O_3$: Er with additive 0.5 wt% of ErO_3 were grown using Verneuil method. The residual concentration of Er in spinel grown crystals was 0.12 wt%. Single crystals of YAG: Er were grown by Czochralski method in vacuum and the crystallophosphors were prepared by the solid phase chemical reaction both crystals of erbium content c_{Er}=1.4 wt%.

The RL spectra in YAG: Er single crystals includes all lines in the visible range related to transitions in Er^{3+} ions (curve 1). In the RL spectra of crystallophosphor there appear wide emission band at about 480 nm which tentatively was ascribed to luminescence of F-type centers formed at anionic vacancies [1]. Therefore, we speculate the incorporation of erbium in the YAG lattice is accompanied with defects formation in anionic sub-lattice.



The attempts to grow spinel single crystals doped with rare earth ions (including erbium) using Verneuil method were not successful. For non-stoichiometric spinel we managed to introduce Er^{3+} up to 0.12 wt%. The main peculiarity of the observed spectra is that sharp emission lines in different transitions of Er^{3+} are not resolved (curve 2). The wide emission bands are in accordance with shape of reflectance bands in Er-doped stoichiometric spinel phosphor powder prepared by combustion method [2]. The explanation of this phenomena is based on the high concentration of cationic and anti-site defects which creates disorder in non-stoichiometric MAS that allow to accommodate the large size rare earth ions in small size tetra- and octahedral positions of spinel lattice.

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SPECTRAL AND PHYSICAL PROPERTIES OF GERMANIUM-DOPED PHOTO-THERMO-REFRACTIVE GLASSES

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Photo-thermo-refractive (PTR) glass is a new class of inorganic photosensitive materials, which is developed for recording of high effective thermostable volume Bragg gratings. In these glasses, nanocrystals of AgBr-NaF grow in irradiated region after the UV irradiation and heat treatment, whose refractive index differs from the refractive index of the non-irradiated glass region [1]. This effect is used for fabrication of holographic optical elements [2].

In present work, the PTR glasses based on the Na_2O-ZnO-Al_2O_3-GeO_2-SiO_2 system and doped with F^-, Br^-, CeO_2, Sb_2O_3 and Ag_2O have been prepared. Germanium oxide concentration was varied from 0 to 34.2 mol. %. The glass synthesis was carried out at temperature of 1440°C in the air atmosphere using a quartz crucible, and the melts have been homogenized with the platinum stirrer. The glass transition temperature measured with differential scanning calorimetry was varied from 478°C to 510°C for different germanium oxide concentration. All samples were irradiated by UV radiation and subsequently heat treated at different temperatures in range from 400°C to 540°C. The refractive index and the absorption spectra of the samples were measured at all stages of UV irradiation and thermal treatment. It was shown that the introduction of germanium oxide into the PTR glass matrix increases the refractive index from 1, 49 up to 1, 66. Effect of germanium oxide on mechanisms of spontaneous thermo-induced crystallization and photo-thermo-induced crystallization was studied in the PTR glass.

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OPTICAL AND SCINTILLATION PROPERTIES OF Nd-DOPED $YAlO_3$ CRYSTALS

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Scintillators are one of the phosphors, and they can convert ionizing radiations to UV-NIR photons immediately. The spectrum of the application is wide, including medical imaging, security, well-logging, environmental monitoring and high energy physics. Recently, the trend of R&D of new scintillators is insulator materials doped with Ce which shows efficient luminescence due to 5d-4f transition of Ce^{3+}. In addition, some other rare earth emission centers which can exhibit 5d-4f transition have attracted much attention [1]. On the other hand, some rare earth emission centers can show 4f-4f transition, and some of them can be applicable for the scintillator. In the case of Nd-doped YAG, it exhibited relatively high scintillation light yield of ~ 10000 ph/MeV under ^{137}Cs X-ray excitation in the pulse height spectrum [2]. Technically, scintillation decay with several μs is acceptable for practical uses. In order to expand studies of Nd-doped scintillators, in this study, we synthesis and evaluate Nd-doped $YAlO_3$ (YAP) crystals.

The sample crystals were synthesized by the floating zone method, and nominal Nd concentrations were 0.1, 0.5, 1 and 2% with respect to Y. After the crystal growth, all the samples were polished for optical characterizations such as transmittance, photoluminescence (PL) and PL decay time. Then, we evaluated X-ray induced radioluminescence spectra, scintillation decay time profiles, and pulse height spectra upon ^{137}Cs irradiation. In the pulse height, Nd-doped YAG which was studied previously [2] was used as a reference.

Fig.1 shows radioluminescence spectra of the samples. Many sharp lines due to Nd^{3+} 4f-4f transitions were detected. Fig.2 demonstrates ^{137}Cs irradiated pulse height spectra. Compared with reference Nd-doped YAG, Nd 0.1% and 0.5% doped YAP showed higher scintillation light yield of 12500 and 6500 ph/MeV, respectively. In the conference, other optical and scintillation properties will be shown and discussed.

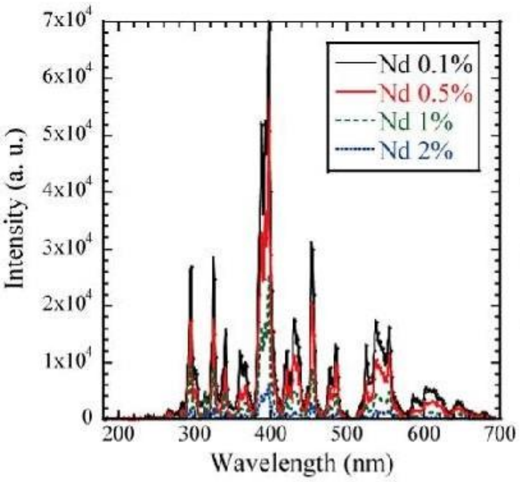

Fig. 1 X-ray excited radioluminescence spectra.

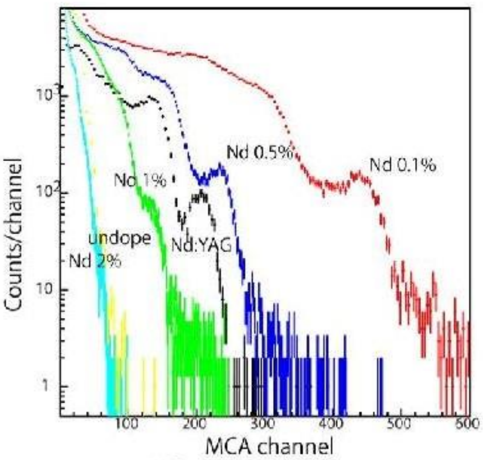

Fig.2 ^{137}Cs pulse height spectra.

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OPTICAL AND RADIATION INDUCED LUMINESCENCE PROPERTIES OF SCANDIUM ACTIVATED Al_2O_3 TRANSPARENT CERAMICS

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Ionizing radiations, having high energy (keV – Mev), can penetrate materials and ionized atoms. They are invisible to human eyes and would be harmful. Thus, radiation detectors are needed to detect and measure the doses absorbed by human bodies. Solid state luminescent materials which were widely used in radiation detectors can be classified into two types. Upon exposure to the ionizing radiations, scintillators can instantly convert the energy into thousands of visible photons. Thus, they are useful for various applications such as medical imaging and security inspection. On the other hand, storage phosphors can accumulate the radiation doses for some period of time. Further external stimulation, either by heat (thermally stimulated luminescence, TSL) or by light (optically stimulated luminescence, OSL), are needed by storage phosphors to read out the dose absorbed as luminescence. They generally have been utilized in personal dosimeters. Among such storage phosphors, C-doped Al_2O_3 crystal is one of the famous dosimeter materials, but other dopant ions have not been examined largely. In order to develop new dosimeter materials, in this study, we examined Sc-doped Al_2O_3 transparent ceramics for the radiation detector material.

The sample crystals were synthesized by the spark plasma sintering method, and nominal Sc concentrations were from 0.01 to 2%. After the synthesis, all the samples were polished for optical characterizations such as photoluminescence (PL) and PL decay time. Then, we evaluated X-ray induced radioluminescence spectra, scintillation decay time profiles, thermally stimulated luminescence (TSL) dosimeter properties including TSL glow curves, dose response functions and fading characteristics.

Fig.1 shows radioluminescence spectra of the samples. Broad emission peak due to F^+ center (300 nm) and F center (400 nm) were observed. Fig.2 demonstrates TSL glow curves of the samples after X-ray irradiation. Some glow peaks appeared by introducing Sc ions, and when we compared with Al_2O_3 crystal, TSL intensity was highly improved. In the conference, other optical, scintillation and dosimeter properties will be shown and discussed.

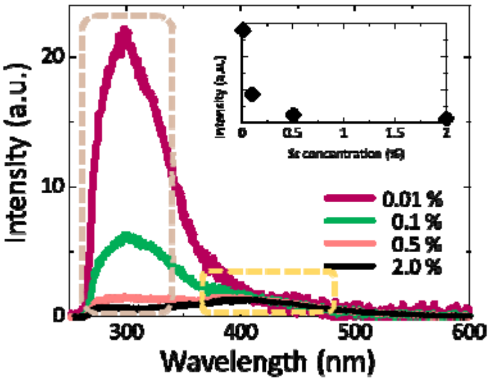

Figure 1. X-ray excited radioluminescence spectra.

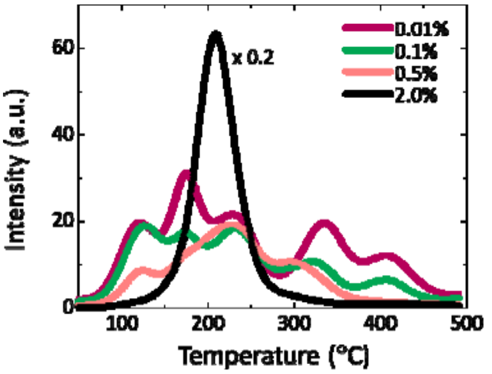

Figure 2. TSL glow curves.

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ACTIVE MEDIA BASED ON BaY_2F_8 SINGLE CRYSTALS FOR LASERS OF DIFFERENT SPECTRAL RANGES

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Single crystals based on inorganic fluorides have a unique combination of chemical properties that allow them to be used not only under normal conditions, but also in corrosive environments. Most of them are insoluble in water; they are insoluble in dilute acids even when boiling, slightly soluble in hot concentrated acids, chemically resistant to most organic solvents. Melting temperatures in comparison with oxides are relatively low (do not exceed 1700C), therefore it is possible to use inexpensive equipment for growing bulk crystals. BaY_2F_8 single crystals activated with rare earth ions are a popular material for developing active media for lasers of different spectral ranges. The technology of growing these crystals is presented in detail in [1]. The report will consider the following issues:

Active media for UV range.

The short-wave limit of the intrinsic transmission (λsw) of most single crystal fluorides is located in the VUV region of specrtrum. This is an advantage of single crystals fluorides in comparison with oxide single crystals for applications in short wavelength region. λsw of single crystal BaY_2F_8 = 125 nm.

The main problems in the development of such media are two: limited choice of solid-state pump sources for direct excitation of laser activity with 5d-4f transitions of rare-earth ions and processes of solarisation of active elements that result from the action of pumping UV radiation. One way to solve both problems simultaneously and implement compact emitters for UV light is to use up-conversion mechanisms for the excitation of 5d luminescence of rare earth ions. This would enable the use comfortable pump sources like laser diodes and prevent solarization processes by pumping with lower energy quanta. As an example, intense UV luminescence in a BaY_2F_8 crystal co-activated by Yb^{3+}, Pr^{3+} and Ce^{3+} ions excited by IR laser diodes will presented.

Active media for the visible range.

The emission on the generation channels of visible range in single crystals Ba (Y, Yb) $_2F_8$:Ho^{3+}, Ba(Y, Yb)$_2F_8$:-Er^{3+}, Ba(Y,Yb)$_2F_8$:Tm^{3+}, Ba (Y,Yb)$_2F_8$:Pr^{3+} will be considered. The efficiency of the various up-conversion mechanisms that were used to excite this luminescence will be discussed.

Active media for IR spectral range.

Excitation of three-micron and two-micron generation in crystals Ba(Y,Yb) $_2F_8$:Ho^{3+}, Ba(Y,Yb)$_2F_8$:Er^{3+}, Ba (Er) $_2F_8$:Tm^{3+}- Ho^{3+} using cross-relaxation laser schemes with quantum efficiency equal to 3 and 2 will be presented. A comparison of the cross relaxation processes occurring in fluoride and oxide single crystals will be discussed.

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ENERGY TRANSFER IN QUANTUM DOT STRUCTURES PROBED BY PHOTOLUMINESCENCE EXCITATION SPECTROSCOPY IN THE TELECOMMUNICATION SPECTRAL RANGE

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The electronic structure of quantum dots and energy transfer mechanisms (specially on a single dot level) available experimentally through photoluminescence excitation spectroscopy are limited mainly to the quantum dots emitting below 1 μm. Within the near infrared region, telecommunication windows of 1.3 μm and 1.5 μm are of special interest, for they correspond to the most desirable wavelengths in optoelectronic applications. Besides the fundamental information on the electronic structure, photoluminescence excitation spectroscopy can provide additional data, e.g., on the confinement regime in nanostructures or relaxation efficiency, when compared with phonon energies. The relaxation processes can be farther enhanced by the continuum of states below the wetting layer ground state. There is also a very limited knowledge and published reports on the carrier transfer from the wetting layer itself to the nanostructures or on the in-plane energy transfer between quantum dots emitting in this application-relevant spectral range.

The report presents photoluminescence excitation study of zero-dimensional III-V nanostructures with the ground state emission in the spectral region of telecommunication wavelengths. The experiment is based on a microphotoluminescence setup adapted to the tunable excitation laser source with external cavity design. Depending on the wavelength, the external cavity is arranged in Littrow or Littman configurations with additional spectrometer-based laser-line filtering. This solution provides continuous wavelength tuning range of around 100 nm with a single laser diode. In addition, pulsed laser system (based on optical parametric oscillator) is available, providing large-wavelength-step but spectrally wide tuning. This solutions can provide the total excitation spectral range of at least 1000-1600 nm. The study aims at expanding the knowledge on the energy transfer processes in quantum dots – in particular, it attempts to provide more detailed insight into the excited states. Additionally, for larger nanostructures (e.g. elongated quantum dots) the energy difference between electronic levels is expected to be relatively low and even comparable with the thermal energy, which is crucial for potential applications, where thermal losses have to be evaluated.

The photoluminescence excitation results are supplemented by standard micro-photoluminescence characterization, identifying the emission spectral range of the investigated nanostructures. The obtained results are confronted with numerical simulations to predict the detailed electronic/excitonic structure versus various morphological and compositional parameters of the system under investigation.

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ELECTRO-OPTICAL PROPERTIES OF AN ARTIFICIAL MOLECULE CONFINED IN SELF-ASSEMBLED $Ga_{1-x}Al_xAs$ NANOCONE

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As a consequence of the rapid and vast development in the field of nanofabrication technologies, the low-dimensional semiconductor systems have been a great deal of interest in the last decades [1, 2]. The manufacturing of semiconductor nano-structures, specially quantum dots, have provided ideal scenarios to study few-particle systems residing into these zero-dimensional clusters with different shapes and sizes as a result of the quantum confinement [1, 2]. The few-particle energy structure may exhibit unique properties for the opto-electronic field which is intrinsic related to the number and type of confined particles, external fields and shape and size of the quantum dot [3, 4]. The range of applications is very wide being of special interest those related to the development of advanced sensors [5]. These notable studies, have inspired the present work in which is calculated the quantum levels of a D_2^+ artificial molecule confined in a $Ga_{1-x}Al_xAs$ pyramid-like nanocone within the effective mass framework and by using an adiabatic/finite elements hybrid technique. Furthermore, the optical response is addressed by using the compact density matrix formalism. The validation of the three-dimensional numerical procedure was performed by comparing it with analytical solutions for strictly two-dimensional systems such as single-electron elliptic-base disks. The set of results are in excellent agreement confirming the accuracy of the proposed model.

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OPTICAL THERMOMETRY BASED ON VIBRATION SIDEBANDS IN Y_2MgTiO_6:Mn^{4+} DOUBLE PEROVSKITE

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The Mn^{4+} doped Y_2MgTiO_6 phosphors are synthesized by the traditional solid state method. Powder X-ray diffraction (XRD), scanning electron microscope (SEM) and energy-dispersive X-ray spectrometer (EDS) are employed to characterize the samples. The Mn^{4+}-doped Y_2MgTiO_6 phosphors show the far-red emission at around 715 nm, which is assigned to the $^2E_g \rightarrow {}^4A_2$ spin-forbidden transition of Mn^{4+}. The temperature dependent luminescent dynamics of Mn^{4+} is described by a complete model associated with electron-lattice interaction and spin-orbit coupling. The non-contact optical thermometry of Y_2MgTiO_6:Mn^{4+} is discussed based on the fluorescence intensity ratio (FIR) of thermally coupled anti-Stokes and Stokes sidebands of the efficient ~ 715 nm far-red emission in the temperature range 10 - 513 K. The maximum sensor sensitivity of Y_2MgTiO_6:Mn^{4+} is determined to be as high as 0.00142 K-1 at 153 K, which demonstrates potential applications for the optical thermometry at low temperature environments.

LUMINESCENCE PROPERTIES OF SODALITE-TYPE $Zn_4B_6O_{13}:Mn^{2+}$

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Luminescence properties of sodalite $Zn_4B_6O_{13}:Mn^{2+}$ are investigated by optical and laser excitation spectroscopy in the temperature range 10 – 300 K. The samples of $Zn_4B_6O_{13}:Mn^{2+}$ are prepared in the carbon reducing atmosphere. The green emission at 540 nm are observed in $Zn_4B_6O_{13}:Mn^{2+}$ for various Mn^{2+} concentration. Optimum Mn^{2+} concentration and critical distances between Mn^{2+} ions in $Zn_4B_6O_{13}$ are obtained by the luminescence intensity as functions of Mn^{2+} concentration. The decays of Mn^{2+} emission depend strongly on Mn^{2+} concentration due to the energy transfer and energy diffusion in $Zn_4B_6O_{13}:Mn^{2+}$. The fine structures consisting of the intense zero phonon line (ZPL) and weak vibrational sidebands are observed at low temperature. The relevant mechanism of excitation bands, ZPL, vibrational sidebands and the bandwidth as functions of temperature are interpreted in detail by energy level diagram of the $3d^5$ transition metal ions and configuration coordinated diagram. The high thermal stability of the $Zn_4B_6O_{13}:Mn^{2+}$ phosphor are observed in the temperature range 10 - 300 K.

GAS SENSORS BASED ON ELECTROSPUN OF CHOLESTERIC LIQUID CRYSTAL CORE MICROFIBERS FOR DETECTING VOLATILE ORGANIC COMPOUNDS

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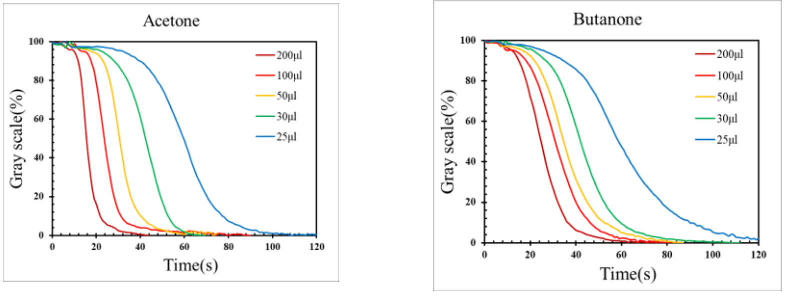
It is well-known that cholesteric liquid crystal (CLC) is self-organized in a periodic helical structure spontaneously, which leads to a periodic modulation of the refractive index and results in a selective Bragg reflection band. The reflection occurs in the planar texture at wavelength $\lambda_0 = \bar{n}P_0$ where $\bar{n}$ and p are the average refractive index and helical pitch of liquid crystal, respectively. The CLC pitch can be changed by external stimuli such as stress, temperature, and chemical composition dissolved in CLC. Owing to this unique property, CLC material can be applied to achieve a visual sensing system displaying color changes as the detection signal. In this work, a novel method is proposed to make a gas sensor based on the electrospun CLC coaxial fiber for real-time detecting volatile organic vapors. The coaxial electrospinning technology was used to fabricate core-sheath polymer composite fibers with encapsulated cholesteric liquid crystal, and then the proposed fibers were applied to monitor the solvents of acetone and butanone respectively. The dynamic response of the CLC fibers to the organic vapor was recorded by the camera under the polarized light microscope. By analyzing the grayscale of the reflected light signal, the reaction of the CLC fibers to the organic molecules was investigated and analyzed. In addition, the response time of the CLC molecular from the planar alignment to disordered state under the disturbance of the organic gas was also studied. Quantitative characterization of reflected light signal is established to explore the dynamic response of organic vapor diffusing into the CLC layer as shown in Fig.1. Based on the experimental results, the pitch of CLCs is increased with the amount of the penetrated organic vapor. The order of CLC directors will lessen during the penetration of organic vapor and finally becomes null as enough amount of vapor molecule is bound with CLC molecules.



(a) (b)

Figure. 1 The measured dynamic response of the reflectance of CLC fibers under different concentrations of organic vapors (a) acetone, (b) butanone

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OPTICAL ANISOTROPY INDUCED AT DIFFERENT WAVELENGTHS IN AZOPOLYMER THIN FILMS: KINETICS AND SPECTRAL DEPENDENCE

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Azopolymers are highly efficient materials able to register the polarization state of light [1]. Their applications include data storage and diffractive optical elements with unique polarization properties [1, 2]. It is well known, that under illumination with linearly polarized light, optical anisotropy (dichroism or birefringence) is induced in the azopolymers due to *trans-cis-trans* isomerization and the subsequent reorientation of the chromophores. The value of the photoinduced birefringence (Δn) is a key factor which determines the possibility to inscribe efficient polarization holographic elements in a given material. Data about the spectral dependence of Δn are rarely presented [3, 4] and to the best of our knowledge, there is no published research about the influence of the recording wavelength on the birefringence spectrum $\Delta n(\lambda)$.

In this article, we present a study of real-time kinetics of birefringence, induced with different pump lasers with wavelengths from 355 to 532 nm in an amorphous azopolymer PAZO. During the real-time measurement, the value of Δn is determined at 635 nm, using a DPSS laser. When saturation is reached, the spectral dependence of the birefringence is calculated, using a method, described by us earlier [4]. Our results indicate that the investigated azopolymer can be used for applications in a wide wavelength range.

Acknowledgements: This work is financially supported by contract DN 18/5 with the National Science Fund of Bulgaria.

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LUMINESCENCE PROPERTIES OF THE $Li_2B_4O_7$: Er, Ag GLASSES

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The luminescence properties of the Er-doped and Er-Ag co-doped glasses with $Li_2B_4O_7$ (Li_2O_2–B_2O_3) basic composition have been investigated using optical absorption, photoluminescence (excitation, emission, decay kinetics), and Judd–Ofelt analysis. The $Li_2B_4O_7$: Er and $Li_2B_4O_7$:Er,Ag glasses of high chemical purity and optical quality were obtained in the air using standard glass technology, described in [1,2]. The XRD patterns of the obtained materials confirm their glassy structure. Spectroscopic and luminescence properties of the Er-doped $Li_2B_4O_7$ glasses were firstly detailed described in [1].

Optical absorption spectra of the Er-doped and Er-Ag co-doped $Li_2B_4O_7$ glasses consist of several narrow bands in the visible and infrared spectral ranges, which belong to characteristic $f-f$ transitions of the Er^{3+} ions. The Judd–Ofelt intensity parameters (Ω_2, Ω_4, and Ω_6) have been calculated using the spectral intensities of the observed absorption bands and least- square fitting. Absorption spectrum of thermally annealed (T_a = 460 °C, t_a = 2 hrs) $Li_2B_4O_7$:Er,Ag glass shows additional broad band in the range of 400 – 430 nm that is attributed to the surface plasmon resonance band of the metallic silver nanoparticles.

The photoluminescence spectra of the Er-doped and Er-Ag co-doped $Li_2B_4O_7$ glasses reveal infrared ($^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, λ_{max} = 1530 nm) and green ($^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition, λ_{max} = 545 nm) emission bands. The radiative properties such as transition probabilities (A_{rad}), branching ratios (β), stimulated emission cross-sections (σ_e), and radiative lifetimes (τ_{rad}) are estimated for observed emission transitions of the Er^{3+} ions and compared with corresponding values for other Er-doped glasses. Besides metallic silver nanoparticles, the Ag impurity is incorporated into the network of $Li_2B_4O_7$: Er, Ag glass as Ag^+ luminescence centres, which are characterised by broad emission band with a maximum about 395 nm that can be efficiently excited in the 330 – 350 nm spectral range.

The luminescence kinetics of the Er^{3+} infrared emission band in the investigated borate glasses were satisfactory described by single exponential decay with lifetimes about 350 μs, whereas the luminescence kinetics of the Er^{3+} green emission band are slightly non- exponential with average lifetime values about 60 μs. Experimental and radiative lifetimes were compared and quantum efficiency (η) for green ($^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition) and infrared ($^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition) emission bands have been estimated.

The enhancement of Er^{3+} luminescence in the $Li_2B_4O_7$: Er, Ag glass have been observed. The enhancement is stronger for the green luminescence ($^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition) of the Er^{3+} ions. The observed enhancement is attributed to energy transfer from the Ag^+ to the Er^{3+} centres as well as local field effects induced by surface plasmon resonance of the Ag nanoparticles.

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ANALYSIS OF ENERGY TRANSFER PROCESSES IN SrI_2: Eu VIA TRANSIENT ABSORPTION SPECTROSCOPY USING PULSED ELECTRON BEAMS

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Development of novel scintillators with high light yield is of considerable interest. Most scintillators are composed of an insulator host and dopants, which act as the luminescence centers. In such scintillators, excited states are initially generated in the insulator host upon exposure to ionizing radiation. Subsequently, the excitation energy is transferred to the luminescence centers, and finally scintillation occurs through radiative transitions of the luminescence centers. Among these basic processes, little is known about the energy transfer process, despite its importance. In the present study, to better understand the energy transfer process, the excited states in the host were analyzed using transient absorption spectroscopy. Furthermore, the SrI_2: Eu single crystals, grown using a "Liquinert" process, were used as the sample.

Figure 1 shows the time-resolved transient absorption spectra of undoped and Eu-doped SrI_2. The spectra of the undoped SrI_2 correspond to the excited state absorption of the host. The temporal profiles of the transient absorption almost correspond to the temporal profiles of the scintillation for the undoped and Eu-doped samples. This correspondence indicates that the transient absorption can be attributed to the excited states of Eu^{2+} for the Eu-doped sample. The observation of entirely different spectra for the undoped and Eu-doped samples indicates that the energy transfer to Eu^{2+} occurs within the time resolution of the measurements.

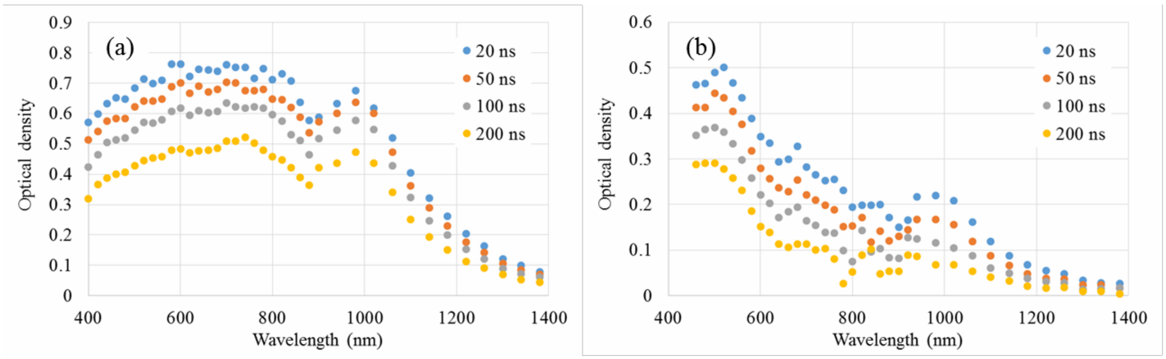

Figure 1. Time-resolved transient absorption spectra of (a) undoped and (b) Eu-doped SrI_2.

ANALYSIS OF RELAXATION PROCESSES OF EXCITED STATES IN $CdWO_4$ BY TRANSIENT ABSORPTION MEASUREMENTS

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$CdWO_4$ has long been used as a scintillator for high-energy photons because of the advantages of high density and relatively high light yield. As far as the origin of the scintillation is concerned, for the origin of the scintillation, involvement of self-trapped holes has been suggested. [1] However, the relaxation processes of the excited states remain unclear. In this study, we analyzed the relaxation processes of the excited states via the transient optical absorption of the excited states on the pico- to microsecond time scales.

Transient absorption spectroscopy was performed using pulsed electron beams from the electron linear accelerator as the excitation source. Figure 1 shows the transient absorption spectra on the pico- and micro-second time scales. A dominant absorption band was observed at around 600 nm. In the microsecond time scale, the optical density decreased with time, at a rate similar to that of the scintillation intensity, which indicated that this absorption band can be attributed to the excited states prior to the scintillation. Interestingly, a blue shift of the absorption band was observed in a picosecond time scale. In addition, the optical density also decreased with time in a range of several hundred picoseconds. The time evolution of the absorption band in the picosecond scale is owing to the relaxation and quenching of the excited states.

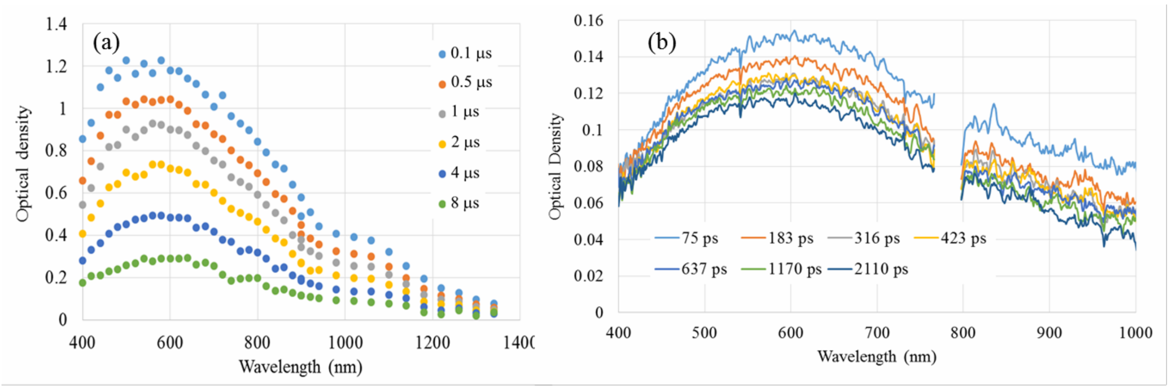

Figure 1. Transient absorption spectra of CdWO4 in (a) micro- and (b) picosecond scales.

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SCINTILLATION PROPERTIES OF Ce-DOPED BaF_2-Al_2O_3-B_2O_3 GLASSES

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Scintillators are one of the phosphor materials, and used in various fields including medical, security, and high energy physics [1]. It is known that some crystal scintillators such as $(Lu,Y)_2SiO_5:Ce^{3+}$ and $Gd_2SiO_5:Ce^{3+}$ exhibit high light yield and short decay time constants due to the 5d-4f transition of Ce^{3+} ions [2,3]. In addition to crystalline materials, rare earth-doped fluorescent glasses are used in some phosphor applications (e.g., laser). Glasses are not only showing excellent in transparency, high formability, mechanical strength, thermal and chemical stability, but also having a large degree of freedom in the chemical composition. In recent years, Shinozaki et al. reported that Eu-doped BaF_2-Al_2O_3-B_2O_3 glass showed high photoluminescence quantum yield [4]. In this research, we select Ce^{3+} ions as a dopant of the BaF_2-Al_2O_3-B_2O_3 glass and evaluated scintillation properties.

The samples were weighed and mixed in a chemical composition of xCeF$_3$-(30-x) BaF$_2$-20Al$_2$O$_3$-50B$_2$O$_3$ (x=0-10), melted in a carbon crucible at 1100 to 1200 °C for 40 min, and quenched to obtain a glass. The glasses were cut and polished to adequate size to research about optical properties (transmittance spectra, photoluminescence (PL) spectra, PL emission maps, and PL decay times), scintillation properties against X-rays (scintillation spectra and scintillation decay time) and thermally-stimulated luminescence (TSL) glow curves.

Fig.1 shows the scintillation spectra of non-doped and Ce-doped glasses under X-ray irradiation. A broad peaks were observed around 280-500 nm for the non-doped glass and 320-400 nm for Ce 0.3~3.0%-doped glasses. When the Ce concentration increased, the peak wavelength became longer due to self absorption. In the conference, we will reported and discuss optical and scintillation properties in detail.

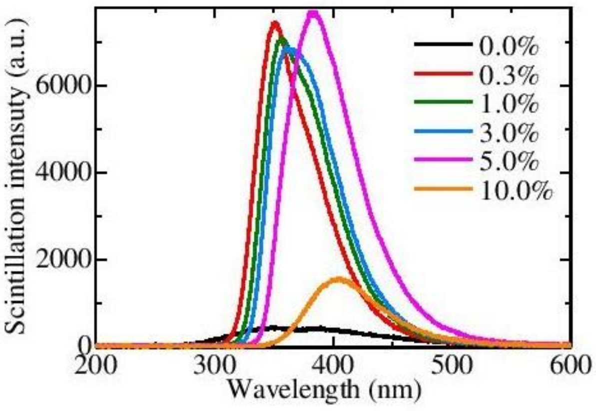

Fig.1 Scintillation spectra of samples.

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RADIATION-INDUCED LUMINESCENCE PROPERTIES OF Ce-DOPED BaO-Al_2O_3-SiO_2 GLASSES

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Silica glass has excellent characteristics such as low thermal expansion coefficient, high heat resistance, high ultraviolet transmittance, and chemical durability. For these reasons many researches have investigated glasses for a long time as to apply them into practical applications [1]. In applications of glasses, optical devices are one of the common usages of glasses, and silica glasses have attracted much attention for such purposes. Although there are so many studies on the structure and optical properties in silica glasses, there are few research of radiation-induced luminescence (scintillation) characteristics of them. In this study, we prepared glasses including silica as a constituent, BaO which has a relatively large effective atomic number, and Al_2O_3 (BaO-Al_2O_3-SiO_2 glass) to study their scintillation properties. As a luminescence center, we selected Ce^{3+} since it can show the luminescence due to the 5d-4f transition.

The samples were prepared by the conventional melt quenching method as follows. After weighing and mixing of $BaCO_3$, Al_2O_3, SiO_2 and CeO_2 to have a chemical composition of 50BaO-25Al_2O_3-25SiO_2 with 0-1% CeO_2, the mixed powder was put in an alumina crucible and melted at 1450°C for 30 minutes. The melt was then quenched on a stainless plate pre-heated at 350°C. Finally, BaO-Al_2O_3-SiO_2 glass was obtained by cooling room temperature. The obtained glass was polished, and researched about optical properties (transmittance spectra, photoluminescence (PL) spectra, PL emission maps, and PL decay times), scintillation properties against X-rays (scintillation spectra and scintillation decay time) and thermally-stimulated luminescence (TSL) glow curves. Fig.1 shows the scintillation spectra of non-doped and Ce-doped glasses. A broad peak was observed between 300-500 nm in all samples, and the scintillation intensity reached the maximum with the Ce 0.5%-doped glass. Fig.2 shows a scintillation decay profile for Ce 0.5%-doped glass. The decay curve was decomposed by three exponential functions. The decay time constants were 5.6, 42.8, and 398.9 ns. The first component is considered to be the instrumental response function, the second component is typical decay time due to Ce^{3+} ions [2]. The third component is attributed to the emission due to the host. In the conference, we will report and discuss optical and scintillation properties in detail.

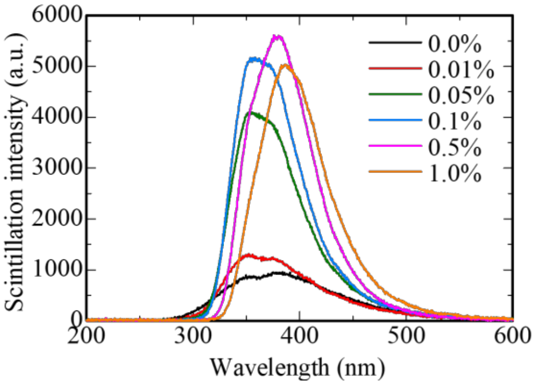

Figure 1 Scintillation spectra of samples.

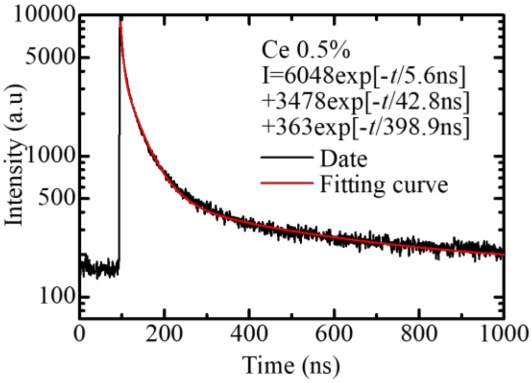

Figure 2 scintillation decay profile of samples.

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LUMINESCENCE AND OPTICAL PROPERTIES OF CERIUM OXIDE NANOPARTICLES

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Cerium oxide (CeO_2) nanoparticles present a promising material for biomedical applications due to its catalytic and antioxidant properties [1-2]. The mechanism of CeO_2 nanoparticles activity is assumed to be related to formation of oxygen vacancies on the particle surface, and as a consequence, changing the oxygen non-stoichiometry [3]. The presence of oxygen vacancies leads to the reduction of Ce^{4+} to Ce^{3+} state. The increase in the Ce^{3+}/Ce^{4+} valence ratio in the nanoparticle surface was found to correlate with the enhance of its catalytic activity [4]. Thus, the presence of Ce^{3+} ions in a surface layer of CeO2 nanoparticles plays a key role in the biological activity of the material. It is known, the Ce^{3+} ions show luminescent properties, while Ce^{4+} ions do not emit. The purpose of the work is to study the luminescence and structural defects of CeO_2 nanoparticles by spectroscopic methods.

CeO_2 nanoparticles was obtained by a pulsed electron beam evaporation in the low pressure gas on NANOBEAM-2 installation [5]. Luminescent study of nanoparticles was carried out by excitation with a laboratory source of ultraviolet radiation; spectra were recorded with MDR-23 monochromator and FEU-106 photoelectric multiplier. The optical absorption spectra were measured with a 9423UVA1002E Helios Alpha spectrophotometer.

The results of optical spectroscopic studies show the presence of cerium ions in two valence states. The observed emission of CeO_2 nanoparticles in the visible region at the 3.0 eV is due to radiative transitions $5d \longrightarrow 4f$ in the Ce^{3+} ion. In addition, a weak band at the 2.5 eV was found in the PL spectrum, which could be associated with the emission of F0-centers, associated with the oxygen vacancies [6]. The optical absorption spectrum consists of a broad intense band in the region of 2.5-6.0 eV, which should be attributed to photoinduced optical transitions with charge transfer from the 2p orbitals of oxygen to the unfilled 4f orbitals of the Ce^{4+} ion [7].

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TEMPERATURE DEPENDENCE OF RADIOPHOTOLUMINESCENCE IN Ag-DOPED PHOSPHATE GLASSES HAVING DIFFERENT ALKALI METALS

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Ag-doped phosphate glasses have been used in fluorescence dosimeter owing to their radiophotoluminescence (RPL) property. RPL is an emission phenomenon caused by light excitation of RPL centers formed after X-ray irradiation. In Ag-doped phosphate glasses, Ag^0 and Ag^{2+}, formed by the transfer of electrons and holes, exhibit blue and orange RPL, respectively. Thus far, RPL center formation process has been analyzed with optical and electron spin resonance measurements [1,2]. However, the process has not been completely understood. Therefore, we aim to elucidate the process from the view of the activation energy and starting temperature of RPL center formation. To obtain this information, we measured the temperature dependence of RPL in Ag-doped phosphate glasses after irradiation with X-ray at cryogenic and room temperatures.

We used Ag-doped Na-Al phosphate glass fabricated by Chiyoda Technol (Na–Al/Ag), Na–K/Ag and Al–K/Ag. Na–K/Ag and Al–K/Ag were synthesized with melting method so that the preparation concentration of Ag becomes 0.1 mol%. We measured temperature dependence of RPL intensity through two procedures. (1) The sample was irradiated with X-ray at 25 K. Subsequently, it was heated from 25 K to 300 K, and while heating the RPL spectra were measured at intervals of 25 K. (2) The sample was preheated to 300 K after it was irradiated with X-ray at 293 K for one hour. Subsequently, it was cooled from 300 K to 25 K, during which the RPL spectra were measured at intervals of 25 K.

Based on the results of (1) and (2), we estimated the temperature dependence of RPL center concentration. In addition, the activation energies were estimated using the Ahrrenius plot. Table 1 shows the activation energies, starting temperatures, and thermal energies at the starting temperatures. In Na–K/Ag and Al–K/Ag, emission from Ag^{2+} was not observed. Therefore, only infromation about Ag^0 is displayed in Table 1. In all the samples, the activation energies are greater than the thermal energies. This indicates that the electron transfer process is not purely a heat-activated process but rather electrons are trapped at certain sites before they are transferred to Ag^+. Figure 1 shows the relationship between the activation energy and mean molecular volume[3]. The activation energy decreased with the increase in mean molecular volume, indicating that the trap depth depends on the size of vacancies. It further suggests that electrons are trapped at negative ion vacancies before forming Ag^0.

Table 1. Activation energies, starting temperatures and thermal energies of Ag^0.

Sample	Activation energy [meV]	Starting temperature [K]	Heat energy [meV]
Na-Al/Ag	20	100	8.6
Na-K/Ag	21	100	8.6
Al-K/Ag	14	25	2.2

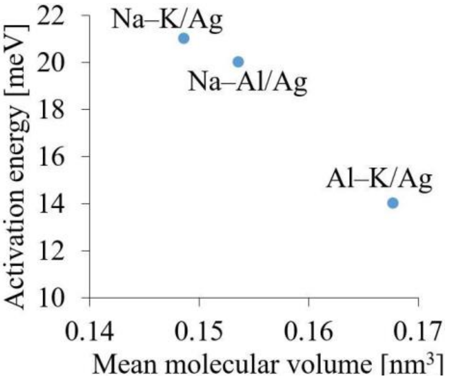

Fig. 1. Relationship between activation energy and mean molecular volume.

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RADIOPHOTOLUMINESCENCE CENTER FORMATION PROCESS IN Ag–DOPED ALKALI HALIDES

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Radiophotoluminescence (RPL) is an emission phenomenon caused by the light excitation of RPL centers, which are formed by the transfer of electrons and holes after irradiation with X-ray. Until now, Ag-doped phosphate glasses have been used in fluorescence dosimeters. In addition to Ag-doped phosphate glasses, certain materials having RPL properties, such as non-doped Mg_2SiO [1] and Ag-doped alkali halides, have been reported. However, there remain unresolved issues regarding the RPL center formation process. In Ag-doped alkali halides, RPL center was revealed by optical measurement, but the formation process is not understood completely. In this study, we aim to reveal the RPL formation process based on the combination of optical and electron spin resonance (ESR) measurements.

The samples were prepared by melting method. First, NaCl and AgCl powders were mixed such that the concentration of Ag is 0.3 mol%, and the mixed powder was sealed in a vacuumed ampoule. Subsequently, the ampoule was heated to 1173 K in an electric furnace, followed by slow cooling to room temperature to obtain NaCl and Ag-doped NaCl (NaCl/Ag) crystals. The samples were X-ray irradiated at 24 Gy. We measured ESR spectra, emission spectra (excitation wavelength: 289, 339 nm), and excitation spectra (emission wavelength: 560 nm).

Figure 1 shows the ESR spectra around 325–345 mT. The signal split into four was observed only in NaCl/Ag after irradiation. If I is the nuclear spin of the nuclei interacting with electrons or holes, the number of splits n of the ESR signal can be expressed by $n = 2*I + 1$. In addition, the nuclear spins of Na and Cl nuclei are 3/2. These results and the splitting of the signal into four of lines indicate that this signal is attributed to electrons or holes that interact with Na or Cl nuclei. Figures 2 and 3 show the excitation and emission spectra. In the emission spectra, two PL bands were observed around 430 nm and 540 nm in only NaCl/Ag after irradiation. In the excitation spectra, the peak which is attributed to Ag^0 was observed around 290 nm. These results demonstrate that electrons are trapped at Ag^+ and form Ag^0. Therefore, the ESR signal is attributed to holes that interact with the Cl nuclei. In alkali halides, holes are trapped by two Cl^- ions and form a V_K center. This suggests that electrons are trapped at Ag^+ and form Ag^0, while, holes are trapped by two Cl^- ions and form V_K centers in NaCl/Ag after irradiation.

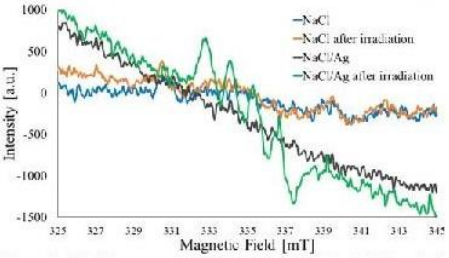

Fig. 1. ESR spectra around 325–345 mT.

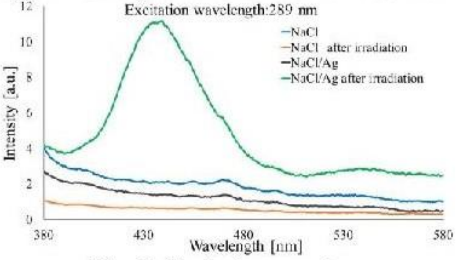

Fig. 2. Emission spectra.
(excitation wavelength: 289 nm)

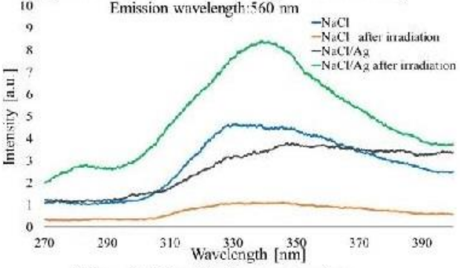

Fig. 3. Excitation spectra.
(emission wavelength: 560 nm)

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EFFECT OF Er^{3+}-DOPING ON $65GeS_2$-$25Ga_2S_3$-10CsCl GLASS PROBED BY ANNIHILATING POSITRONS

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The Er-doped chalcohalide glasses such as $65GeS_2$-$25Ga_2S_3$-10CsCl are shown to provide a large number of different Er^{3+} transitions among glassy matrixes, which can be used for up- and down- conversions [1]. Specifically in this glass, the excitation with 800 nm laser pulses of ~fs duration at room temperature results in three up-conversion lines well detected at ~530, 550 and 660 nm. The decrease in the temperature causes the ~530 nm emission to cease under similar excitation conditions.

In this report, we studied modification of atomic-deficient free-volume structure of chalcohalide $65GeS_2$-$25Ga_2S_3$-10CsCl glass doped with 0.6 and 1.0 at. % of Er^{3+} employing the method of positron annihilation lifetime spectroscopy. The detected positron-electron annihilation lifetime spectra were reconstructed from unconstrained x2-term analysis employing two-state simple trapping model for only one kind of positron trapping free-volume defects [2, 3].

It was proved that reduction in the positron trapping rate was primary free-volume void-evolution process in this Er^{3+}-doped glass, like in many other chalcohalide and chalcogenide glass matrices affected by rare-earth doping [4-6]. The microstructure nature of the observed effect of rare-earth doping in this chalcohalide glass is comprehensively explained in terms of comMACatundaive contribution of changed occupancy sites in Ga-modified glassy matrix available for rare-earth ions and annihilating positrons.

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INVESTIGATION OF THE EFFECT OF PHASE TRANSITIONS ON THE ACCUMULATION OF RADIATION DEFECTS IN LITHIUM-POTASSIUM SULFATE

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Crystals of lithium-potassium sulfate ($LiKSO_4$) belong to a group of crystals with the ion-covalent nature of the chemical bond. The covalent bond is realized in the tetrahedral sulfate anion. A feature of lithium-potassium sulfate crystals is the presence of two polymorphic phase transitions in the temperature range 80-300 K: at 180 K and 250 K in the heating regime. According to the published data, the temperatures of the phase transition in lithium- potassium sulfate crystals in different sources lie in the range 170-180 K and 240-250 K [1]. This is due to the fact that the temperature of the phase transition is sensitive to small changes in the stoichiometric composition of the compound.

Some aspects of the effect of structural phase transitions on recombination luminescence in lithium-potassium sulfate crystals are considered.

Crystals of lithium-potassium sulfate, grown from aqueous solutions, are transparent in the wavelength range 200-800 nm. It is established that when crystals are exposed to ionizing radiation, the crystals do not stain. After irradiation with X-ray quanta at the temperature of liquid nitrogen, the spectra of thermally stimulated luminescence (TSL) were measured.

The TSL peak at 260 K in the lithium-potassium sulfate crystal does not change shape with increasing radiation dose. This makes it possible to measure the accumulation of the light sum as a function of the irradiation temperature without separating it into individual peaks. Qualitatively, this peak of TSL is similar to the high-temperature peak in potassium sulfate, which is associated with a SO_3^- defect.

In crystals with complex anions or cations, radiation defects can be conditionally divided into primary and secondary defects. The first include those defects that are formed as a result of the decay of electronic excitations, the latter - as a result of the transformation of the former. Of all the radiation defects known in sulfates, only SO_3^- radicals result in a mechanism for the conversion of hole radiation defects SO_4^-. This occurs when the former interact with atomic oxygen. The implementation of the proposed channel for the formation of SO_3^- ions presupposes the migration of oxygen in the crystal. Obviously, migration processes are structurally sensitive.

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INVESTIGATION OF SPECTRAL PROPERTIES OF CHLORIDE PHOTO-THERMO-REFRACTIVE GLASSES DOPED BY Nd

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Nowadays, one of the promising areas of Photonics is the creation of optical elements and devices based on three-dimensional phase holograms in the form of Bragg gratings. One of these materials are photo-thermo-refractive (PTR) glass. They have high diffraction efficiency (~90%), high refractive index modulation (Φ n~ 0.001), high transparency in the visible and near-infrared bands. Competitive advantage over organic media is high chemical resistance, optical, thermal and mechanical strength, unlimited information storage. In spite of the fact that FTR glasses are widely used today for creation of modern base of Photonics (filters, selectors, combine harvesters, multiplexers, etc.) their composition and structure are constantly modified and improved. Since holograms can be recorded in this material, when activated by its rare-earth ions, it is possible to create devices such as lasers with distributed feedback and distributed Bregg reflector, it is also possible to obtain laser generation. There is a small amount of work devoted to the study of the properties of such glasses and the creation of elements on them [1-4]. Therefore, the urgent task is to develop new holographic media.

The paper synthesizes and studies the FTR glass composition SiO_2-Na_2O – ZnO – Al_2O_3 – Cl - f – SB_2O_3 – CeO_2 – Ad_2O-Nd_2O_3. The samples under study are plane-parallel polished plates with a thickness of 1 mm. the absorption Spectra of FRP glasses were measured on a lambda 650 spectrophotometer (PerkinElmer). Measurement of the excitation spectra of luminescence and luminescence in the visible and near IR regions, as well as the quantum yield was carried out on the integrating sphere Hamamatsu C9920-02G. The excitation wavelength was 360nm and 808nm. Glasses were irradiated with different dose of UV- irradiation (1, 4, 6, 10 j) at room temperature. Glass transition temperature was determined by differential scanning calorimeter STA6000 (Perkin-Elmer). The samples were thermally treated at temperatures above and below the glass transition temperature.

The work shows a change in the refractive index in irradiated and non-irradiated areas, as well as its change depending on the dose of UV radiation. Observed shift of the peak plasmon resonance of silver nanoparticles with increasing doses of UV irradiation, with the position of the peaks of the bands of neodymium have not changed. Luminescence spectra show broad luminescence in both the visible region of silver and the IR region of Nd. The influence of radiation dose on the shape of luminescence spectra was observed. At the time of writing, the maximum quantum yield was 27%.

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DIPHENYLSULFONES META-SUBSTITUTED BY DIFFERENT DONOR MOIETIES AS TADF EMITTERS

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Thermally activated delayed fluorescence (TADF) [1] is shown by organic molecules due to the reverse intersystem crossing [2] from triplet excited to singlet excited states caused by the thermal motion of atoms and the following charge transfer emission. This approach allows to employ triplet excitons by converting them to singlet excitons for luminescence and overcome spin statistical 25% limit of internal quantum efficiency of organic light emitting diodes (OLEDs). Employment of TADF emitters for the fabrication of OLEDs became widespread in recent years due to the possibility of replacing high-cost phosphorescent emitters based on rare metals. In 2012 Adachi et al [3] reported on the first class of deep-blue TADF emitters designed using diphenylsulfone moiety as an acceptor. The advantage of this type of acceptor moiety is in tetrahedral geometry of sulfonyl group which helps to avoid conjugation in the compound thus leading to strong intramolecular charge transfer. In addition, diphenylsulfone moiety has electron-withdrawing properties caused by significant electronegativity of oxygen atoms [4].

Motivated by the above given information, we synthesized and characterized a series of new donor-acceptor-donor type diphenylsulfone-based TADF materials and studied them in host-guest systems in order to disclose relationship between structure and properties and to test the optimized systems in OLEDs.

The optical, thermal, and photoelectrical properties of the synthesized compounds have been investigated. All the compounds were found to be capabale to form glasses with glass transition temperatures ranging from 82 to 91 ^{o}C. They exhibited high thermal stabilities, with 5% weight loss temperatures exceeding 385 ^{o}C. Strong solvatochromism arising from the intramolecular charge transfer in the excited state was evidenced by bathochromic shifts of emission maxima with increasing solvent polarity. The compounds containing acridine and phenoxazine moieties showed relatively high photoluminescence quantum yield (up to 35%) in the non-doped solid state, long delayed fluorescence lifetime (in μs range) and small singlet-triplet energy splitting (ΔE_{ST}) that is attributed to thermally activated delayed fluorescence. These compounds were tested as emissive species for the fabrication of OLEDs. The sky-blue and green devices showed maximum brightness of 3200 and 12300 cd/m^2 and maximum external quantum efficiency of 6.3 and 6.9%, respectively.

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SPECTRAL-LUMINESCENT PROPERTIES OF CARBON NANOPARTICLES SYNTHESIZED FROM SOLUTIONS OF AMINOCAPROIC ACID

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At the present time, the spectral-luminescent properties of colloids of luminescent particles based on heavy (Cd, Pb, Zn) and rare earth (Nd, Er, Tm, Ho) metals are intensively studied. However, a serious drawback of such systems is their toxicity for bioobjects [1]. Colloidal solutions of carbon nanoparticles (CNPs) are considered as an alternative.

These compounds are distinguished by environmentally compatibility, simplicity and variety of obtaining methods, as well as high photostability [2-4]. Various organic and inorganic compounds such as nanodiamonds, graphite, carbon nanotubes, citrate, chitin and other poly- and monosaccharides can be used as starting compounds for the CNPs synthesis [2-4]. A characteristic feature of the CNPs is the presence of "tunable" visible luminescence. This property is due to the π-domain structure and the presence of functional groups on the CNPs surface [2]. The spectral-luminescent characteristics of these compounds can also vary depending on the initial materials and synthesis conditions. Management of these characteristics is an important task and is of considerable interest for researchers [2, 4]. In this connection, the actual task is the development of synthesis methods and searching for new materials for obtaining CNPs with controlled dimensional and luminescent properties.

In this work, colloids of CNPs from a solution of aminocaproic acid were first obtained. Synthesis was carried out by hydrothermal treatment at excess pressure in a microwave reactor.

The results of the investigation of the luminescent properties of CNPs colloids obtained from an aminocaproic acid solution reveal the presence of a tunable luminescence in the 325-600 nm range when excited by radiation with $\lambda_{exc.}$ = 280-520 nm (Fig. 1).

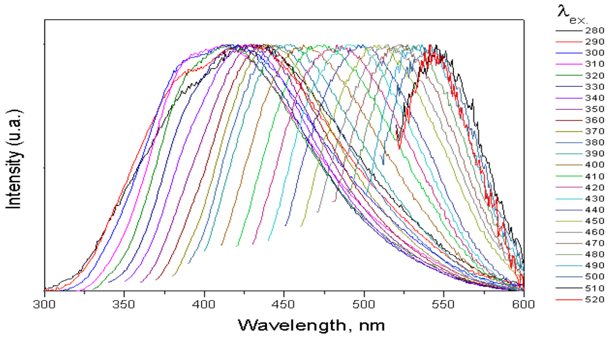

Figure.1 Luminescence spectra of a CNPs colloid obtained from aminocaproic acid solution

The appearance mechanisms of the broadband "tunable" luminescence of CNPs colloids, obtained from aminocaproic acid solution, are discussed.

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HIGH POWER MID-INFRARED SUPERCONTINUUM SOURCE FOR STAND-OFF SPECTROSCOPY

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Spectroscopy in the mid-infrared (mid-IR) spectral range is of particular interest for applications in military, automotive, food, and pharmaceutical industries. Quantum cascade lasers (QCL) are the most commonly applied laser source for this task. Despite their technological maturity, they still have many limitations – e.g. they provide low output power with limited tunability of output wavelengths per laser. Therefore, alternative solutions to these light sources are searched for. In this context, high-power mid-IR supercontinuum (SC) generators appear very interesting, mainly owing to their unique properties, of which the most important are their broad spectrum spanning over several hundreds or even thousands of nanometers, high spectral power density (>1mW/nm) over a broad bandwidth, high spatial coherence, directionality and brightness, compared to those exhibited by conventional lasers including QCLs. These features make SC sources a perfect tool for high sensitivity stand-off detection [1-3].

The paper presents a stable, high power mid-IR SC source built with the use of properly selected commercially available components. A 1.55 μm MOPA laser system emitting 1 ns pulses at 500 kHz repetition rate was used as a source of high peak power pump pulses whereas a thulium-doped single-mode fiber was used as a nonlinear medium. The maximum average SC power exceeds 8.5 W corresponding to ~29 W of pump power at 790 nm. The output spectrum spreads from ~1.5 to 2.65 μm (Fig. 1) and the output power stability was measured to be below 3%. This laser system is linearly scalable, highly efficient and it covers a spectral region where O–H stretch vibrations occur. All this features make the developed SC source suitable for stand-off detection of various chemical compounds.

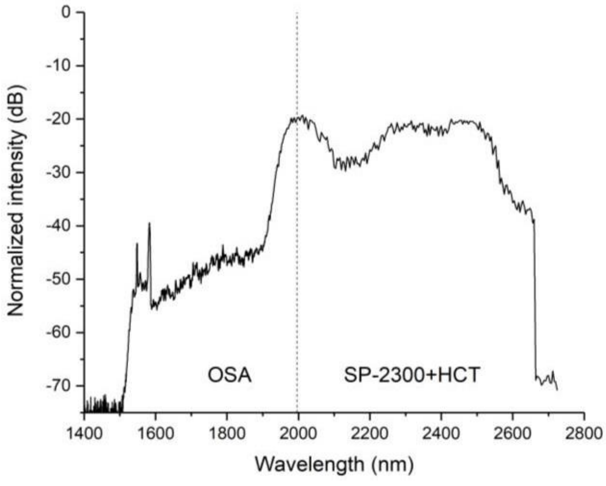

Figure. 1 Supercontinuum output spectrum measured by optical spectrum analyser and monochromator (cancatenated)

This work was supported by the National Science Centre, under project No. UMO-2014/14/M/ST7/00868.

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OPTICAL RESPONSE OF A D_2^+ MOLECULAR COMPLEX IN AN ELLIPTICAL $Ga_{1-x}Al_xAs$ NANODISK

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Very recently, the manufacturing of new low-dimensional nanostructures has rapidly evolved allowing to obtain diverse and exotic morphologies such as the Pr-doped ZnO/SnO2 nanoflowers [1], ZnO nanospindles [2], and being of special interest, the graphene nanoflakes [3]. The range of applications varies from materials reinforcement [3], gas sensors [1], field emission displays [2], among others. A detailed study of the morphology of these nanosystems have been performed by scanning/transmission electron microscopy techniques, X-ray diffraction and energy dispersive X-ray spectroscopy [2]. Their composition and optical responses have been characterized via photoluminescence techniques [3]. In particular, the experimental studies reporting nanoflakes with different shapes, sizes, compositions and irregularities, motivate the formulation of theoretical models to study the quantum confinement of few-particle systems in such nanostructures in order to tailor customizable few-particle energy spectra.

These remarkable findings, have motivated the present contribution in which is analyzed the energy structure of an artificial D^{2+} molecular complex confined in a non-uniform elliptical $Ga_{1-x}Al_xAs$ nanodisk. The energy structure is analyzed within the effective mass framework by using an adiabatic/finite elements hybrid technique. In addition, the optical response is investigated within the compact density matrix formalism. Validation of the numerical procedure was carried out through the comparison with analytic solutions (like those obtained for single- electron disks) showing a good accordance between the set of results.

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Te^{4+}/Yb^{3+} CO-DOPED TELLURITE GLASS: A PROMISING CONVERTER FOR SOLAR CELLS

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During the tellurite glass synthesis, it can be expected that the TeO_2 participate both as a network conditional former and also in the ionic form (Te^{4+}) into the glass. The Te^{4+} cations present electronic configuration ns^2-type which has parity-allowed transition exhibiting strong visible emission intensities [1]. Recently Te^{4+}-doped tellurite glass was optically investigated and the results indicate that the material has potential for application in optical devices. When it is co-doped with Yb^{3+} ions, it can be studied to improve the conversion efficiency of Si solar cells [2]. In this study, lithium tellurite glasses with nominal composition $80TeO_2$- $20Li_2O$ (mol%) doped with 0.5, 1.0, 2.0 and 4.0 mol% of Yb_2O_3 were prepared in an ambient atmosphere by the conventional melt-quenching method. The reagents TeO_2, Li_2CO_3 and Yb_2O_3 were melted at 850°C for 1 h. The melt was poured into a stainless steel mold (at ~260 °C) and was subsequently annealed for 5 h. From the samples were performed excitation-emission maps measurements, and Te^{4+} and Yb^{3+} lifetimes and luminescence quantum efficiencies (η). Fig. 1 shows the obtained excitation-emission maps for the undoped (a) and for the 2.0wt.% Yb^{3+}-doped (b) tellurite glasses. It is possible to note that the undoped sample exhibits a broad and intense absorption band in the UV region followed by a broad emission band centered at 645 nm, which are characteristics of Te^{+4} ion. This emission is reduced when Yb^{3+} is incorporated into the glass structure, and as a consequence, the emission of Yb^{3+} in the near-infrared is increased when the doped glass is excited between 300 and 550nm (see Fig. 1(b)). The observation of the Yb^{3+} emission under excitation in the (UV-Vis) region indicates an energy transfer process among Te^{4+} and Yb^{3+} ion. The efficiency of the energy transfer process (η_{ET}) from Te^{4+} and Yb^{3+} it was quantified by rate equations by measuring the heat generated in the sample through thermal lens spectrometry technique. The determined η_{ET} values are in good agreement with those determined by lifetime measurements: as function of the Yb^{3+} concentration, η_{ET} reaches 120% for the sample with 4.0% mol of the Yb_2O_3.

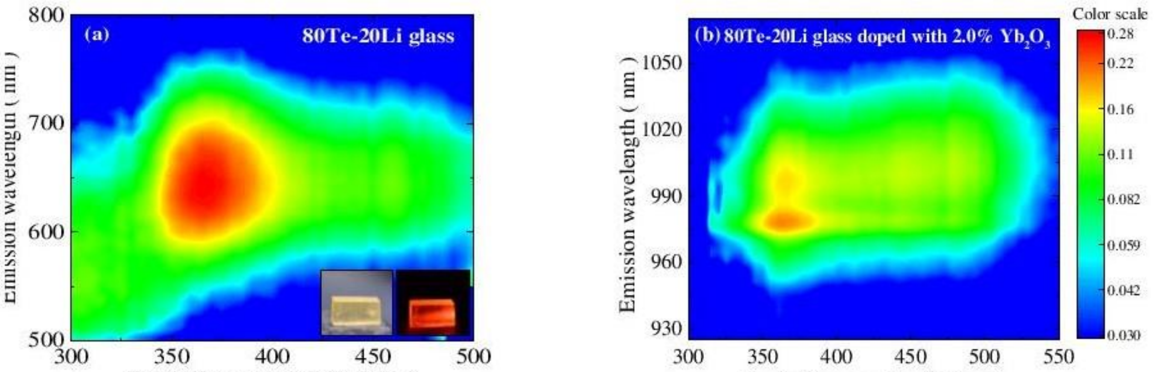

Figure 1. Excitation-emission maps for undoped (a) and Yb^{3+}-doped (b) $80TeO_2$-$20Li_2O$ glass. The inserted photographs show the undoped sample without and with laser excitation (405 nm).

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SYNTHESIS AND CHARCTERIZATION OF TWO-DIMENSIONAL $PtSe_2$ FILMS

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Transition metal dichalcogenides (TMDCs) are semiconductors of the MX_2 type, where M is a transition metal atom (such as Mo or W) and X is a chalcogen atom (such as S, Se or Te). TMDCs exhibit a unique combination of atomic-scale thickness, direct bandgap, strong spin–orbit coupling and favorable electronic and mechanical properties, which make them interesting for fundamental studies and for applications in high-end electronics, spintronics, optoelectronics, energy harvesting, flexible electronics, DNA sequencing and personalized medicine [1].

Here we report the synthesis and investigation of $PtSe_2$ films obtained by CVD thermally assisted selenization of pre-deposited platinum films. The thickness of the $PtSe_2$ films was controlled by respective sputtering time for pre-deposition of Pt layers. The Raman scattering was studied as a function of the film thickness and laser light polarization (Fig.1). The Raman active modes were identified and found to display a position and intensity dependence with film thickness [2]. The stoichiometry of the $PtSe_2$ films was confirmed by X-ray photoelectron spectroscopy.

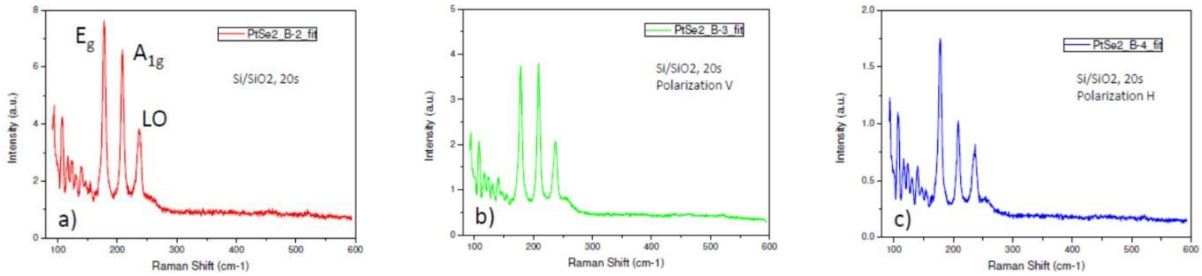

Figure. 1 Raman spectra of $PtSe_2$. Pt sputtering time 20s on Si/SiO_2 substrates: a) standard mode; b) vertical polarization; c) horizontal polarization

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Acknowledgements:

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MAGNETIC AND DIELECTRIC PROPERTIES OF $CaMn_2O_4$ SINGLE CRYSTALS

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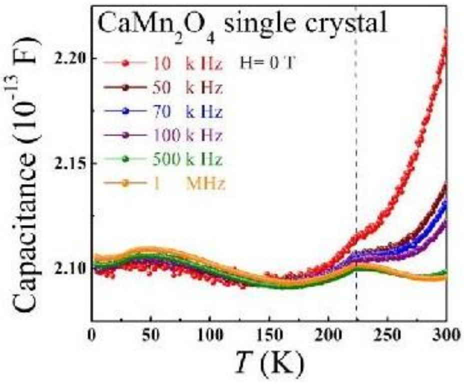
$CaMn_2O_4$ is the only manganese oxide of the group XMn_2O_4 (X = Ca, Ni, Cu, Mn, Zn, Cd, Mg, and Li) which crystallizes in an orthorhombic structure under ambient pressure. For various applications it is necessary to prepare single crystals with high-quality. Large-sized single crystals of $CaMn_2O_4$ were grown using the high-temperature solution method [1]. Crystal structure characterization was determined by X-ray single crystal diffraction. The structure was found to belong to the orthorhombic space group Pbcm with unit cell parameters a = 3.1478(2)Å, b =9.9750(6)Å, and c = 9.6647(7)Å.

Temperature and pressure dependences of the magnetic and dielectric properties (capacitance, dielectric constants, polarization, magnetization, T_N, pyrocurrent) were measured in order to assess the quality of the single crystals.



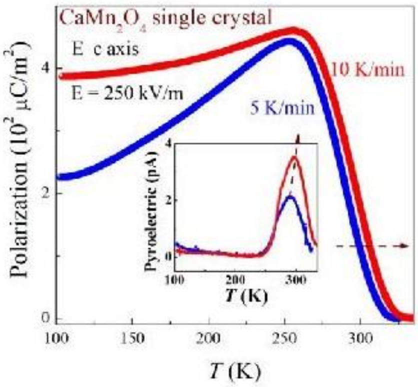


Figure 1 Dielectric constant of $CaMn_2O_4$ single crystals; Figure 2 Polarization of $CaMn_2O_4$ single crystal

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RELATIONSHIP BETWEEN THE STRUCTURAL CHARACTERISTICS AND PHOTOLUMINESCENCE PROPERTIES OF (Ca, Ba) $Y_{2-x}Eu_xGe_3O_{10}$ PHOSPHORS

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Germanates of lanthanide elements are largely studied by different research groups due to their promising applications for lasers, optical fibers, scintillators and phosphors [1–4]. The basic structural units $[GeO_4]^{4-}$ of germanates, combining in different ways, may form complex anions: $[Ge_2O_7]^{6-}$, $[Ge_3O_{10}]^{8-}$, $[Ge_3O_9]^{6-}$, $[Ge_4O_{12}]^{8-}$ etc. The structural diversity, the high thermal/chemical stability and sufficient water resistance make germanates one of the most attractive inorganic materials as hosts for lanthanide ions.

In this report, we study the structure-luminescence relationships in the $CaY_{2-x}Eu_xGe_3O_{10}$ (x = 0.1-1.0, Δx =0.1) and $BaY_{2-x}Eu_xGe_3O_{10}$ (x = 0.1-1.0, Δx =0.1) solid solutions. The compounds have been prepared by an EDTA-assisted route using $CaCO_3$ ($BaCO_3$), La_2O_3, Nd_2O_3 and GeO_2 as reagents. Powder XRD study has revealed that $CaY_{2-x}Eu_xGe_3O_{10}$ and $BaY_{2-x}Eu_xGe_3O_{10}$ crystallize in the monoclinic system with the space group $P2_1/c$, Z = 4 and the space group $P2_1/m$, Z = 2, respectively. The crystal structure of all compounds contains isolated trigermanate anion, $[Ge_3O_{10}]^{8-}$. The calcium, yttrium and europium ions are distributed among three different sites coordinated by seven oxygen atoms in the lattice of $CaY_{2-x}Eu_xGe_3O_{10}$. This distinguishes the compounds from the $BaY_{2-x}Eu_xGe_3O_{10}$ series where cations occupy two unique sites. The crystal structure of $BaY_{2-x}Eu_xGe_3O_{10}$ can be described as a tree-dimensional framework formed by infinite zigzag chains of edge-sharing Y/EuO_6 octahedra, connected by $[Ge_3O_{10}]^{8-}$, Ba atoms are located in channels in irregular eight-fold coordination of oxygen atoms.

The photoluminescence spectra (λ_{ex} = 280 or 393 nm) of phosphors consist of several intense peaks in the orange-red spectral range, which correspond to the characteristic transitions from the excited $^5D_0$ level to the ^7F_J (J = 0–4) levels in Eu^{3+} ions. The peak at 605–630 nm caused by the $^5D_0 \rightarrow {}^7F_2$ transition is most prominent and strong that confirms a low symmetry of the Eu^{3+} sites in $CaY_2Ge_3O_{10}$ and $BaY_2Ge_3O_{10}$ hosts. In the case of $CaY_{2-x}Eu_xGe_3O_{10}$, the maximum of the peak depends on the excitation wavelength, that are attributed to the presence of several sites in the lattice. The relationships between the crystal structure and the luminescence characteristics: the energy of the charge transfer transition, the values of 4*f*–4*f*/CTB and $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ intensity ratios have been also revealed. Note that the CTB is more intensive compared to the peaks associated with 4*f*-4*f* transitions for the all samples. This observation suggests that the studied phosphors can be considered as optical materials for LEDs if the diode-chips provide an incoming light below 300 nm.

The work was supported by the Russian Science Foundation (project No. 16–13–10111). The crystallographic study was carried out at the multiple–access center for X–ray structure analysis at the Institute of Solid State Chemistry, UB RAS (Ekaterinburg, Russia).

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ENERGY STRUCTURE AND OPTICAL RESPONSE OF A TWO-COUPLED DONORS IN NON-UNIFORM QUANTUM STRIP UNDER EXTERNAL PROBES

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Two-coupled donor system (D_2^+) is analogous to the single ionized hydrogen molecule H_2^+. The D_2^+ molecular complex energy structure display bonding and antibonding states [1] and it is possible to increase the energy difference between the ground state and the first excited state in order to obtain charge qubits [2].

In this work, we calculate the energy sates of a D_2^+ complex confined in a multi-hilled semiconductor nanostructure with a cylindrical stripe geometry under orthogonal electric and magnetic fields. The energy structure is calculated by using the adiabatic approximation combined with diagonalization procedure. The presence of structural hills yields vibrational states and a quenching of the Aharanov-Bohm oscillations [3-4]. The D_2^+ molecular complex stability and the Aharanov-Bohm oscillation patterns are highly sensitive to the number of hills while the electric field breaks the electron rotational symmetry and removes the energy degeneration between low-lying energy states. The optical response is calculated by using the well-known density matrix method. We show that the optical absorption and refractive index change are strongly affected by the electric field which induce optical transparency effects due to the suppression of the off-diagonal dielectric polarization response in the system.

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SHALLOW DONOR IN ELONGATED QUANTUM RING: ENERGY SPECTRUM AND NON-LINEAR OPTICAL PROPERTIES

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The energy estructure, dipole momentum, and polarizability induced by an off-axis donor in InAs/GaAs elongated volcano-shaped quantum dot in the presence of external electric and magnetic fields are theoretically investigated. The numerical calculations are carried out by using the adiabatic approximation and the Kane model, which takes into account the effect of non-parabolicity of the conduction band. We show that estimated donor energies are essentially lower than corresponding values, obtained by means of the effective mass approximation. The mixing of the donor's energies, the variation of the dipole moment, the electric polarizability and the charge distribution induced by the electric and magnetic fields are consistently described with our simple formalism, in which the adiabatic potential is related directly to the morphology of the elongated quantum ring. In this structure, the charge density in two lowest "bonding" and "anti-bonding" states tends to align along of one of two symmetry axes. The donor-electron Coulomb attraction leads to an increase of the energy gap between these states and provides a strong polarization of the anti-bonding state. The out-of- plane magnetic field decreases the overlapping of the corresponding wave functions, while the in-plane electric field increases their mixing and provides the reordering of the energy levels. We have found that the dependency of the polarizability on the external electric field in these conditions displays a phase transition to a donor state with a giant dipole moment.

The optical response is calculated by using the well-known density matrix method. We analyze the effect of the external probes: electric and magnetic fields and the quantum ring geometrical parameters on the change in the refractive index and the absorption coefficient.

SYNTHESIS, CRYSTAL STRUCTURE AND OPTICAL PROPERTIES OF NOVEL Sm^{3+} -DOPED GARNET-TYPE TANTALUM-BASED PHOSPHORS

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Lanthanide doped garnet hosts are in great demand due to their wide applications as active laser media and phosphors for white light-emitting diodes (wLEDs). In recent years, the lithium-containing garnets $Li_xLn_3M_2O_{12}$ (Ln = La, Y; M = Zr, Nb, Sn, Sb, Te, Hf, Ta; x = 3–7) have attracted a lot of interest mainly as potential electrolytes in solid-state lithium ion batteries. The replacement of La^{3+} or Y^{3+} by optically active lanthanide cations in the structures allows one to obtain phosphors emitting in the visible spectral range. The $Li_xLn_3M_2O_{12}$ compounds doped with Eu^{3+} were recently considered as promising efficient luminescent materials for white LEDs [1–2]. Because of their good excitation profile, stable luminescence properties at high temperature, red color purity and high quantum yield, the cubic garnets $Li_3Ln_3Te_2O_{12}$ (Ln = Y, Gd) doped with Eu^{3+} and Sm^{3+} ions are potential red phosphors for near-UV chip-based white LEDs and for display devices [2, 3]. The present report is an overview on the synthesis, crystal structure refinement, results of Raman spectroscopy and luminescence study of new reddish orange phosphors based on the cubic garnet $Li_{5+x}A_xLa_{3-x}Ta_2O_{12}:Sm^{3+}$ (A = Ca, Sr; x = 0, 1).

Rietveld refinement of room temperature powder X-ray diffraction patterns shows that these compounds crystallize in the cubic system (sp.gr. $Ia\bar{3}d$, Z = 8). The FTIR and Raman spectra have been measured, the maximum phonon energy of $Li_{5+x}A_xLa_{3-x}Ta_2O_{12}$ (A = Ca, Sr; x = 0, 1) is about 800 cm^{-1}. The excitation spectrum of $Li_{5+x}A_xLa_{3-x}Ta_2O_{12}:Sm^{3+}$ (A = Ca, Sr; x = 0, 1) in the range of 200–300 nm consists of two overlapping wide bands centered at 230 and 250 nm, which are attributed to the O^{2-}–Sm^{3+} and O^{2-}–Ta^{5+} charge transfer bands, respectively. The series of sharp peaks observed at wavelengths longer than 300 nm belongs to the *f–f* transitions from the ground state $^6H_{5/2}$ to higher excited states in Sm^{3+} ions. A suitable red-emitting ultraviolet LED phosphor should show absorption at around 400 nm (LED excitation wavelength). The strongest excitation peak caused by the $^6H_{5/2}\rightarrow{}^4K_{7/2}$, $^6P_{3/2}$ transitions is observed at 407 nm indicating that $Li_{5+x}A_xLa_{3-x}Ta_2O_{12}:Sm^{3+}$ phosphors are potential candidates for near UV-based LEDs. The photoluminescence spectra contain several lines centered at 568, 615, 658 and 712 nm associated with the $^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2 and 11/2) transitions, respectively. Under 407 nm excitation, the CIE chromaticity coordinates of $Li_6CaLa_2Ta_2O_{12}:Sm^{3+}$ phosphor (0.60, 0.39) are close to those of the commercially available $Y_2O_3:Eu^{3+}$ (0.62, 0.37) red phosphor.

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LUMINESCENCE OF DEFECTS AND IMPURITY IONS IN TITANIUM DOPED SPINEL CRYSTALS

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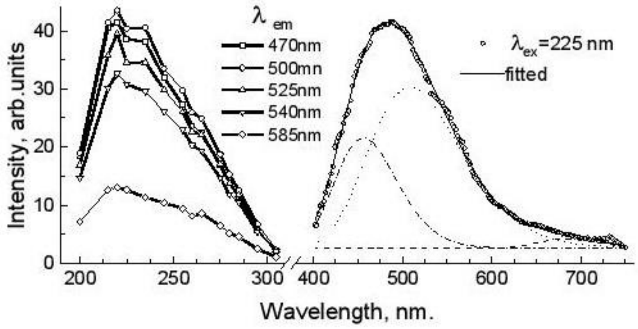
The photo- and radioluminescence of non-stoichiometric magnesium aluminates spinel crystals ($MgO{\cdot}2.5Al_2O_3$) doped with titanium dioxide to concentration of 0.2 and 0.5 wt% (MAS:Ti) are investigated. The Verneuil grown single crystals of dimensions of 10-20 mm in diameter and 20-50 mm in length have stripped coloration in bluish. For investigations the boles were cut into slices of 1.5 mm in thickness along the direction of crystal growth and polished to optical finish. As-grown crystals demonstrate two absorption bands at maxima about 800 and 470 nm. In UV range a strong absorption edge arising from 300 nm was observed.

Emission spectra in MAS:Ti cotaines a wide blue emission band at 490 nm and near IR-band at abot 800nm. Izumi at al. [1] assigned 490 nm band to the charge-transfer de-excitation of Ti^{3+} ions into the valence band the hole created by the band-to band excitation, although, no correlation was observed between Ti^{3+} amount and TiO_2 content. Jouini at al. [2] upon laser excitation at wavelength of 266 nm observed strong blue emission of maximum at 455 nm and shoulders at about 400 and 500 nm.

In this paper we provided the measurements of radio-luminescence at excitation by X-rays and found wide non-elemental emission bands at wavelength of about 500 and 790 nm. The deconvolution of the first band into Gaussian curves reveals the existence of overlapping bands at wavelength of 456 and 518 nm. In photo luminescence spectra we also registered wide band consisting as in the case of the radio-luminescence of two components the relative intensity of which depends on wavelength of excitation light. The excitation spectra demonstrate several overlapping bands which were identified with charge transfer transitions and transition in defect centers.



Incorporation of transition metals into spinel lattice having the large concentration of intrinsic defects leads to formation of complexes of defects and impurity ions of different sizes [3]. The measured excitation spectra in the UV-range (also absorption spectra in this range) and blue emission show the existence of the titanium contained complexes and anion vacancies accompanied the incorporation of titanium ions.

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TIN SULFOSELENIDE (SnSSe) – A NOVEL TERNARY SEMICONDUCTOR FOR PHOTOVOLTAIC APPLICATION

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Since solar energy is an alternative renewable energy source in replacing oil and coal to reach the world's energy demand, a rapid increased interest and focused research in the field of photovoltaics has been going on all over the world. The performance of a solar cell is highly dependent on the properties of the material with which it is made. Many materials are available, which exhibit suitable properties for photovoltaic applications, but earth abundant and eco-friendly materials capable of converting solar energy to electrical power at low cost and high processing stability are very few. Recently, tin sulfoselenide (SnSSe), a novel ternary compound belongs to IV-VI group semiconductors attracted much interest of researchers in solar energy conversion. This material possesses the properties of both tin sulphide (SnS) and tin selenide (SnSe), which are proved as good absorber materials for solar cell fabrication. Hence, the aim of the present study is synthesis and characterization of SnSSe thin films. Therefore, vacuum thermal evaporation technique has been employed to prepare SnSSe thin films at different substrate temperatures ranging from 200°C to 350°C and the structural properties of the as-deposited films were carried out using grazing incidence X-ray diffractometer (GIXRD). It was observed that all the as-deposited films were of orthorhombic crystal structure with (111) plane as their preferred orientation and the crystallinity has been improved with increase of substrate temperature. Further, some of the structural parameters such as crystallite size, dislocation density, lattice strain and structure factors were also evaluated.

EVIDENCE OF Yb^{2+} STATE AS ELECTRON TRAP IN $Y_3Al_2Ga_3O_{12}$:Ce^{3+}-Yb^{3+} PERSISTENT PHOSHORS

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Persistent phosphors, which emit light after ceasing excitation light, has been widely used in many applications; luminous paints in the dark for hazard signboards and road markers, and luminescent markers for *in-vivo* imaging. Almost all bright and long persistent phosphors have been developed in Eu^{2+}- or Ce^{3+}-doped compounds codoped with Ln^{3+} (trivalent lanthanide ions).

In lanthanide ions-doped persistent phosphors, the vacuum referred binding energy (VRBE) diagram including the Ln^{3+}/Ln^{2+} ground state (GS), conduction band (CB) and valence band (VB), which was proposed by Dorenbos, is known to be a useful tool.[1] Using the VRBE diagram, the trap depth of lanthanide ions and the threshold of charging wavelength can be predicted. For instance, Bos et al. reported the systematic energy shift of the electron trap depth by changing codopant ion in YPO_4:Ce^{3+} phosphors and the good agreement between the estimated trap depth from the thermoluminescence (TL) and that predicted from the energy diagram [2-4]. Also some persistent phosphors such as $SrSi_2AlO_2N_3$:Eu^{2+}-Ln^{3+} and $Ca_3Si_2O_7$:Eu^{2+}-Ln^{3+} show the similar systematic trap depth shift by the type of Ln^{3+} based on the VRBE diagram [5, 6].

However, there is no clear evidence of the formation of Ln^{2+} state in almost all persistent phosphors co-doped with Ln^{3+}. In this study, we investigated the valence state changing of Yb^{3+} into Yb^{2+} in $Y_3Al_2Ga_3O_{12}$:Ce^{3+}-Yb^{3+} transparent ceramic persistent phosphors by absorption spectra in visible to near-infrared region. Before blue light charging, there is almost no absorption band of Yb^{2+}:4*f*-5*d* transition. On the other hand, after blue light charging, a clear broad band at around 580 nm due to the Yb^{2+}:4*f*-5*d* transition was observed. Based on these results, it is demonstrated that Yb^{3+} ions act as electron trap by capturing one electron in $Y_3Al_2Ga_3O_{12}$:Ce^{3+}-Yb^{3+} persistent phosphors.

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THERMAL IONIZATION QUENCHING OF $CaAlSiN_3:Eu^{2+}$

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$CaAlSiN_3:Eu^{2+}$ is a widely applied phosphor in white LEDs (w-LEDs) because of strong blue absorption and efficient red luminescence with high thermal quenching temperature. The good stability against thermal quenching has been well established, but the mechanism for the luminescence quenching at high temperatures has not been elucidated yet. In this report, we investigate the possibility of thermal ionization quenching of $CaAlSiN_3:Eu^{2+}$ red phosphor by thermoluminescence (TL) and persistent luminescence techniques. Figure 1 shows the TL glow curves of $CaAlSiN3:Eu^{2+}$ by UV charging and 550 nm charging. In the TL glow curve by UV charging at 100 K, two broad TL glow bands were observed around 160 and 390 K. The higher TL glow band was not observed by 550 nm charging at 300 K, but it was observed by 550 nm charging at above 400 K which corresponds to the onset temperature of luminescence quenching. Because the 550 nm light excites the lowest 5*d* level of Eu^{2+}, we conclude that the luminescence quenching of $CaAlSiN_3:Eu^{2+}$ at high temperatures is caused by the thermal ionization [1].

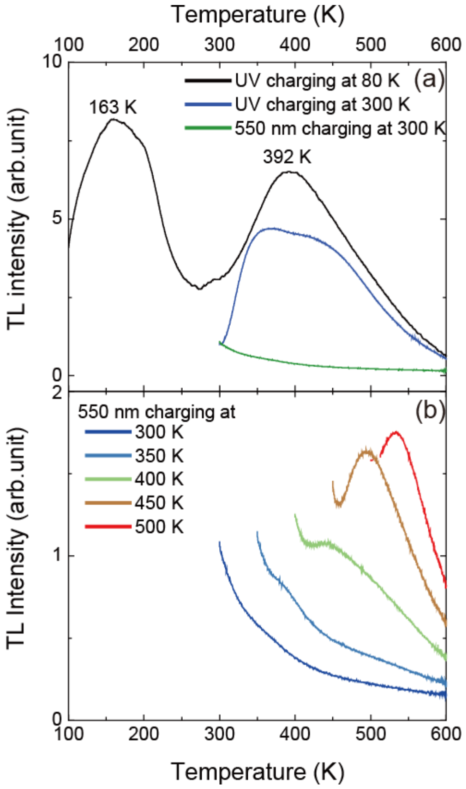

Figure 1. TL glow curves (a) by UV charging at 80 K and 300 K and by 550 nm charging at 300 K and (b) by 550 nm charging at different temperatures.

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PLASMON EFFECT OF ISLAND SILVER FILMS IN NANOSIZED FILMS OF ORGANIC DYES

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The distance dependence of the plasmon effect of silver island films on the spectral-luminescent properties of Rhodamine B (RB) and Nile red (NR) in solid films was studied. Island silver films (ISF) were deposited by the thermal vacuum deposition of $AgNO_3$ followed by thermal annealing of the film at a temperature of 240 °C for 10 minutes. The maximum absorption of ISF is manifested at 420 nm. Then films of amphiphilic derivatives of RB or NR were deposited onto the ISF by using of Langmuir-Blodgett (LB) technology. The film thickness was equal to 5 monolayers of the dye. The distance between the ISF and dye LB film was changed with monolayer of fatty acid (FA), whose thickness was about 2.1 nm. The number of layers of stearic acid was equal to 1, 3, 5, and 7 monolayers. The absorption, fluorescence spectra and fluorescence decay kinetics of the produced films were measured.

Investigation of the influence of the distance between the dye and ISF on the plasmon effect in LB films of the oxazine dye has shown that there are no shifts of the absorption and fluorescence bands or their noticeable change in the half-width in the presence of silver. However, the fluorescence of NR was quenched slightly in direct contact with the ISF film. With increasing distance between the Ag films and the dye, the luminescence intensity of the latter increases and reaches a maximum at 3 monolayers of FA. Similar data were obtained for the rhodamine dye. Measurements show that in the direct contact of the dye with silver nanoparticles, the intensity of the luminescence of the dye increases by 15%. The maximum increase in intensity - by almost 25%, was recorded at a distance from the dye to the ISF ~ 6 nm. Further growth of the distance leads to a decrease in the luminescence intensity of the dye to almost the original value.

The observed changes are associated with an increase in the rate of electronic transitions in the dye molecules between the S_1 - S_0 states in the near field of the island metal film, that was evidenced by a decrease in the dye fluorescence lifetime.

Table 1. Spectral-luminescent parameters of RB and NR LB films at various distance to the silver island film

Sample	N	λ^{abs}_{max}, nm	$\Delta\lambda^{abs}_{1/2}$, nm	λ^{f}_{max}, nm	$\Delta\lambda^{f}_{1/2}$, nm	I, a.u.	□, ns
RB	Neat	552	25	580	37	2.23	1.8
SIF+FA+RB	0	552	25	580	36	2.54	1.6
	1	552	25	580	35	2.51	1.4
	3	552	25	580	35	2.94	1.0
	5	552	25	580	35	2.43	1.6
NR	Neat	566	86	615	30	0.28	4.3
SIF+FA+NR	0	566	86	616	30	0.262	4.3
	1	566	86	616	30	0.274	4.0
	3	566	86	616	32	0.333	2.2

OPTICAL CHARACTERIZATION OF Er^{3+}-DOPED $Ge_{20}Ga_5Sb_{10}S_{65}$ GLASS FOR MID-IR PHOTONICS

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Chalcogenide glasses are known as one of the most versatile functional media for active device applications in IR photonics. These special glasses possess an excellent transparency in visible and IR region of spectrum, which makes them very appealing for many advanced applications, such as solid state lasers operating in mid-IR, bio-sensors, low-loss optical waveguides for atmospheric and space telecommunication, etc. Once doped with rare-earth ions, such as Er^{3+}, these glasses significantly improve their functionality due to the numerous radiative transitions of rare earth ions in the near and mid-IR region.

In this work, the $Ge_{20}Ga_5Sb_{10}S_{65}$ glass doped with different concentration of Er^{3+} ions (0; 0.1; 0.5; 1.0 mol. %) was studied using optical transmission and fluorescence spectroscopies. The experiments were performed at room (TR) and liquid nitrogen (TLN) temperatures. Typical optical transmission and fluorescent spectra are shown in Fig. 1 at the example of 1 mol. % Er^{3+} doped $Ge_{20}Ga_5Sb_{10}S_{65}$ glass.

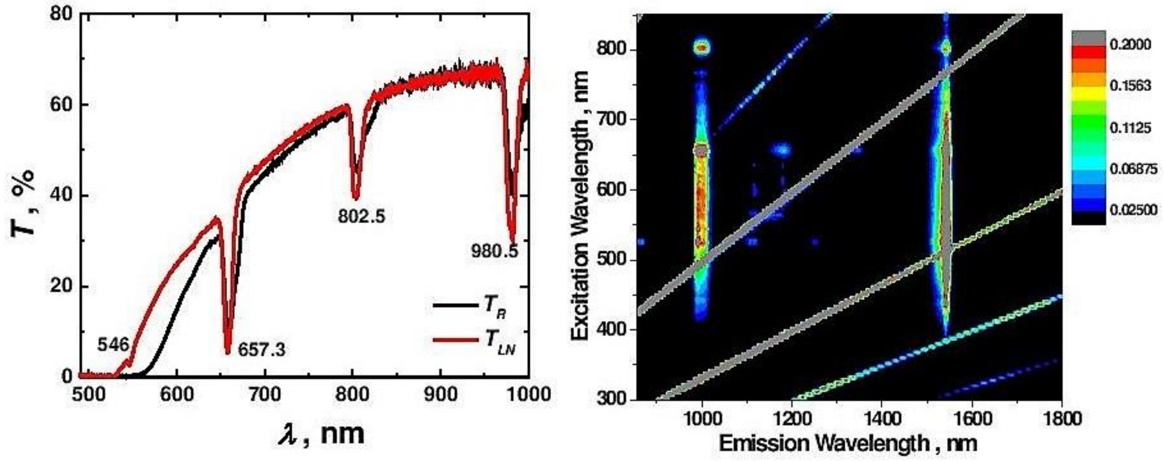

Figure 1. Vis-NIR transmission at T_R and T_{LN} temperatures (left)
and T_{LN} fluorescence spectrum (right) of the glass doped with 1.0 mol. % Er^{3+}.

The observed at T_R absorption peaks at □ 657, 803 and 981 nm correspond to $^4I_{15/2}\rightarrow{}^4F_{9/2}$, $^4I_{15/2}\rightarrow{}^4I_{9/2}$ and $^4I_{15/2}\rightarrow{}^4I_{11/2}$ transitions of Er^{3+} ions, respectively. At T_{LN} temperature, it is possible to observe also the absorption at 546 nm, which corresponds to $^4I_{15/2}\rightarrow{}^2H_{11/2}$ ($^4S_{3/2}$) transition. The strongest emission in the low-temperature fluorescence spectra is observed at □1 μm and ~ 1.5 μm identified as $^4I_{11/2}\rightarrow{}^4I_{15/2}$ and $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transitions of Er^{3+} ions, respectively.

SPIN-SPIN RELAXATIONS OF Nd^{3+} IONS IN Y_2SiO_5 AND YVO_4

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The problem of quantum state conversion of microwave photons into optical photons and vice versa can be resolved by using impurity rare-earth ions in dielectric crystals. These ions exhibit long optical coherence lifetimes for communication via optical photons, have the electron spin that can offer hybrid coupling between optic photons and superconducting qubits and often have non-zero nuclear spin for implementation of long lived quantum memory. Y_2SiO_5(YSO) and YVO_4 single crystals doped by ^{143}Nd ions are examples of such systems. The aim of this work is to compare the dependence of the spin-spin relaxation times of the impurity ^{143}Nd and ^{145}Nd ions in the YSO and YVO_4 monocrystals.

The Y_2SiO_5 and YVO_4 crystals were grown by the Czochralski method in iridium crucibles in the slightly oxidizing atmosphere (99 vol. % Ar and 1 vol. % O_2). The measurements of the spin-spin relaxation times were carried out on a Bruker ELEXYS E580 EPR spectrometer at the frequencies 9.64 and 9.82 GHz, respectively. Temperature dependences of the Nd^{3+} spin-spin relaxation time T_2 in the single crystals a) Y_2SiO_5; b) YVO_4. The spin-spin relaxation time at 4K depends on the resonance magnetic field that was established for neodymium ion doped in the Y_2SiO_5. The temperature dependencies of the spin-spin relaxation times for several resonance lines in YSO and $YVO_{\$}$ are shown in Figure. The strong temperature dependence of the T_2 value was attributed to the effect of the spectral diffusion caused by the hyperfine interaction with magnetic nuclei of the crystal matrix. This spectral diffusion can be efficiently eliminated in the Carr-Purcell-Meiboom-Gill (CPMG) pulse protocol (see Fig 1b). This work was supported by the Russian Science Foundation (project no. 16-12-00041).

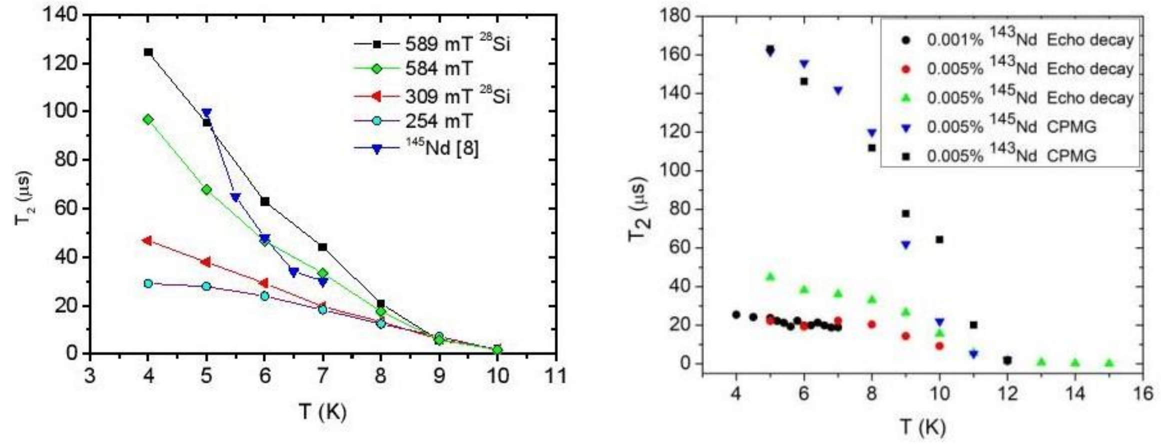

Figure 1. Temperature dependences of the Nd^{3+} spin-spin relaxation time T_2 in the single crystals a) Y_2SiO_5; b) YVO_4.

SOME OPTICAL PROPERTIES OF DIVALENT COBALT DOPED K (Mg, Zn)F_3 PEROVSKITES

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Optical absorption spectra of fluoroperovskites K (Mg, Zn)F_3 doped with divalent cobalt have been studied last years [1]. In the paper [1] we presented the fine structure of optical energy levels and the Ham reduction of their spin-orbit splitting, due to electron-phonon interaction between phonons of fluorine ligands and energy levels of active metal ion.

The aim of this paper is to present new results concerning optical properties of Co^{2+} doped in title systems. We used the same cluster model $[CoF_6]^{4-}$ obtained by doping the divalent cobalt ion that substitutes Mg^{2+}, respective Zn^{2+}, without charge compensation. Based on the exchange charge model of crystal field [2] we have calculated the dependence of the crystal field strength 10*Dq* on interionic distances *R* between the Co^{2+} impurity ion and F^- ligands of K(Mg,Zn)F3: Co^{2+} systems. The obtained results were extrapolated by the power law and was shown that 10*Dq* depends on *R* as $1/R^n$, with *n* deviated from the value $n = 5$, predicted by the simple point charge model of crystal field, that being explained by the covalent exchange effects properties and electron-vibrational interactions. The last type of interaction is characterized by typical parameters as electron vibrational coupling constants, Huang-Rhys factors and Jahn-Teller stabilization energy. Moreover, extracted from these calculations, the distance dependence of the crystal field strength 10*Dq* allowed us to estimate these parameters, obtaining favorably close values to the corresponding experimental results.

We also investigate the geometry of the $^4T_{2g}$ excited state of cobalt ion and, also, calculated the values for optical parameters of Co^{2+}.

All the calculations were done using the optimized geometry of K (Mg, Zn)F_3:Co^{2+} systems, in the frame of DFT methods as implemented in CRYSTAL14 code [3].

The obtained data were compared between them and with the experimental ones and the results are satisfactory.

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ON HUMIDITY SENSITIVITY OF MAGNESIUM AND ZINC GALLATE SPINELS

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The demand of industry, environmental monitoring, pharmacy, agriculture for highly efficient and inexpensive humidity sensing stimulates researchers to seek for new functional materials. The oxide ceramic materials have become a high spot on this topic due to several advantages, in particular chemical stability, fast response and high sensitivity [1]. Recently, oxide gallate spinel compounds showed good biocompatibility and possibility to be applied as gas sensitive media [2, 3]. In particular, $MgGa_2O_4$ and $ZnGa_2O_4$ spinels are materials with semiconductor properties which shows efficient emission in a broad spectral range depending on used activator ions [2, 4]. Finally, due to this combination of properties, these compounds can be investigated with a lot of different techniques and used in broad application fields [1-4].

The $MgGa_2O_4$, $ZnGa_2O_4$ compounds were synthesized via high-temperature solid-state technique using equal molar portions of initial powders to form a stoichiometric spinels doped with Mn^{2+} and Mn^{2+}, Eu^{3+} ceramic materials. The ceramic samples were characterized with a few spectroscopic methods (XRD – X-ray Diffractometry, TEM – Transmission Electron Microscopy, PALS – Positron Annihilation Lifetime spectroscopy). In addition, the luminescent properties and electrical conductivity were studied at different humidity environment of the atmosphere.

The XRD analysis confirmed successful formation of spinel phase in all samples. The TEM and STEM diffraction showed formation of ceramic samples with a broad size distribution of crystallites of irregular shape and orientation. The PALS measurements exhibited a high-intensity maximum with a characteristic decay time of water contained voids that directly testifies the existence of water-absorbance porous in both Mn^{2+} doped and Mn^{2+}, Eu^{3+} co- doped ceramics. Investigation of the luminescence spectra showed the changes of the total and relative intensity of emission bands attributed to Mn^{2+} and Eu^{3+} ions at different humidity. The electrical conductivity measurements showed high changes of the complex resistance of the samples at different frequencies of the applied voltage.

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SPECTROSCOPIC STUDY OF Nd^{3+} AND Yb^{3+} CO-DOPED TELLURITE GLASS FOR SOLAR CELLS

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Tellurite glasses (TL) show interesting properties like reasonable thermal stability, high solubility of rare-earth ions and low phonon energy compared to other glasses. Nd^{3+} ion is one of the most investigated rare earth ions mainly due to the high emission quantum yield from $^4F_{3/2}$ to ^4I_j (j=9/2, 11/2, 13/2 and 15/2) in the near-infrared spectral region. The co-doped system Nd^{3+}/Yb^{3+} have been calling the attention due to its potential for application in the photovoltaic cells. In this system, the neodymium ion acts as an absorber due to the large number of energy levels of Nd^{3+} located in the visible region, at the same time it presents an energy level ($^4F_{3/2}$) near of energy level $^2F_{5/2}$ from Yb^{3+} favoring the process of energy transfer mechanism from Nd^{3+} to Yb^{3+} ions. For another side, the Yb^{3+} ion is interesting for solar cells because of its simple energy level configuration of only two levels, which present a broad emission band in the maximum absorption of silicon. Figure 1 shows the absorption spectra of the studied tellurite glasses. The Nd^{3+} and Yb^{3+} ions present broad absorption bands, which is desirable for solar excitation and the overlap of the levels $^4F_{3/2}$ (Nd^{3+}) and $^2F_{5/2}$ (Yb^{3+}) is promising for the energy transfer form Nd^{3+} to Yb^{3+}. The inset of Figure 1 (a) shows the linearity of the incorporation of the Ytterbium ion in the glass. Figure 1b show the visible luminescence spectrum of Nd^{3+} (see Figure 1). The excitation spectrum in the range of 330 to 505 nm for the Nd^{3+}/Yb^{3+} co-doped TL glasses demonstrated that with blue excitation between 431 and 490 nm ($^2P_{1/2}$,$^2G_{9/2}$, $^4G_{11/2}$, $^2K_{15/2}$, and $^2D_{3/2}$ levels) (inset in Figure 1(b)) the emission intensity at 610 nm decreases with Yb^{3+} concentration. These results indicate the effect of the energy transfer occurs not only from the $^4F_{3/2}$ from Nd^{3+} but also from the blue energy levels from Nd^{3+} to Yb^{3+}. These results indicate that the pair Nd-Yb in TL glass is a promissory candidate for solar cells sensitizer.

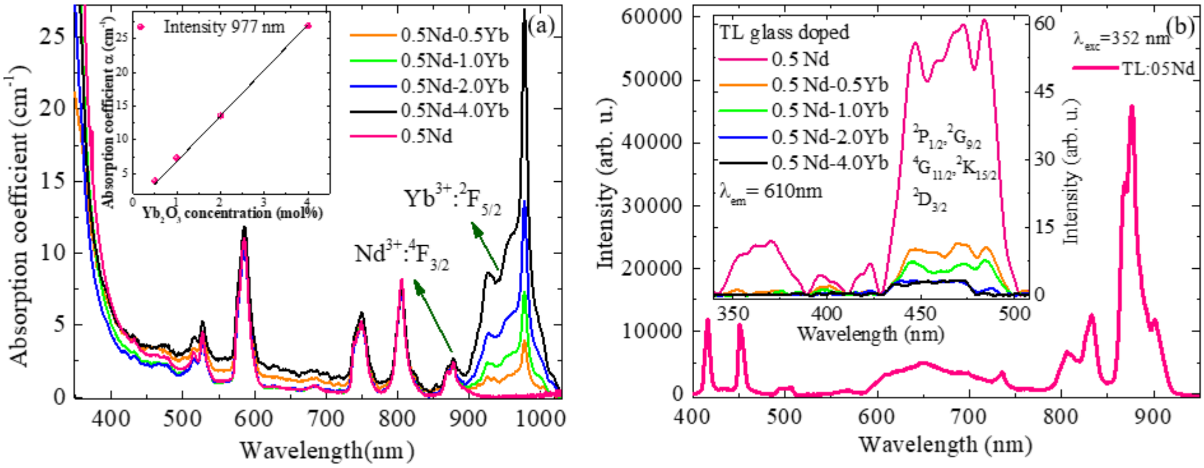

Figure 1. (a) Absorption spectra for the 0.5Nd and 0.5Nd-xYb (x=0, 0.5, 1, 2, and 4 mol%) co-doped TL glasses and the inset shows the peak intensity for absorption coefficient at 977 nm as a function of the concentration of Yb^{3+}. (b) Emission spectra for the 0.5Nd doped TL glass, with □$_{exc}$=352 nm and the inset, shows the excitation spectra for the 0.5Nd and 0.5Nd-xYb (x=0, 0.5, 1, 2, and 4 mol%) co-doped TL glasses with emission detected at 610 nm.

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BLACK LIGHT EMITTERS ON COLLOIDAL CdSe NANOPLATELETS

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Colloidal semiconductor nanocrystals are essential materials in modern nanotechnology. They are used for photodetection, serve as active media in light-emitting diodes, lasers and displays, and applied in biomedicine for diagnostics and drug delivery. They appear in various compositions and shapes, most common being quantum dots, tetrapods, nanorods and nanoplatelets. Among these, nanoplatelets are novel two-dimensional nanocrystals that continue to amuse scientists with their unique properties. Only their thickness is nanoscale and consists of few atomic layers while their lateral dimensions can reach several microns. They are excellent luminophores and suit well for optoelectronic applications, thanks to their flat geometry.

Therefore we developed a stable and repeatable synthesis procedure for obtaining ultrathin nanoplatelets and studied their optical characteristics to show that these nanocrystals will allow to broaden the line of pure-colored semiconductor light emitters and enrich them with devices operating in UV range, that would be extremely useful for medical lasers, as well as for integrating them in optical fibers, microfabricated waveguides and lab-on-chip systems [1].

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$Eu^{2+,3+}/Pr^{3+}$ CO-DOPED CALCIUM ALUMINOSILICATE GLASS FOR TUNABLE WHITE LIGHT DEVICES

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White-light-emitting diodes (WLEDs) have greater advantages when compared to the traditional fluorescent and incandescent lamps as low consumption. Many efforts have been done to develop WLEDs with acceptable colorimetric parameters to lighting (high color rendering index, CRI and correlated color temperature, CCT) [1]. Ce^{3+}: YAG is the most used phosphor combined with blue excitation. This WLED has some drawbacks due to low red emission component, turning it with low CRI (~ 70) and high CCT (~ 6500K) values. It is well known that Pr^{3+} is among the ions to promote this red emission component under blue excitation to increase CRI. In this study we report the use of Eu^{2+3+}/Pr^{3+} co-doped calcium aluminosilicate (CAS) glass as phosphor for white light generation under blue and violet excitation. A prototype of WLED is developed by using different sample powder layers with combined 445 and 405nm tunable LED excitation. In Figure 7 there are the photoluminescence (PL) spectra obtained for 0.5 wt.% Eu^{2+}/1.0 wt.% Pr^{3+} co-doped CAS glass for different excitation powers of both violet and blue LEDs. The applied current in the LEDs where chose to produce high CRI values and acceptable D*u*'*v*' values, with high tunable CCT range. It was observed that the (*x*, *y*) coordinates produce CRI values above 90 and CCT values tunable from 5140 – 5702K, with D*u*'*v*' values less than the required limit (<0.02). These results were promising to the development of high-quality WLEDs.

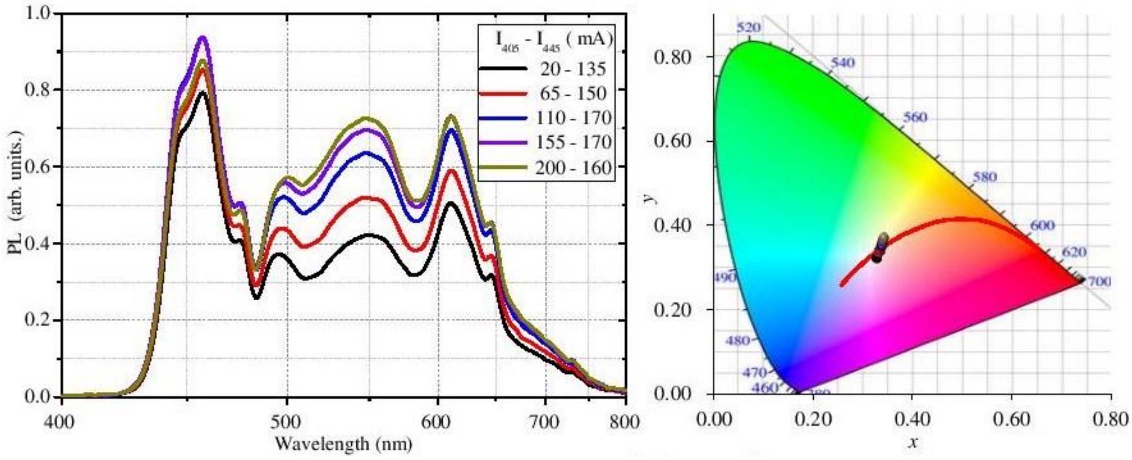

Figure 1. Photoluminescence (PL) spectra of $0.5Eu^{2+,3+}/1.0Pr^{3+}$ co-doped CAS glass for different LED's currents of 405 and 445nm. b) CIE 1931 diagram showing the coordinates obtained for each spectrum.

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TAILORING OF ZnO LUMINESCENCE PROPERTIES BY CONTROLLED DOPING

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Pure zinc oxide naturally exhibits two kinds of luminescence – weak exciton-related emission in UV and strong defect-related emission in visible spectral ranges. The intensity of the excitonic luminescence can be increased by doping ZnO with donor ions, such as Ga^{3+} or In^{3+}. Doping by Ga^{3+} ions and post-preparation treatment play a significant role, as shown in [1], and lead to complete disappearance of defect-related luminescence in the visible spectral region and to the enhancement of narrow emission at 389 nm. As shown in [2], slow components are completely absent in ZnO: Ga scintillation decay within ns–100 ps time scale under nanosecond pulse soft X-ray excitation.

The principle of band gap modulation consists in shifting the conduction band edge by affecting the energy levels of 2p orbital of Zn^{2+} by foreign ions and their energy levels. These foreign ions may occupy either the lattice position of Zn^{2+} ions or interstitial positions. If the concentration of foreign ions is sufficient, the bottom edge of the conduction band shifts. Doping by appropriate ions, such as Cd, Mg, Ca or Sr leads to the narrowing or broadening of the band gap. In summary, the changes in the band gap structure will be directly affected by the electron configuration of doping ion in the crystal lattice and with increasing concentration the shift of BG increases. The effect of doping ion can be observed as “red” or “blue” shift in emission spectra to lower or higher energies.

Cadmium and magnesium ions were chosen for the investigation of the ZnO band gap modulation, based on the previous promising results. It was shown that the concentrations up to 1mol% of Cd in ZnO structure have no effect on the intensity and position of exciton- related emission in UV range, but the increasing intensity of defect-related emission in visible range was observed. At higher Cd concentrations, modulation of the band gap and appropriate shift of emission maxima were observed. Significant blue or red shift of the UV emission maxima was obtained with the maximal admixture of 13 mol % of Cd or Mg ions, without any emission in the visible spectral range. It was manifested that the UV exciton-related emission can be shifted in the range of 376-425 nm at the cost of the decrease in total luminescence intensity.

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REFRACTIVE INDEX CHANGES OF SPHERICAL QUANTUM DOT WITH HYDROGENIC IMPURITY IN MAGNETIC FIELD

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Linear, nonlinear and total refractive index changes of a spherical quantum dot with on-center hydrogenic impurity in the external static magnetic field are studied. Expressions for the refractive index changes are derived with the help of the density matrix formalism for a two-level system, and analyzed from the theoretical point of view. Their behaviors with respect to the incident photon energy is examined, as well as their dependence on the magnetic field strength, quantum dot radius, laser intensity and relaxation time.

The blue shift of refractive index changes for quantum dots with large radii is observed when the applied magnetic field is increased, while the red shift of the examined quantities, with increasing the magnetic field strength is noticed for quantum dots with small radii. Total refractive index change turns its slope from negative to positive values when the incident photon energy is close to the transition energy when laser intensity increases, which is closely connected to the group velocity of the laser light.

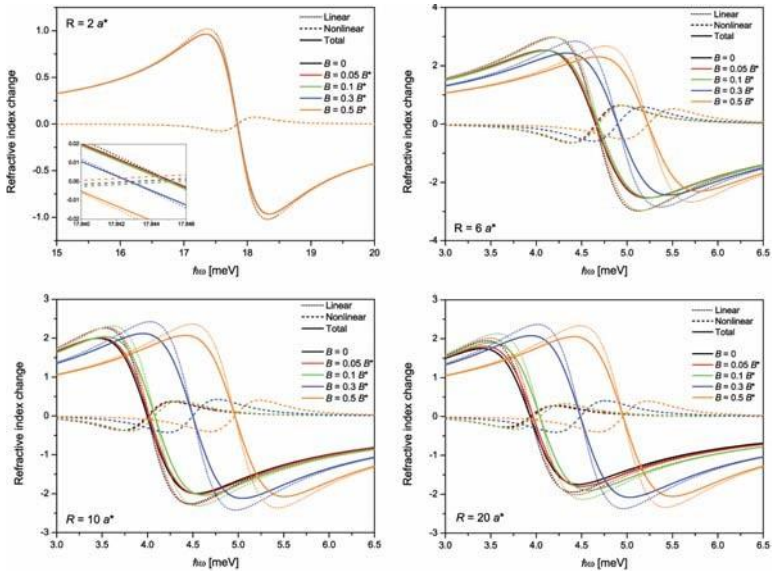

Figure1. Linear, nonlinear and total refractive index changes as functions of the incident photon energy, calculated for several values of quantum dot radius and magnetic field strength.

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Nd^{3+}-DOPED TELLURITE GLASS FOR FLUORESCENT THERMOMETERS

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The temperature sensors are commonly used in several technological and scientific applications. However, there is a lack of appropriate sensors in some cases, e.g., thermocouples are not suitable for measurements near installations with high electromagnetic interference (near electromagnetic coils), or for biological applications where the device requires reduced instrumental dimensions and high sensitivity (measurements at micro and nano scale to cellular temperature mapping, for example). Fluorescent thermometers based on fluorescence intensity ratio (FIR) technique of some trivalent lanthanide ion (Ln^{3+}) has attracted a great interest due the possibility of the change of the electron population in two thermally coupled levels, predicted by the Boltzmann's distribution, that change the emission intensity associated with these levels with the temperature [1,2]. In the present study the Nd^{3+}- doped tellurite glass (TL: Nd^{3+}) with nominal (in wt. %) composition [$80.0TeO_2+20.0Li_2CO_3+ 0.5Nd_2O_3$] was excited at 583nm (dye laser), in 299 – 371K temperature range (Fig. 1a). It can be observed a decrease of the emission at 893nm, due to the decrease of population of excited state $^4F_{3/2}$ by thermal excitation to upper levels $^4F_{5/2}$,$^2H_{11/2}$, and $^4F_{7/2}$, confirmed by the increase observed in the emission bands at 816 and 760nm ($^4F_{5/2,\ 7/2} \rightarrow {}^4I_{9/2}$ transitions). The calculated relative sensitivity of this material reaches 1.63%K^{-1} at 299K, comparable with values found to other Nd^{3+} doped systems [3]. The results indicate that the material is promising for application as temperature sensor.

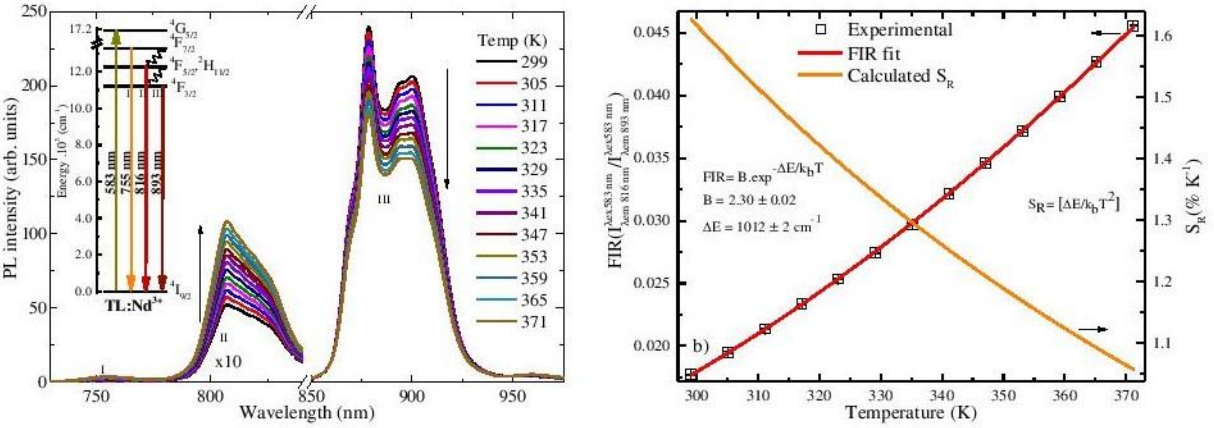

Figure 1. a) Photoluminescence (PL) spectra of Nd^{3+}-doped TL glass with excitation at 583 nm, for different sample temperatures (from 299 to 371K). The emission intensity in I and II designed area was multiplied by 10 for best visualization; b) FIR fit and relative sensitivity calculated for the ratio between the areas of the bands II and III.

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NEW PERSPECTIVE ON MECHANOLUMINESCENCE: INCREASING THE SIGNAL VISIBILITY THROUGH RECOVERY

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Monitoring the health of structures for the prevention and detection of early-stage damages requires easy-to-use and non-invasive stress sensing devices. Elastico-mechanoluminescent (EML) stress sensors consisting of a phosphor powder embedded in a polymer matrix are gaining a lot of interest in this area, allowing repetitive full field visualization of the stress distribution present in the material under loading conditions [1]. Many phosphors, including $SrAl_2O_4:Eu^{2+}$(, Dy^{3+}) [1, 2], $ZnS:Mn^{2+}$ [3] and $BaSi_2O_2N_2:Eu^{2+}$ [4], have been found to be eligible for use in EML sensors, exhibiting a linear relation between the mechanoluminescence intensity and the applied load in addition to wide pressure ranges and sensitivity to a variety of mechanical stresses and deformations: compression, tension, friction, impact, ultrasound, [5-7].

The practical implementation of these EML sensors however is currently obstructed by relatively low signal visibility, the restriction to real-time measurements and the need for dark conditions [8]. Efforts to eliminate these drawbacks have mainly concentrated on reducing the unwanted persistent luminescent behavior or afterglow, for instance by using long delay times between the excitation and mechanical stimulation of the phosphor [9]. In this discussion, the ML behavior of the phosphor $BaSi_2O_2N_2:Eu^{2+}$ is investigated in depth, elucidating the underlying mechanism and the trap depth distribution of the phosphor through a combination of ML, thermoluminescence and optically stimulated luminescence. The obtained results indicate an alternative to the previously proposed solutions, namely the recovery of the ML signal. In our approach, signal acquisitioning can take place at a chosen time long after the initial loading of the material, eliminating the undesired afterglow and improving the ML signal visibility. A working mechanism is derived and extensively tested. From this, it became clear several other phosphors possess the possibility of displaying this behavior, increasing the potential of exploiting this phenomena for use in ML based applications.

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OPTICAL AND SCINTILLATION PROPERTIES OF Ce-DOPED BaBrI CRYSTALS

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BaBrI doped with Eu^{2+} ions was discovered as a prospective scintillator [1]. It exhibits high light yield and gamma-ray energy resolution. The vacuum refereed binding energy (VRBE) diagram of lanthanide ions doped BaBrI crystal was given in [2, 3]. In these articles a possibility of 5d-4f emission of Ce^{3+} ions was proposed. However, there has not yet been an spectroscopic study of Ce^{3+} ions in BaBrI crystals. Despite the fact that Ce-doped crystal has a number of indisputable advantages over the Eu-doped one due to faster decay time and temperature stability of light yield. Therefore, Ce-doped BaBrI crystals will be important high-performance scintillator with applications in homeland security, medicine, and well logging. In this paper we present the results of study Ce-doped BaBrI crystals.

The stable phase of BaBrI crystal at room temperature has the orthorhombic $PbCl_2$ structure with space group D_{2h}, Pnma [1, 2]. The elementary cell has a centre of inversion, the local symmetry of all cation and anion sites corresponds only to the point group C_S with a single symmetry plane parallel to the *bc*-plane. Ce^{3+} ions substitute Ba^{2+} ions and can be compensated interstitial anions or oxygen O^{2-} ions. Photoluminescence measurements performed at 300 K in BaBrI:Ce^{3+} show a resolved luminescence doublet peaking at 363 and 391 nm, and a second band with an unresolved peak at 480 nm. These can be assigned to two Ce^{3+} luminescent sites. In excitation spectra several peaks in 230-340 nm region were found. The doublet photoluminescence peaked at 363 and 391 nm may be assigned to Ce^{3+} ions on the unperturbed Ba^{2+} sites. The unresolved peak at 480 nm could be attributed to Ce^{3+}-O^{2-} complexes. The decay time constant of Ce^{3+}-related emission was estimated at about 30 ns.
Photostimulated and thermostimualted luminescence, and temperature dependence of photo- and x-ray excited luminescence measurements were performed.

In this paper we estimate U (6, A) parameter of VRBE model based on the experimental data and discuss possible nergy transfer mechanism to Ce3+-realated centers. The scintillation properties of Ce-doped BaBrI crystals are also measured.

The research was supported by grant of Russian Science Foundation RSF 17-72-10084

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MULTIPLE APPLICATIONS OF LUMINESCENCE TECHNIQUES

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Thermally stimulated luminescence and optically stimulated luminescence are the phenomenon of emission of light from a solid which has been previously exposed to ionizing radiation under conditions of increasing temperature or optical stimulation, respectively. Luminescence is exhibited by a host of materials, glasses, ceramics, plastics and some organic solids. Apart from being a tool for the study of defects in solids, luminescence techniques have other multiple applications in various fields, especially for detection of irradiated food, dating in archaeology and geology, and in medical dosimetry.

Currently, there are certain regulations in Macedonia concerning safety requirements of irradiated food. Also, detailed procedures for sampling, measurement and analysis of results for detection of irradiated food are not defined. Implementation of standardized luminescence techniques in the field of detection of irradiated food is critical for aligning national regulations with European legislation.

Most of Macedonian cultural heritage objects are still waiting for scientific dating, conservation and restoration, making it very important to emphasize the need for enhancing characterization capabilities. Geology is one of the earliest disciplines to accept nuclear based techniques in its fold in a variety of applications, such as dating of mineralization, igneous activities, sedimentation and evaluation of growth rate of beaches and sand dunes. These techniques have been found useful in dating specimens of geologically recent origin where all other conventional methods fail. Of particular interest in Macedonia is evaluation of dynamics of landslides, which are common in this region. Furthermore, there is no institution in Macedonia that deals with radiometric dating. Therefore, enhancing national capacities in the field of geoarchaeological dating is essential for implementation of national legislation in this field.

The quality of current widespread use of ionising radiation in medicine can be achieved mostly by accurate determination of energy absorbed from the radiation field and, if possible, the distribution of this absorbed energy within the material. Thermoluminescence dosimetry can provide a perfect passive measurement i.e. integrated irradiation levels over extended periods, even of the order of years. Thus, it finds immense use in the monitoring of doses received by radiation workers. Thermoluminescence dosimetry has proved to be a useful method in the determination of patient absorbed dose, for improving radiographers' techniques and design of equipment to reduce patient absorbed dose, and for providing a measurement database for epidemiological analysis of population radiation absorbed dose from diagnostic radiology.

Establishing Laboratory for application of luminescence techniques for multipurpose applications is based on the issue of interdisciplinary approach. In this paper the idea and roadmap for establishing such Laboratory is elaborated, arising from the fact that the same luminescence techniques could be implemented in different fields of applications. This is of great importance, especially for developing countries, where infrastructure and human capacities in research institutions are limited, and prices of provided services should be reasonable.

SINGLET OXYGEN GENERATION USING LuAG:Pr^{3+}@SiO_2-PpIX NANOCOMPOSITE MATERIAL

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Due to LuAG:RE^{3+} (RE = rare-earth elements) single crystal and fiber applications in many fields, including high-energy particle physics, medical imaging and security measures [1], there is a growing interest in the usage of LuAG:Re^{3+} powders. Due to the luminescence properties, such nanopowders may be used as a light-emitting core of the nanocomposite material for X-ray induced photodynamic therapy (PDTX) [2]. PDTX uses tumor-destroying agents based on the nanoparticles (NP) conjugated with photosensitizer (PS) molecules. The agent accumulates preferentially in the target cells; subsequently, the external X-ray irradiation excites the scintillating NP, emitting secondary radiation, which activates the PS molecules. Their deexcitation via non-radiative energy transfer (ET) leads to the production of the reactive oxygen species, where the singlet oxygen is the most cytotoxic [3].

Due to its high effective atomic number, luminescence intensity and overlap of Pr^{3+} emission and protoporpyrin IX (PpIX) absorption bands, LuAG: Pr^{3+} may be a good candidate for a core of the PDTX agent. In this work, we present a concept of preparation of the singlet oxygen producing LuAG:Pr^{3+}@SiO_2-PpIX nanocomposites for PDTX application. LuAG: Pr^{3+} nanoparticles with the average size of about 30 nm were prepared using photo-induced method [2]. Subsequently, the surface coating procedure with SiO_2 amorphous layer was performed via sol-gel route. Finally, NPs were conjugated with a photosensitizer molecule (PpIX). Morphological characteristics of the materials were obtained from the X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM). Energy transfer (ET) and luminescent properties of the nanocomposites were studied by radioluminescence (RL) and photoluminescence (PL) experiments. The singlet oxygen generation in the system was demonstrated by APF chemical probe sensitive to the singlet oxygen presence. Quenching studies, using NaN_3 as an $^1O_2$ inhibitor, also confirm the presence of $^1O_2$ in the system and rule out the parasitic reaction of APF with OH radicals.

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FABRICATION OF TILTED LONG PERIOD FIBER GRATING BASED ON POLYMER- STABILIZED ALIGNED LIQUID CRYSTAL

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A novel and simple method is proposed to fabricate the tilted long-period fiber gratings (TLPFGs) based on liquid crystal-filled hollow core fiber by using polymer stabilized alignment (PSA) technique in this study. The periodic fringing field is utilized to create the desired gradient refractive index profile in the LC/monomer layer, which is later stabilized by UV curing to form polymer networks for controlling the preferred direction and pretilt angle of LCs on the wall surface of the fiber core in the UV-illuminated region. As a result, the tilted LCF grating is then successfully realized with phase separation of the LC molecules and UV-curable prepolymer mixture. The polymer networks used here offer the anchoring effect on the alignment of LC molecular on the surface, and thus provide satisfactory electro-optical performance for the LC-based fiber device. In addition, TLPFGs with different tilted angles are easily achieved by modulating the grating mask and the LCF during phase separation process as shown in Fig.1. The structures of the TLPFG devices are evaluated by using a cross-polarized optical microscope (POM) and the optical spectrum analyzer (OSA), respectively. The optical properties of the LC fiber devices are investigated by the optic spectrum analyzer under different applied voltages. We found the red-shift of the resonant wavelength of the TLPFG device occurs with the applied voltages.

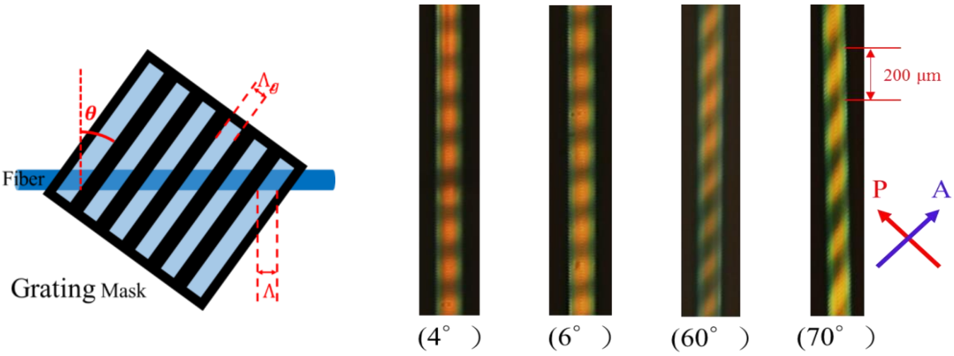

Figure. 1. The TLPFGs with different tilt angles are observed under crossed polarization microscope.

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OPTICAL ABSORPTION SPECTRA OF Ni^{2+} EIGHTFOLD CUBIC COORDINATION IN (Cd, Ca) F_2 CRYSTALS

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Crystals with fluoride structure provide the possibility of investigation optical spectra of an impurity transition metal ion in cubic eightfold coordination, when the ion is substituted on cation sites. If the doped ion has degenerated ground state than, due the static Jahn-Teller (JT) effect the geometry of the unit cell crystal could be distorted from a cube to an octahedra [1]. In this paper we present the results of theoretical investigation of optical spectra of divalent nickel ion doped in (Cd, Ca)F_2 structure. As results of doping, Ni^{2+} will substitute cation (Cd^{2+}/Ca^{2+}) without charge compensation, in cubic coordination. The strong trigonal distortion of the eighfold cubic coordination $[NiF_8]^{6-}$ as due to the T Jahn-Teller will distort the cubic unit cell to an octahedra, with trigonal site symmetry of divalent nickel. The analysis of new cluster $[NiF_6]^{4-}$ follow a recent methodology [2] combining two methods: the semi empirical crystal field, in the framework of the exchange charge model (ECM) [3] and the *first principle* multireference configuration interaction method, respectively. Both methods of calculations are applied to the $[NiF_6]^{4-}$ cluster embedded in an extended point charge field of host matrix ligands constructed according Gellé-Lepetit procedure [4]. The ECM theory has been used to calculate the ligand field parameters used for simulation of optical absorption spectra. The *first principle* wave functions approaches, such as complete active space self-consistent field (CASSCF) and N-electron valence second order perturbation theory (NEVPT2) are also used for the energy terms calculation. In addition, *ab initio* ligand field theory (AILFT) [5] allows to extract all ligand field parameters and spin-orbit coupling constant from such calculations. The obtained results are discussed and the comparisons with measured values shows a reasonably agreement, which justifies this new route of investigation.

The results of taken into account the static trigonal JT effect, combined with the new methodology above aforementioned, allows the calculations of optical spectra of impurity ions doped in eightfold cubic coordination.

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FIRST-PRINCIPLE CALCULATIONS OF OPTICAL ABSORPTION SPECTRA AND EPR PARAMETERS FOR Cr^{3+} DOPED DIPOTASSIUM TETRACHLOROPALLADATE

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Palladium (II) complexes have attracted considerable attention due its anti-viral, -malarial, -fungal and -microbial activities [1]. An impurity ion like Cr^{3+} doped in a host lattice K_2PdCl_4 increases number of applications in chemical, electrical, electronic, glass industries etc. Thus, investigations on local structures and behaviour of Cr^{3+} in K_2PdCl_4 are the scientific and practical significance. The aim of the present work is to explore the optical absorption spectra and electron paramagnetic resonance (EPR) parameters for the Cr^{3+} centres in K_2PdCl_4 crystal by involving *first principle* calculations. In order to do this, we have carried out the geometry optimization of the title system by means of density functional theory (DFT), method implemented in Crystal 14 software [2].By doping, Cr^{3+} substitutes K^+, with charge compensation and the local symmetry decreases from tetragonal to orthorhombic one, due to Jahn –Teller static effect. We have modeled these effects on the $[CrCl_6]^{3-}$ cluster embedded in an extended point charge field of host matrix ligands, based on Gellé Lepetit procedure [3]. The computation of the energy levels and EPR parameters of Cr^{3+}: K_2PdCl_4 system have been done using *first principle* calculations of multireference configuration interaction wave functions approaches, such as complete active space self-consistent field (CASSCF), N- electron valence second order perturbation theory (NEVPT2) and spectroscopy oriented configuration interaction (SORCI), implemented in ORCA program [4].

The obtained results are compared with experimental data [5] and the agreement is quite reasonable, which confirm the validity of the used method. This method could be applied for similar calculations with the transition metal ion doped into another optical material. The present study demonstrated that this new methodology, larger describes in [6], reproduce well the experimental results.

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M-SHAPED QUANTUM WELLS FOR ACTIVE REGION OF INTERBAND CASCADE LASER

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There has recently been reported a significant progress in various concepts of coherent radiation sources in the MIR. As one of very efficient solutions there evolved the interband cascade lasers (ICLs), proven to have several advantageous features, like broad tuning range of the emission [1-3], minimized influence of the Auger related carrier losses [4], and a very low power consumption [5]. However, in order to fully utilize the potential of ICLs, many parameters of these multilayer structures need to be further optimized. This concerns especially the active region which is composed of a cascade of type II quantum wells (QWs) made of broken gap materials, InAs and GaInSb, forming the so called “W-like” quantum well due to the shape band edge profile of InAs/GaInSb/InAs layers, with usually AlSb external barriers.

In this work, we discuss a possibility of implementing a novel type-II QWs design, which we called M-shaped, being a combination of reversed combination of layers compared to “W” QWs, i.e. GaInSb/InAs/GaInSb with a double QW for confinement of holes, which affects many important factors, as e.g. the overlaps of the conduction and valence band confined states or sensitivity to system parameter changes (as compositions, layer thicknesses, or electric field). We have modelled the electronic structure and optical properties of such QWs considered as to be grown on a GaSb substrate. The calculations have been carried out within the eight-band $k\cdot p$ theory including strain. There has been considered the use of a double well M-design and a triple type II quantum well structure of that kind, with respect to their utilization in lasers. There will be reported such issues as variation of compositions and thicknesses and external factors crucial in operational devices as e.g. electric field. We have obtained that such a design allows preserving the large optical matrix elements in spite of indirect in the real space character of the optical transition, allows for simultaneous red shift of the transitions and exhibits low sensitivity to different structure nonuniformities. In order to verify the application prospect the results will be confronted with the common W-design QWs. For instance, there has been obtained a significant tunability of optical transition’s oscillator strength and hence also the characteristic lifetimes by external bias, which would make M-structures beneficial in construction of absorber and gain sections of a passively mode-locked laser devices. In this context, the approach with M-design QWs is technologically less challenging to fabricate than the previously considered solutions of triple QWs or W-shaped QWs involving the GaAsSb alloy of rather demanding epitaxial growth.

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ENERGY STRUCTURE AND OPTICAL RESPONSE OF A NEUTRAL DONOR IN NON-UNIFORM HEIGHT QUANTUM RIBBON WITH AZIMUTHAL BARRIERS POTENTIAL UNDER EXTERNAL PROBES

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Semiconductor quantum rings with non-uniform height have been reported by using cross-sectional scanning tunneling microscopy. It is well known that the presence of neutral hydrogenic impurities tends to modify substantially the electronic properties. In this regard, we investigate the energy structure of an off-axis neutral donor D0 confined into non-uniform height and very narrow quantum rings with azimuthal barriers potential under threading magnetic field and radial electric field. Structural measurements allow to conclude that the quantum ring present several peaks and its height-to-base radius aspect ratio is very small. This experimental fact permits us to implement the adiabatic procedure in order to separate the electron rapid motion in axial direction from slow rotational motion. The corresponding angular Schrödinger equation with effective potential, which includes geometrical effects related to non-uniform height quantum ring profile and azimuthal barriers potential can be solved by using diagonalization method. The optical response is calculated by using the well- known density matrix.

The results of calculation show that the Aharanov-Oscillation patterns and optical response (linear and nonlinear absorption coefficients and change in refractive index) are strongly affected by the angle between azimuthal barriers, donor position and the number of peaks present in the quantum ring. It is possible to observe that he Aharanov-Bohm oscillation can be suppressed by the presence of peaks in the height profile of the quantum rings, which also affect the optical response, yielding a blue shift in the absorption peaks by increasing the height of geometrical hills. Nevertheless, these effects can be reversed by applying an electric field perpendicular to the magnetic field direction.

FACILE FABRICATION METHOD OF PHOTOMASK FOR THE UV REGION USING POLYIMIDE TAPE AND LASER

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In this presentation, we report a new method to form photomaks for the UV region by diffrent laser processing parameters. Among polymers, polyimide (PI) is well known for its excellent properties, including a low dielectric constant, good biocompatibility, outstanding mechanical properties, thermal properties, and chemical resistance [1]. And the PI is known to have low absorption in X-ray region [2]. So, many researchers had conducted the fabrication of masks for x-ray lithography using PI and gold. However, in the Ultraviolet(UV) region, since PI tape so called Kapton tape has a high absorptivity, we proposed that UV mask can be fabricated by removal process of PI without any other material coating or sputtering.

The Kapton tape removal process used a 355 nm nanosecond laser, and the mask was exposed on a wafer coated by ma-P 1205 photoresist using a 360 nm CW laser. Ultrafast-laser processing of PI tape had been studied through parameter controls such as the number of the irradiation, processing time and scanning speed. The facile fabrication of PI photomasks can be easy to apply various patterns like images, characters and shapes.

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ENERGY STRUCTURE AND ELECTROMAGNETICALLY INDUCED TRANSPARENCY OF NEUTRAL DONOR IN A MULTI-HILLED GaAs QUANTUM RIBBON

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The theoretical study of the energy spectrum and optical response of off-axis donor in a GaAs quantum ribbon with anisotropic rim height under the presence of constant crossed electric and magnetic fields is presented. The calculations are carried out within the effective mass and parabolic approximation, using an adiabatic approach combined with a diagonalization scheme. The rim height of the quantum ribbon has been modeled by including a phenomenological two-parametric function that accounts for realistic features of multi-hilled semiconductor nanostructure obtained from atomic force microscopy images. The first phenomenological parameter is introduced to control the number of quantum ribbon structural hills and the second one to deal with the height of the hills. It is shown that both the depth and the number of structural hills tend to substantially affect the Aharanov-Bohm oscillation pattern which can be quenched or restored by applying an electric field in an appropriate direction. The effect of the changes in the geometry and in the applied electric field onto the optical absorption and refractive index change are discussed. The phenomenon of electric- field-induced optical transparency in the system is particularly highlighted.

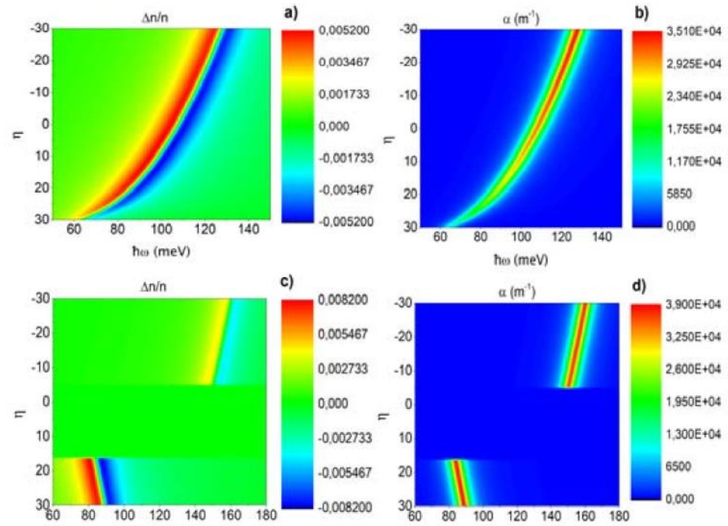

Figure 1. Optical properties for the neutral donor as a function of the applied electric field for: (a) a system with one hill (upper panels); (b) a system with two hills (lower panels).

Eu^{3+} STRUCTURAL PROBE IN $La_2Mo_2O_9$ AND La_2MoWO_9 UNDER UV EXCITATION

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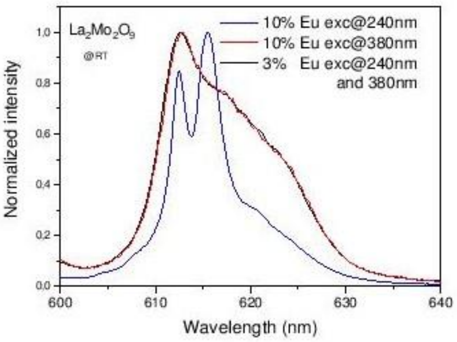
In our objective to find out new optical ceramic materials we focused our research on Rare Earth doped tungstates, molybdates and mixed molybdatotungstates materials. The cubic structure in one of the main requirement to fabricate transparent ceramics. However the structure within these families generally depends both of the dopant Rare Earth ion itself such Nd, Yb or Eu and also of their concentration [1, 2].

We have compared the structural and spectroscopic properties of both, micro- crystalline Eu^{3+}-doped $La_2Mo_2O_9$ and La_2MoWO_9. Series of samples were synthesized by the high-temperature solid-state reaction. XRD analysis has shown a structural dependence on Eu^{3+} ion concentration. If only the cubic phase is observed in the La_2MoWO_9 compound whatever the Eu^{3+} concentration, monoclinic phase exists for low concentration up to 7 mol% of Eu^{3+} ions in $La_2Mo_2O_9$, then for higher concentration the cubic phase is obtained.

Investigation of the spectroscopic properties leads to more complex behavior according the concentration in both matrixes. If europium-site selective excitation measurements with high spectral resolution, allow us to evidence multisite character and site distribution in both $La_2Mo_2O_9$ and La_2MoWO_9 compounds, UV excitation (240 & 380 nm) measurements prove to be a good tool to quickly analyze the main phases existing in these crystals according the concentration and temperature ; Figure1. Moreover we will discuss the origin of the various components observed in the absorption bands (in the range 200-400nm) that we clearly highlighted in these molybdates/tungstates: a broad blue emission band is observed under excitation in the high energy range (230-290nm), whereas no emission appears for longer excitation wavelengths (300-400nm); Figure2.



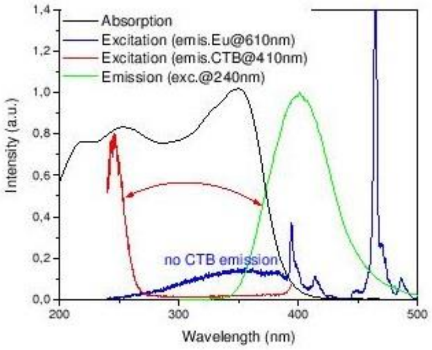


Figure1 (left): $^5D_0 \rightarrow {}^7F_2$ emission spectra under excitation at 240 and 380 nm in $La_2Mo_2O_9$ Eu.
Figure 2 (right). Absorption, excitation and emission spectra in La_2MoWO_9: Eu

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$Ti^{3+,\,4+}/Eu^{2+,\,3+}$ CO-DOPED LOW SILICA CALCIUM ALUMINOSILICATE GLASS FOR WHITE LIGHTING

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Low calcium aluminosilicate glasses (LSCAS) containing rare earth ion [1] or transition metal [2] are widely reported in the literature, especially for their potential application as phosphors for white light emission diodes (WLEDs). In the present work the LSCAS glass was co-doped with titanium and europium ions to be investigated for WLEDs application, with the possibility of tunable color temperature. The glass composition in wt% was 39.5-x Al_2O_3 (5N), 47.4 CaO (5N), 7 SiO_2 (5N), 2.0 TiO_2 (5N), 4.1-x MgO (5N), x Eu_2O_3 (4N) where x = 0.1 and 0.5. The mixture was melted under vacuum atmosphere at 1600ºC for two hours. All emission spectra were collected by a HR4000 Ocean Optics spectrometer. The coordinates (*x*, *y* and (*u′*, *v′*) were determined by the emission spectrum of the samples under excitation at the ultraviolet (300nm) and blue (445nm). Figure 1a) shows a broad visible emission band around 525nm which is attributed to Eu^{2+} and $Ti^{4+,3+}$. The peak centered at 613nm is due Eu^{3+}, and it increases with the Eu_2O_3 concentration. A red shift of the broad emission band can also be observed with Eu addition. This result indicates that the addition of Eu_2O_3 in LSCAS:$Ti^{3+,4+}$ induces the reduction from Ti^{4+} to Ti^{3+}. Figure 1b) shows in CIE 1931 x-y chromatic diagram the observed changes in the emission for different excitation wavelengths in the LSCAS doped with 0.1 wt% of Eu_2O_3. The results indicate that is possible to tune the emission color according to the excitation

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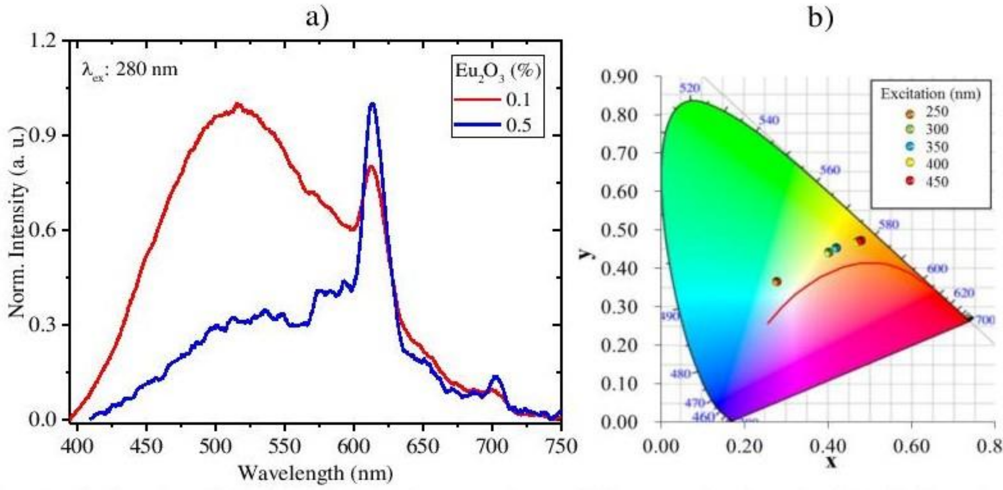

Figure 1a) Emission band 0.1% and 0.5% Eu samples at 280nm excitation. b) CIE 1931 color diagram from sample doped with 0.1 wt% of Eu_2O_3.

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TERNARY COMPOSITES WITH PBS QUANTUM DOTS FOR HYBRID PHOTOVOLTAICS

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Hybrid photovoltaics based on conjugated polymers and fullerene derivatives possess technological flexibility and high performance. However, they usually suffer from low absorption efficiency. Semiconductor quantum dots (QDs) may replace fullerene derivatives, acting as both light absorber and electron acceptor. In this case, light absorption can be tuned over a wide spectral range and cover near-infrared. Unfortunately, such devices still suffer from low efficiency, which mostly caused by inefficient charge transfer. To overcome these limitations, the concept of ternary composite should be developed.

The third component facilitates charge separation and transfer in the hybrid of conjugated polymers and QDs. In the current research we studied the introduction of fullerene and graphene derivatives into the PbS QDs - P3HT polymer blend. We studied optical properties of the blends using steady-state and time-resolved photoluminescence spectroscopy to establish the efficiency of charge transfer. Using atomic-force and confocal fluorescence microscopy, we monitored the morphology of the thin films made from ternary hybrids. We demonstrated that accurate ligand-exchange approach allows to improve thin films quality, components compatibility, and charge transfer efficiency.

PHOTOPHYSICS AND CONTROL OF CHARGE TRANSFER STATES IN TRIPHENYLAMINE DERIVATIVES VIA METHYLAMINE CONNECTOR

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To overcome difficulties in fabricating small microelectronic devices, a high demand for multifunctional charge transport and emissive optoelectronic materials emerges. It is well known, that triphenylamine compounds with additional substitutions in phenyl *para* positions demonstrates high charge carrier mobility. Emission properties although suffers from low fluorescence quantum efficiency with high charge transfer state fluorescence characteristics, poor packing in solid state with strong fluorescence concentration quenching which are strongly dependent on surrounding medium.

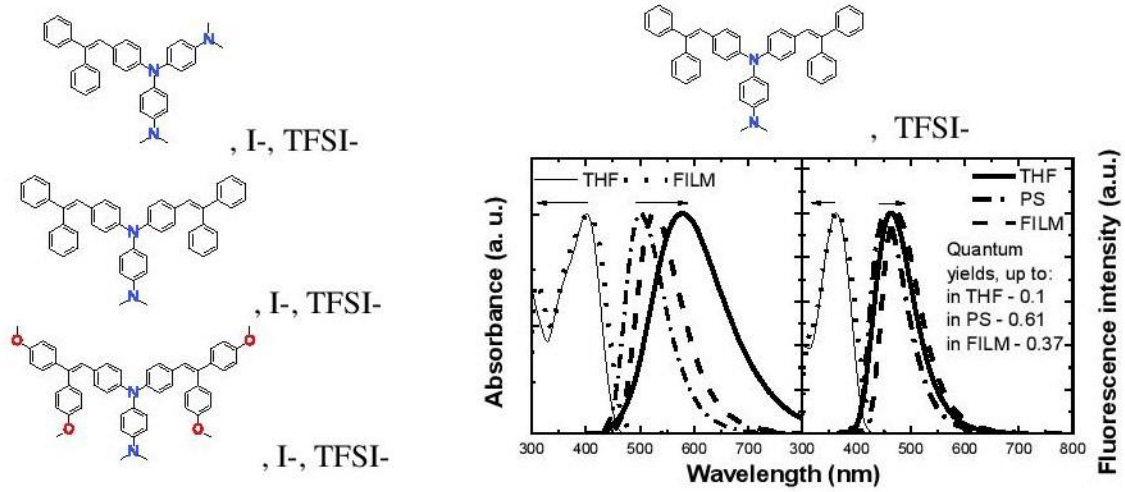

Figure 1. Triphenylamine derivatives with additional phenylethenyl and methylamine substitutions. Typical optical absorption and emission characteristics for one of the compounds are also shown.

In this paper we demonstrate new triphenylamine derivatives, with additional phenylethenyl as electron accepting and dimethylamine as electron donating moieties. To get deeper insight in excited charge transfer state relaxation and formation, the ratio of electron donating and accepting moieties was changed. Moreover, electron donating dimethylamine moiety was additionally stabilized with iodine (I-) and bistriflimide (TFSI-) ions to suppress charge transfer to triphenylamine core. Wide variety of optical and electrochemical techniques were employed for investigation. Balanced modification of triphenylamine core and control of charge transfer state enabled highly effective emission (fluorescence quantum yield up to 0.61) with low fluorescence concentration quenching in solid state (fluorescence quantum yield up to 0.37). Moreover, adittional modification with I- and TFSI- ions suppressed charge transfer state relaxation and compounds demonstrated local excitation type relaxation with medium - independant characteristics of emission spectra. Meanwhile, high charge carrier mobility (up to 10^{-2} cm^2/Vs) was preserved.

KCl: Yb^{2+}: CN^{-} CRYSTALS FOR PHOTONICS APLICATIONS

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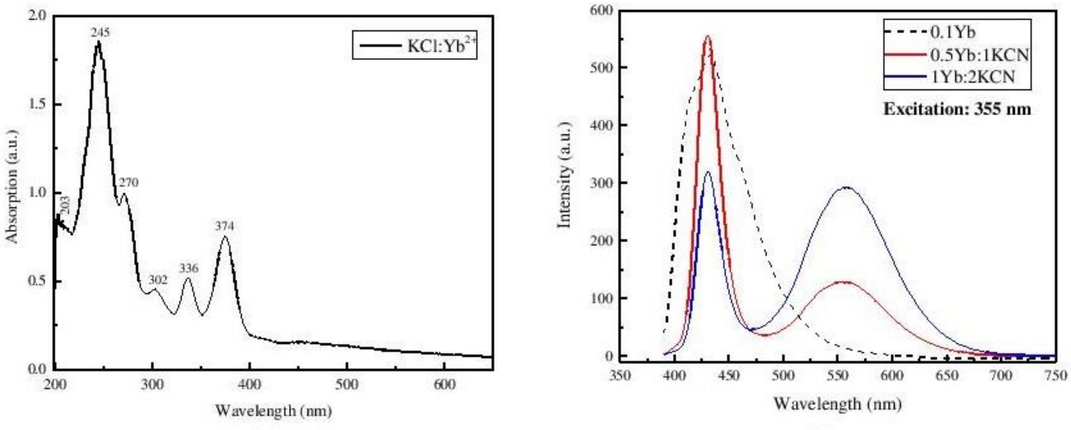
KCl crystals co-doped with Eu^{3+} and CN^{-} have attracted greater attention due to their potential for the development of white-light-emitting diode (WLED) devices [1]. The broad range of yellow-green emission band observed in the KCl: Eu^{2+}/KCN sample originates from the energy transfer from Eu^{2+} ion to CN^{-}[1]. Another pair that can show similar optical properties is Yb^{2+}/CN^{-} because of the similarity of the energy levels of Yb^{2+} [2] compared with Eu^{2+}. The interaction of the ion Yb^{2+} with CN^{-} cause a strong perturbation in Yb^{2+} levels, resulting in a red shift of the blue emission band Yb^{2+}. Therefore, the optical properties of the KCl: Yb^{2+}:CN^{-} crystals, with different concentrations of the Yb^{2+} and CN^{-}, should be investigated to verify their potential application WLED and solar cells sensitizer. The samples were prepared using the modified Bridgman method in an argon atmosphere. The growth rate was 4 mm h^{-1} with the vertical descent. Double doping was performed with a nominal concentration of (0,5% $YbCl_3$: 1% KCN) and (1.0% $YbCl_3$: 2% KCN). The crystals obtained by this method exhibited good optical quality. Figure 1(a) shows the absorption spectrum of the KCl+1.0% $YbCl_3$, confirming only the presence of the divalent ion Yb^{2+}, which show absorption bands in the UV-Violet region (200-400 nm). Figure (1b) shows the emission spectrum of the co-doped KCl:Yb^{2+}/CN^{-} crystals compared with the single doped. The concentration increase of the KCN reduces the intensity of the isolated ion emission Yb^{2+} band centered at 430 nm and favors the higher agglomeration of Yb^{2+}/ CN^{-} pairs that show a broad emission band centered at 550 nm a with displacement towards the red region. The strong absorption in the UV-violet and the broad emission band in the visible suggests that this crystal presents the potential for white light LEDs phosphorus or sensitizer for silicon- based solar cells.



(a) (b)

Figure 1 a) Absorption crystal KCl: Yb^{2+}. b) Emission band of crystals[KCl:1%Yb]; [KCl:0.5%Yb:1%KCN]; [KCl:1.0Yb:2KCN] with excitation at 355nm.

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A PHOTOTHERMAL SPECTROSCOPY STUDY OF OVERTONES AND COMBINATION BANDS IN SOLVENTS

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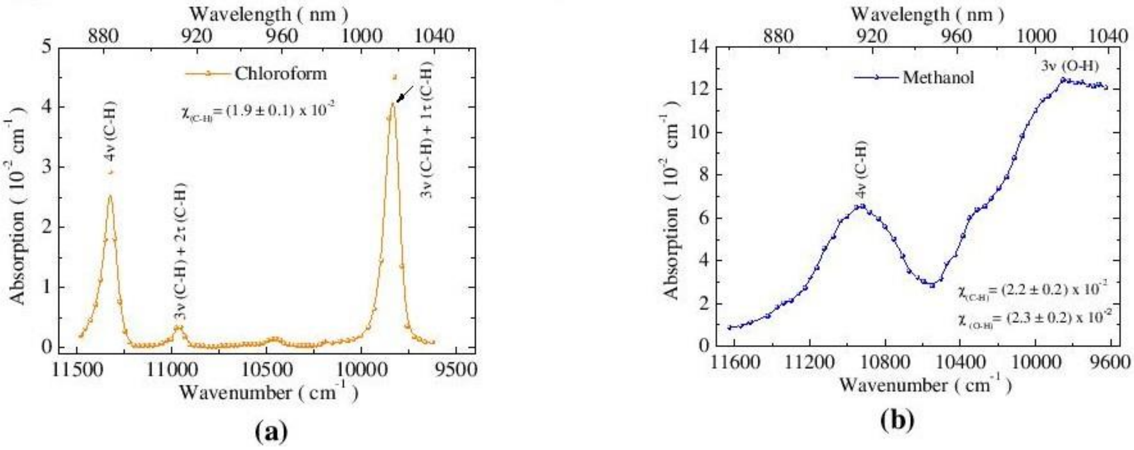
The dual-beam mode-mismatched Thermal Lens (TL) technique in the near-near infrared (N-NIR), was applied in the study of solvents using a tunable cw excitation laser (Ti^{3+}:Sapphire) in the range 9600 to 11500 cm^{-1}. Absorption spectra due to overtones and combination bands of the C-H and O-H stretching bonds were obtained and the anharmonicity constants (χ), dissociation energies and thermo-optical properties were calculated.

Figure 1 shows the TL absorption spectra in the N-NIR for the chloroform (a) and methanol (b), attributed to overtones and combination bands. In the chloroform spectrum is noted an absorption due to the third overtone of the C-H stretching mode (4ν C-H) at 11325 cm^{-1} and combination band at 9823 cm^{-1}. The anharmonicity constants (χ) obtained are in agreement with the literature [1, 2]. Fig. 1.b shows the methanol spectrum with 4ν C-H and 3ν O-H lines, much broader than compared to the lines observed in Fig.1.a. Similar spectra were obtained for dichloromethane and ethanol.

The thermal diffusivity values were also determined in all solvents: chloroform (0.85 ± 0.02) x 10^{-3} cm²/s^{-1}, dichloromethane (0.93 ± 0.03) x 10^{-3} cm²/s^{-1}, methanol (1.06 ± 0.02) x 10^{-3} cm²/s^{-1} and ethanol (0.89 ± 0.03) x 10^{-3} cm²/s^{-1}, in good agreement with the literature.

Most of TL results reported have no selectivity since they were obtained with single wavelength excitation. We obtained spectra with high selectivity since the signal due to the absorption lines are two order of magnitude higher than the background (blank) absorption ~ 2 10^{-4} cm^{-1}. In conclusion, the TL technique with N-NIR tunable excitation of a Ti-sapphire lasers is a technique with high selective and sensitivity suitable for many analytical applications such environmental monitoring [3].



(a) **(b)**

Figure 1. TL absorption spectra in the N-NIR for the **(a)** chloroformand **(b)** methanol.

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COMPARATIVE STUDY OF $Gd_2(Hf, Zr, Ti)_2O_7$ CRYSTALLINE SCINTILLATORS

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Scintillators convert incident ionizing radiation into thousands of ultraviolet-visible photons, and they have been used in different fields of radiation measurement including medical imaging, security and so on. Among scintillators, heavy element-based materials with high effective atomic number are advantageous in high energy radiation detection. Up to now, $Bi_4Ge_3O_{12}$ scintillator, which were developed in 1973, has been mainly used. In order to develop a scintillator which is a substitute for $Bi_4Ge_3O_{12}$, we focus on hafnium-based oxide as a new heavy element material. Since hafnium-based oxide has a quite high melting point of 2400 °C, it is difficult to grow a single crystal; therefore, only a few studies on hafnium-based oxide polycrystalline powder or ceramic have been reported [1, 2]. In this study, $Gd_2Hf_2O_7$ and $Gd_2(Hf_{0.99}M_{0.01})_2O_7$ (M=Zr, Ti) single crystals were synthesized using Floating Zone furnace with Xenon lamp, which is suitable for crystal growth showing high melting point materials. We evaluate the photoluminescence and scintillation characteristics of these crystals for the first time.

Fig. 1 shows the X-ray induced radioluminescence spectra of the synthesized single crystals. All the samples exhibit a broad emission around 500 nm, which would be owing to oxygen vacancy since it has similar emission wavelength and shape to those of $La_2Hf_2O_7$ reported in the past study [3]. Among the samples, the Ti-doped sample shows the highest emission intensity. In order to expect the emission origins, the radioluminescence decay profiles were evaluated. The decay curve is approximated by a sum of two exponential functions. The faster component is originated from the experimental function while the other is owing to oxygen vacancy. In this presentation, we also report the photoluminescence and afterglow characteristics to understand the emission mechanisms systematically.

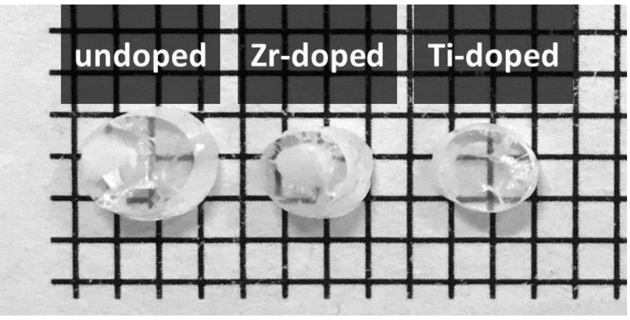

Figure. 1. Photograph of synthesized crystals.

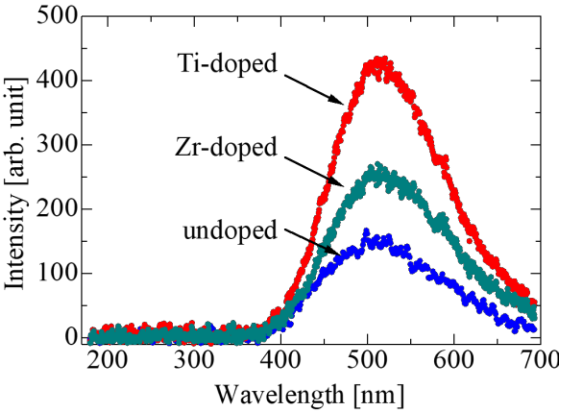

Fig. 2. X-ray induced radioluminescence spectra of $Gd_2(Hf,Zr,Ti)_2O_7$ crystals.

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OPTICAL SPECIFICITIES OF MOLECULAR CRYSTALLINE NANO-FILMS

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The main advantage of the theoretical approach is essential knowledge of the mechanisms that allow us to comprehend the experimental conditions that we have to fulfill to be able to get the desired results. This paper presents review of our current achievement in the field of theoretical optics of ultrathin films and possible ways to materialize the same in the field of nano-technology. Analytical analysis of the impact of the boundary parameters on the changes of the fundamental physical properties of the nanofilm, as compared to the same properties of bulk samples with identical crystalline and chemical structure, is impossible. Thus, a software package has been developed and applied to perform the numerical analysis and plot graphic displays of the relation between microscopic and macroscopic properties for a specified set of values of the boundary parameters. This proved that the outer environment of the film affects the given fundamental optical properties of a dielectric nano-film, i.e. that their choice/change directly controls the optical characteristics of the film. Such an approach could be considered as a kind of optical nano-engineering.

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DISTRIBUTION OF Yb^{3+}AND Yb^{2+} IONS ALONG THE YbF$_3$ DOPED BaF$_2$ CRYSTALS

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BaF$_2$ is known as the fastest scintillator with decay time of 600 ps at 220 nm. In addition to its fast emission component, BaF$_2$ has an unwanted slow emission component at 310 nm that can be suppressed by doping the crystal with rare-earth ions. Exposed to radiations various absorption bands appear due to the formation of color centers; this effect is usually related to impurities and/or structural defects in the crystals. The dopants which changes its valence from +3 to +2 under irradiation, such as Yb, are useful in eliminating the color centers [1].

The purpose of this paper is to study the distribution of Yb^{2+} and Yb^{3+} ions along the YbF$_3$ doped BaF$_2$ crystal. The influence of YbF$_3$ concentration on the Yb ions distribution along the crystal and on the segregation coefficient has also investigated.

BaF$_2$ crystals doped with 0.05; 0.1 and 0.2 mol % YbF$_3$ were grown in our crystal research laboratory using vertical Bridgman method [2]. The crystals were cut from the bottom to the top into 10-17 slices. The strongest characteristic absorption band of the Yb^{3+} ions is at 968 nm and of the Yb^{2+} ions at 353 nm. The corresponding absorption coefficient (for every slice), was estimated from the absorption spectrum. The absorption coefficient is proportional to the impurity concentration (the Beer-Lambert law), so the dopant distribution along the crystal can be estimated from the absorption spectra. The influence of the YbF$_3$ concentration on the Yb^{3+}and Yb^2 ions distribution along the crystals is shown in Fig.1a, b. The segregation coefficient (k) was calculated using the procedure described in [3]; the value of k depends on the YbF$_3$ concentrations (Fig.2).

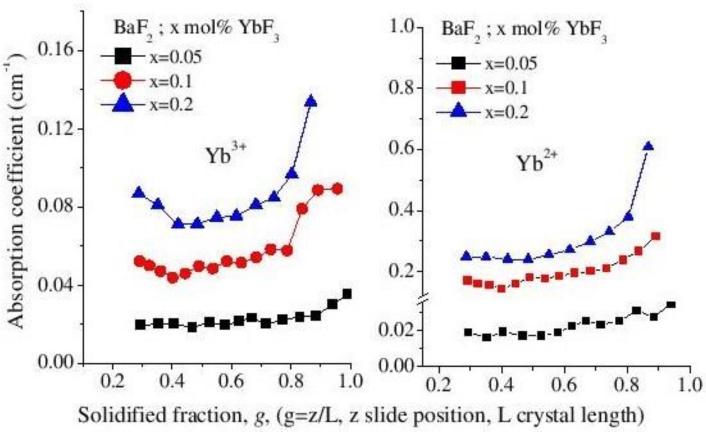

Figure 1. Distribution of the Yb $^{3+}$ and Yb^{2+} ions along the BaF$_2$:YbF$_3$ crystals.

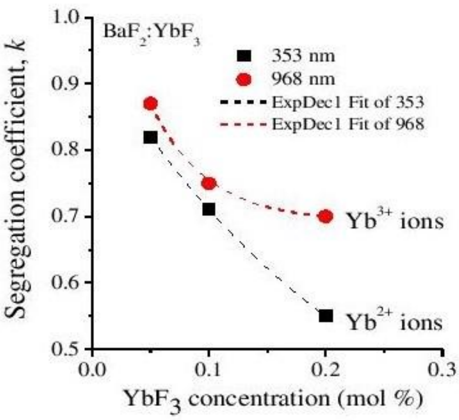

Figure 2. Influence of YbF$_3$ concentration on the segregation coefficient of BaF$_2$:YbF$_3$ crystals.

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Eu^{3+}, Dy^{3+} DOPPED WHITLOCKITE BASED PHOSPHATES FOR OPTICAL DEVICES

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Light-emitting diodes (LEDs), having received a lot of attention as promising solid-state light sources because of the efficient and direct conversion of electricity into light, are actively used in different applications, for instance, the production of plants [1]. The whitlockite-type structure is a universal matrix for the implementation of the lanthanide luminescent properties due to termal, chemical stability [2].

The whitlockite-type structure phosphates with REE $Ca_{9-x}Mg_xRE(PO_4)_7$, ($0 < x < 1$) were synthesized by standart solid-state reaction from stoichiometric amounts of $CaCO_3$, $CaHPO_4 \cdot 2H_2O$, $MgCO_3$, RE_2O_3 (RE= Dy^{3+}, Eu^{3+}). Synthesis was carried out in the air for 120 hours with an intermediate mixing.

As shown on PL spectra of $Ca_{9-x}Mg_xDy(PO_4)_7$ the most intensive transitions of Dy^{3+} are observed at blue (470 nm) and yellow (575 nm) region of visible spectrum which correspond to transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$, respectively (fig. 1a). The transitions $^5D_0 \rightarrow {}^7F_J$ ($J = 0 – 4$) of Eu^{3+} are present on PL spectra, which were registered at excitation wavelength 395 nm (fig. 1b). The most intensive line on the spectra corresponds to the transition $^5D_0 \rightarrow {}^7F_2$ (615 nm). In the both systems non-linear dependence of an integral intensity on concentration of Mg^{2+} is observed. The higher value of the integral intensity for Eu^{3+} dopped system is observed in value of magnum $x = 0.5$. System with Dy^{3+} shows the maximum of integral intensity in $x = 1$. Such behavior can be explained by the different site occupancy of cations in lattice cell of whitlockite matrix and concentration quenching processes.

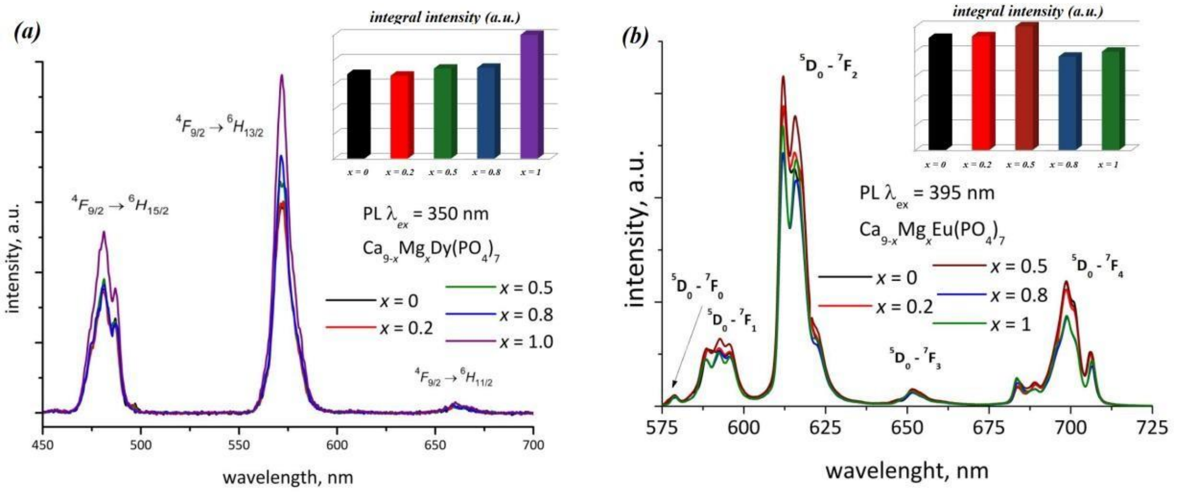

Figure. 1. PL spectra and integral intensity for $Ca_{9-x}Mg_xRE(PO_4)_7$

This work was supported by the Russian Science Foundation (16-13-10340), Foundation of the President of the Russian Federation (MK-3502.2018.5).

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COOPERATIVE ENERGY UPCONVERSION ENHANCEMENT IN β-NaYF$_4$ Tb^{3+}/Yb^{3+} NANOCRYSTALS THROUGH Mn^{2+} CODOPING

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The Tb^{3+} up-conversion phosphors are promising for biological applications due to their long luminescence lifetime and their spectral fingerprint being different from commonly known materials co-doped with Yb^{3+}/Er^{3+} and Yb^{3+}/Tm^{3+}.

Due to the absence of intermediary energy level and large energy mismatch between Yb^{3+} and Tb^{3+}, it is very difficult to achieve efficient UC emission of terbium ions doped nanocrystals under NIR photoexcitation. The UC emission of Tb^{3+} can be only obtained by relatively in-efficient cooperative energy transfer (CET) from a pair of excited Yb^{3+} ions [1]. Recently, new approach to the energy transfer between lanthanide ions and metal transition ions has been investigated [2]. One of the most promising composition exploits Mn^{2+} ions, which are suitable to form Mn^{2+}-Yb^{3+} dimers, efficiently harvest NIR photoexcitation and transfer the energy to the $^5D_4$ energy level of Tb^{3+} ions, ultimately leading to generation of relatively intense Tb^{3+} UC emission under 975 nm excitation.

In the present work we have investigated the impact of Mn^{2+} ions on the enhancement of UC intensity and energy transfer process in β-NaYF$_4$: Tb^{3+}, Yb^{3+}, Mn^{2+} colloidal nanocrystals (Figure 1a). The upconversion emission intensity obtained from the nanoparticles doped with 10% Mn^{2+} ions increased up to 30-fold in comparison to corresponding nanoparticles without Mn^{2+} ions. Additionally, as a proof of the concept, the surface of nanoparticles was coated with proteins and conjugated with folic acid, and such biofunctionalized nanoparticles were subsequently used for bioimaging of HeLa cells (Figure 1b).

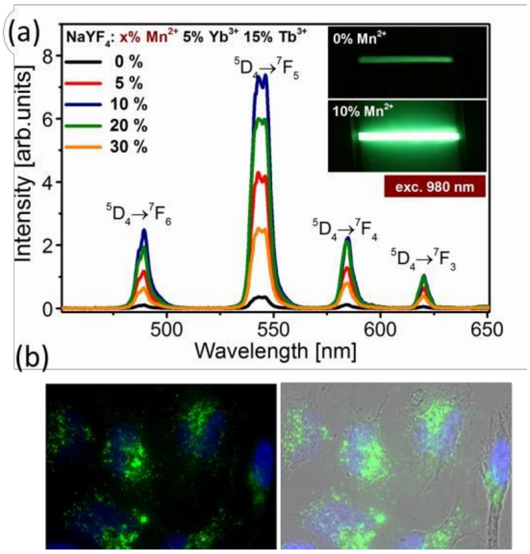

Figure 1. (a) Upconversion spectra of colloidal β-NaYF$_4$: 5% Yb^{3+}, 15%Tb^{3+} nanoparticles doped with different amount of Mn^{2+} ions under 975 nm excitation. (b) The microscope images of HeLa cells after incubation with folic acid-conjugated NaYF$_4$:Yb^{3+}, Tb^{3+}, Mn^{2+} nanocrystals (40x magnification). Green color represents upconversion fluorescence, blue color – fluorescence from nucleic acid stained with DAPI.

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ENERGY TRANSFER PROCESSES BETWEEN RARE EARTH IONS IN SILICA MATERIALS OBTAINED BY SOL-GEL METHOD

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Among rare earth ions, trivalent Tb^{3+} and Eu^{3+} are of great practical importance and their luminescence is frequently using as green and red components in photonic applications [1]. Owing to quite well overlapping of emission band of donor (Tb^{3+}) and absorption band of acceptor (Eu^{3+}), the efficient $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer process is also possible [2]. Thus the tunable multicolor luminescence could be obtained from Tb^{3+}/Eu^{3+} co-doped phosphors, which are considered as promising sources for visible light generation in photonic devices.

The aim of this work was to study the luminescence properties of silica sol-gel materials singly and doubly doped with Tb^{3+} and Eu^{3+} ions. The luminescence behavior of synthesized sol-gel materials was characterized based on emission spectra and their decays. The obtained sol-gel materials exhibit bright multicolor emission from the 4f levels of Tb^{3+} and Eu^{3+} ions. Furthermore, the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer process with its efficiency equal to about 19% is observed. Also, co-doping with Tb^{3+} led to prolongation of luminescence lifetime of Eu^{3+} up to ~24%. Based on the experimental results we suggest that the Tb^{3+}/Eu^{3+} co-doped sol-gel materials could be considered as good candidates for potential photonic applications.

Acknowledgment: The National Science Centre (Poland) supported this work under research project 2016/23/B/ST8/01965.

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X-RAY AND NEAR-INFRARED EXCITED UP-CONVERSION EMISSION PROPERTIES OF Er DOPED SESQUIOXIDES NANOPARTICLES

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Recently, up-conversion of Er doped nanoparticles have become more attractive due to their potential for applications in bioimaging, therapy and photovoltaics [1, 2]. Compared to up-conversion emission excited in the near-infrared (NIR) at 980 nm, the UPC emission excited at 1500 nm and measured in the near-infrared range extended up to 1100 nm is only scarcely reported in literature [2]. Herein, we present NIR to NIR up-conversion and X-ray excited luminescence of Er doped sesquioxides (Y_2O_3 and Lu_2O_3) nanoparticles. The emission properties of the doped nanoparticles were optimized by varying Er concentration and co-doping with Li ions.

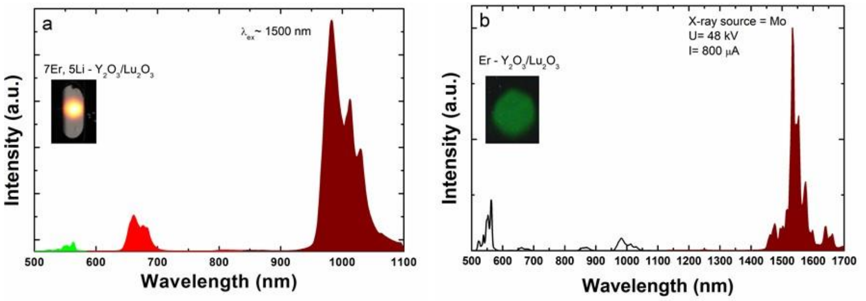

Figure 1. (a) Up-conversion emission spectra of Er – Y_2O_3/Lu_2O_3 under 1500 nm excitation and (b) X ray induced emission spectra of Er – Y_2O_3/Lu_2O_3 (Mo source with maximum debit dose of 2 Gy/s). Digital photos of the emitted light both under 1500 nm and X-ray excitations are also included.

The up-conversion mechanisms were investigated in terms of: time-gated up- conversion emission and excitation spectra and up-conversion emission decay. The X-ray induced emission properties were measured in the 450 to 1700 nm range, under varying X-ray debit dose. Under UPC excitation at 1500 nm, the emission of Er doped Y_2O_3 and Lu_2O_3 display a relative intense emission at 980 nm accounting for up to ~99% of the total emission (for 1% Er doping concentration). Moreover, under X-ray excitation of Er- Y_2O_3 and Lu_2O_3, the emission is dominated up to 80% by the near-infrared emission of Er at 1500 nm [3]. Preliminary results on NIR luminescence thermometry under NIR pulsed excitation are also presented.

In all, our investigations reveal interesting near-infrared emission properties of Er - Y_2O_3 and Lu_2O_3 nanoparticles under both optical and X-ray excitation that render them attractive for bio-imaging in the second/third biological windows as well as photovoltaics and dosimetry applications.

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PHASE TUNING OF Er DOPED ZrO_2 AND CORELATION WITH UP-CONVERSION EMISSION PROPERTIES

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Recently, Er single doped nanoparticles have gain more interest due to their potential for applications in bioimaging, therapy and photovoltaics [1, 2]. ZrO_2 is acknowledged as an excellent host for lanthanide dopants due to its low phonon energy, high chemical and thermal stability, transparency in the visible region, high value of refractive index and ease of doping with trivalent Ln ions [3, 4].

Herein, we present our recent investigations regarding the correlation of the structural phase, dopant distribution and up-conversion emission properties in Er, Li-ZrO_2 nanoparticles. Monovalent Li was chosen as an optical inert and phase tuning dopant, whilst Er was selected as an up-conversion activator and phase stabilizer.

The X-ray diffraction, Raman and High-Resolution Transmission Electron Microscopy measurements were performed to analyse the structural and morphological properties of the nanoparticles. The up-conversion mechanisms were investigated in terms of the up-conversion emission intensity dependence on the pump power, time-gated up-conversion emission and excitation spectra and down/up-conversion emission decays measured in the 450 to 1700 nm spectral range.

Our findings show that, by tuning the phase of zirconia host and Er concentration, the up-conversion emission shape (colour) and intensity of Er, Li-ZrO_2 nanoparticles display attractive properties for photovoltaics and bio-imaging applications.

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LUMINESCENCE PROPERTIES INVESTIGATION OF $MgTiO_3$:Mn^{4+} FOR NANOTHERMOMETRY

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Luminescence properties of $MgTiO_3$:Mn^{4+} nanoparticles (NPs), synthesized by sol gel assisted molten salt synthesis, have been investigated [1]. The deep red luminescence of tetravalent manganese ion in octahedral environment within the perovskite host presents drastic variations with temperature [2]. Thus these 63.1 ± 9.8 nm in diameter particules are potential candidates for local temperature measurements. Both emission spectra and decay profiles are studied, showing that $MgTiO_3$:Mn^{4+} nanomaterials are multi-reading temperature nanoprobes. Specifically, the monitoring of R-lines variation allows the temperature determination between -250 °C and -90 °C with a maximal sensitivity of 0.9 $\%°C^{-1}$, while the study of the intensity ratio between the $^2E \rightarrow {}^4A_2$ (R-line) and the $^4T_2 \rightarrow {}^4A_2$ transitions permits to investigate a larger temperature range (-200 °C to 50 °C) with a sensitivity between 0.6 $\%°C^{-1}$ and 1.2 $\%°C^{-1}$ over this range. Finally, the lifetime value, corresponding to a combination of transitions from two excited energy levels (^2E and $^4T_2$) in thermal equilibrium toward the fundamental $^4A_2$ state, drastically decreases with an increase of temperature. The associated sensitivity reaches an impressive high value of 4.1 $\%°C^{-1}$ at 4 °C. Therefore, according to their optical features, luminescent $MgTiO_3$:Mn^{4+} nanoparticles are suitable candidates for the temperature determination at the nanoscale over several temperature ranges.

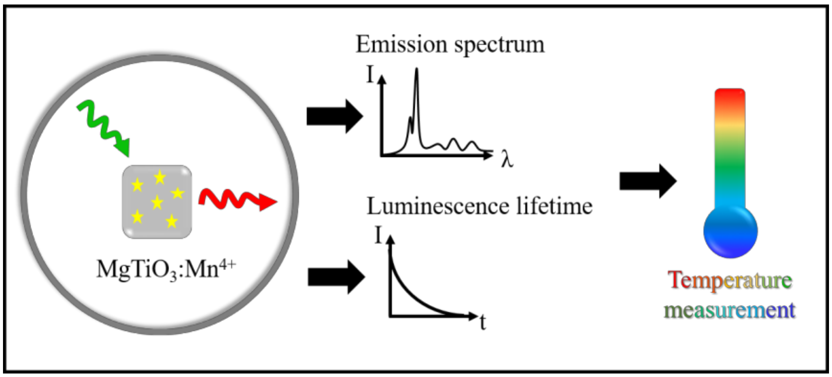

Figure 1. Schematic representation of temperature determination using MgTiO3:Mn^{4+} nanoparticles

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GRAPHENE NANOPARTICLES IN POLIMER DISPERSED LIQUID CRYSTALS

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Polymer-dispersed liquid crystals (PDLCs) are composite materials that consist of submicron-size droplets of liquid crystal (LC) randomly dispersed in a polymer matrix. Recently they found applications in switchable and energy saving windows (smart glasses), light shutters and projection displays. In contrast to the liquid crystal displays, PDLCs show unique advantages such as easy fabrication, polarization independence and rapid response time. Nevertheless, high driving voltage due to the strong surface anchoring effects of the polymer matrix wall is among the shortages. Therefore enormous efforts have been made for lowering the driving voltage.

One of the most efficient ways to expand the applicability of PDLC is by doping with nanoparticles (NPs). Recently graphene attract great attention due to the exceptional properties as excellent electrical, optical, chemical and mechanical behavior. For example, the two-dimensional honeycomb structure of graphene shows remarkable interactions with the LC molecules. A small quantity of graphene in a nematic LC makes the electro-optic switching faster because the graphene can improve the electro-optic response of the nematic LC phase. Moreover, the rod shapes of LC molecules tend to align along to the graphene hexagons.

Here we study the effect of graphene, graphene oxide (GrO) and reduced Graphene Oxide (r-GrO) on the morphology and switching voltage of PDLC films. The existence of graphene nanoparticles (in relatively small concentration) in PDLC structure has been confirmed by Raman spectroscopy analysis. Doping with GrO and r-GrO increases the sizes of LC droplets and leads to a decrease of the driving voltage (Fig.1).

The results open great potential applications in nanoelectronic devices, sensors, and electrochemical energy storage systems.

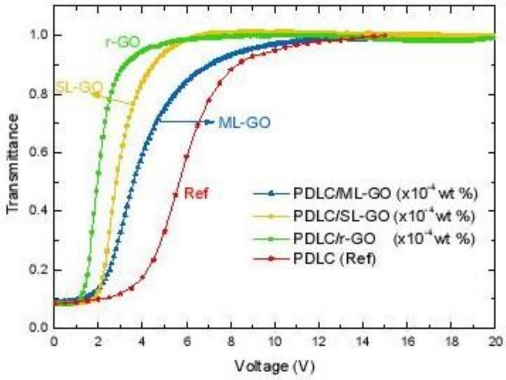

Figure 1. Voltage -transmittance modulation characteristics of GO and r-GO doped PDLC films.

Acknowledgement

Financial support by the Bulgarian National Scientific Fund under Project DH 08/15 2016 and DCOST 01/15 are gratefully acknowledged.

OPTICAL SPECTROSCOPY OF MID-INFRARED GaSb-BASED RESONANT TUNNELING STRUCTURES WITH GaInAsSb ABSORPTION LAYER FOR APPLICATION IN GAS SENSING

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Resonant tunneling structures (RTS) play an important role in a large variety of nowadays electronic and optoelectronic semiconductor devices. Besides being applied in high-speed electronic circuits and even as THz emitters, resonant tunneling is the basic underlying physical principle used in various optoelectronic devices, such as quantum cascade lasers (QCL), interband cascade lasers (ICL) and interband cascade detectors (ICD). Compared with conventional RTSs based on the GaAs or InP material system as mostly employed in QCLs, the InAs-GaSb-AlSb material system offers a broad spectrum of bandgap energies and band alignments from staggered (type-I) to broken (type-II) [1] which e.g. enables their exploitation in light emitting and detecting optoelectronic devices covering the mid-infrared spectral range [2,3]. Substantial flexibility for band gap engineering offers the ability to design and study RTSs with various band alignments, i.e. AlSb/GaSb/AlSb, AlSb/InAs/AlSb.

In this work, we present a comprehensive investigation of the band structure of such a complex layered system. Methods of Fourier-transform spectroscopy were employed to investigate structures based on two asymmetric hybrid AlSb/InAs type-II barriers within a GaSb matrix. In this quantum system, the AlSb layer function as common type-I barrier for electrons and holes, whereas the InAs part functions a trap for electron confinement, while enhancing the hole barrier within the valence band. We find light emission in the mid-infrared spectral range between 3 and 8 μm. Formation of quasi-bound states in the region between the InAs/GaSb interface and the AlSb barriers was confirmed, allowing for resonant tunneling of carriers across the structure [4]. Since the structure under investigation contains two asymmetric type II quantum wells, two quasi-bound states were found.

The exact energy structure of such complex systems is often not well known, due to for example interface layer formations.

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OPTICALLY TRANSPARENT THIN FILMS BASED ON SEMICONDUCTOR SINGLE-WALLED CARBON NANOTUBES: THERMOELECTRIC PROPERTIES

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Currently, new flexible thermoelectric converters are created and explored. Great prospect is semiconducting single-walled carbon nanotubes (SWCNTs) to use them in the flexible thermoelectric converters. Transparent conducting electrodes based on SWCNTs are one of the main candidates able to replace transparent conductive oxides in optoelectronics. Thus, it is possible to realize several functional properties such as electrical conductivity, high optical transparency and thermoelectric properties within a single material. Thin films of SWCNTs can be used for transparent flexible electronics as power supplies positioned on transparent substrates.

The method of separation of single-walled carbon nanotubes (Tuball) based on aqueous two-phase extraction (ATPE) was used. ATPE made it possible to obtain semiconductor SWCNTs with a purity of more than 98 %. Thin films based on semiconductor SWCNTs (Fig. 1a) were obtained by vacuum filtration.

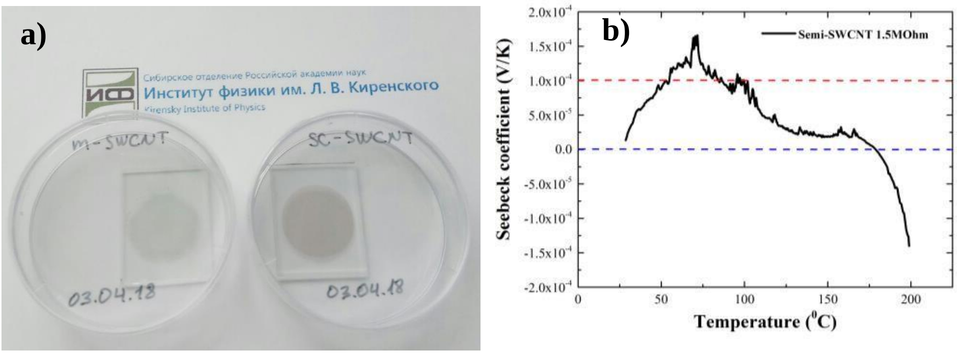

Figure 1. Image of the m- and s-SWNT films (a) and temperature dependence of the Seebeck coefficient for thin film based on semiconductor SWCNT (b).

For the first time, studies of the thermoelectric properties of thin films based on semiconductor nanotubes obtained from SWCNT (Tuball) have been carried out. Studies have shown that the Seebeck coefficient was greater than 100 μV/K in the temperature range from 50 to ~ 100 °C (Fig. 1b). It was found that at temperatures of ~ 150-180 °C the sign of the Seebeck coefficient changed. The surface resistance of thin films based on semiconductor SWCNTs was ~ 1.5 - 2.5 MΩ.

The study was carried out at the expense of a grant from the Russian Science Foundation (project No. 17-72-10079).

THEORETICAL ANALYSIS ELECTRONIC STRUCTURE AND NON-LINEAR OPTICAL PROPERTIES OF p-SUBSTITUTED o-AMINOMETHYLPHENOLS

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The structure–property relationships are investigated in a series p-substituted o-(N-dialkyl) aminomethylphenols, $XC_6 H_5CH\ _2Y$ (X=p-OCH_3, CH_3, H, F, Cl, Br, $COCH_3$, $COOCH_3$, and NO_2, Y=o-N $(C_2 H_5)_2$ and –$N(CH_3)_2$.
An ab initio HF and DFT methods were used to calculate HOMO-LUMO levels, HOMO/LUMO energy gaps, and electric properties, dipole moment(μ), polarizability(α) and first hyperpolarizability(β).
The studied properties of the titled compounds very sensitive to the choice of the basis set and theoretical level of investigation.The calculated dipole moments of o-aminomethylphenols at the B3LYP/6-311+G(d,p) level theory closely related to the known experimental values. The HOMO-LUMO analysis explains the charge transfer taking place within the molecules. A linear relationship has been revealed between HOMO-LUMO gap and intramolecular hydrogen bond energy the obtained from the quantum theory of atoms in molecules (QTAIM).
The β value depends on the nature of para-substituents and charge distribution in the o-aminomethylphenols. For o-(N-diethyl) aminomethylphenols, o-DEAMPH were obtained a linear correlations between β values as well as the Hammett substituent constants, σ_p^- (R^2 =0.9898) and dipole moments, μ (R^2 = 0.9888). A considerable deviation from linearity was observed for X= F, Cl and Br. This trend is also preserved for relationships β values with geometrical parameters. The β value of halogenaminomethylphenols depending on the method of calculation and decreases in the following order: Br>Cl≥F. The influence of the halogen substituents on the β value of the o-DEAMPH is analyzed. The linear correlation also revealed between the β value and total energy density at the bond critical point of the H-N distance of the o-DEAMPH (based QTAIM): $\beta= -39.3755 +10.6805\ \rho^{cp}$ (R^2 =9819). It is found that the substituent volume in o-position of p-substituted o-(N-dialkyl) aminomethylphenols does not influence the β value. The β value is a lesser sensitivity to p-substituents effect at ab initio HF method calculation.
The relationships between nonlinear optical (NLO) properties and the electronic, geometric parameters of the o-DEAMPH are discussed. The predicted properties of the o-DEAMPH confirms that the investigated compounds are an attractive object for future studies of NLO properties.

ENHANCEMENT OF INFRARED PHOSPHORESCENCE PROPERTIES IN LITHIUM SPINEL MATERIALS WITH CHROMIUM DOPED

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In recent years, chromium doped spinel phosphors which are novel luminescent materials with advanced physical-chemical properties, have attracted significant attention owing to their promising near-infrared phosphorescence properties and potential applications in the field of in-vivo tissue imaging and night vision systems. Lithium gallate LiGa5O8 crystal has a stable inverse spinel structure and the emission of the Cr^{3+} doped gallate is in the NIR range (710- 740 nm). Extensively the optical performance of the Cr^{3+} doped spinal has been investigated, however, there is limited study on the co-doped spinals.

In this study, it is aimed to investigate the effect of rare earth and transition metal co-doping on phosphorescence properties of Cr^{3+} doped $LiGa_5O_8$. For this purpose, Cr^{3+} doped $LiGa_5O_8$ was synthesized by wet chemistry and conventional solid state methods. Rare earth elements of Nd, Pr, Eu, Gd, Dy, Ce, Yb and transition metal of Bi were used as co-dopants. Optical performance and structural properties of the co-doped samples were characterized by using Spectrophotometers and X-ray Diffraction techniques. It is observed that, the addition of Dy and Gd, decreases the emission intensity, while, Nd, Pr, Eu, Ce, Yb and Bi increases the intensity.

UNIFIED CONFIGURATION-ENTHALPY MODEL DESCRIBING OPTICAL RESPONSE ORIGINATED FROM PHYSICAL AGEING AND HIGH-ENERGY IRRADIATION IN CHALCOGENIDE GLASSES

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The unified configuration-enthalpy model based on conjugated configuration-coordinate and thermodynamic-enthalpy diagrams is developed to describe the phenomenology of optical response in structural metastability of chalcogenide glasses activated under combined effects of physical ageing and high-energy irradiation [1,2] (Fig. 1).

This model foresees the glass stabilization in the ground state and short-lived excited state, the former being presented by interconnected states (i.e. metastable rejuvenation-induced, metastable irradiation-induced and most stable physically-aged ones) linked by thermally-activated over-barrier and tunneling through-barrier transitions. Effect of irradiation is reflected by vertical transitions of atomic sites into excited state followed by spontaneous relaxation into irradiation-induced sub-state.

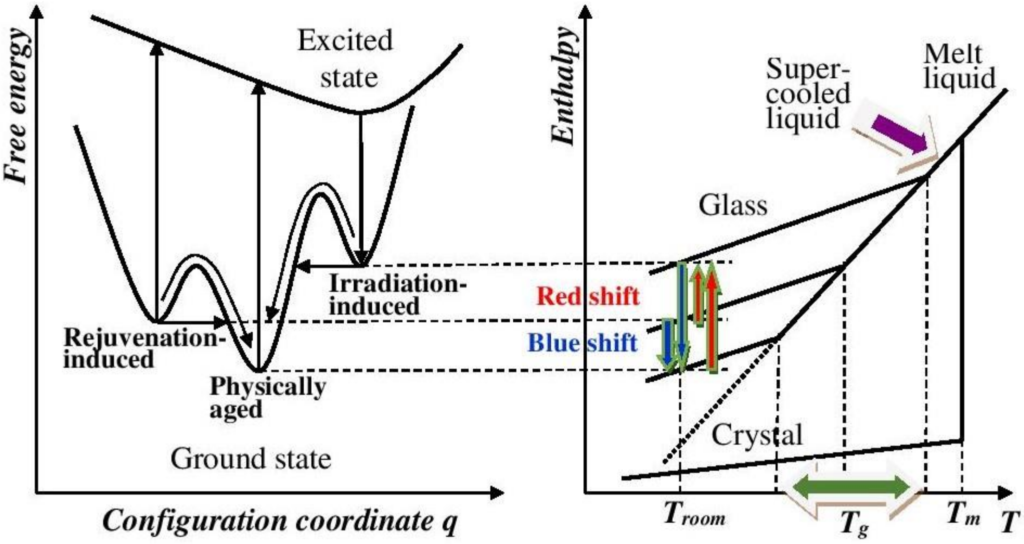

Figure 1. The conjugated configuration-coordinate and enthalpy diagrams describing structural metastability states in chalcogenide glassy semiconductors.

The thermodynamic-enthalpy diagram conjugated to this part (right-sided of Fig. 1) allows complete parameterization of corresponding optical responses related to these sub-states, which can be defined in blue or red shift in optical absorption edge of chalcogenide glasses.

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PLASMONIC METASURFACES MODELED FOR IMPROVED IR ABSORPTION

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Plasmonic metasurfaces are a novel concept in nanophotonics which have the role of tailoring the shape of the optical fields by nano-structuring the substrates [1]. This type of structures are a subclass of metamaterials and can be considered advanced effective materials in the sense that the sizes of the nano-antennas are much smaller than the wavelength of the field such that they can be considered homogeneous. Essentially, metasurfaces are nano-platforms consisting in periodic arrays of metallic nano-antennas, of various shapes and sizes sustaining plasmonic resonances [2], patterned on a substrate. These types of metamaterials have a large variety of application among witch are perfect absorber or reflector [3].

In this paper we present a plasmonic metasurfaces composed of nano-antennas with geometrical parameters bellow 300 nm, used for improved absorption in narrow wavelengths intervals of the IR domain. Our metamaterial is obtain by nano-patterning an array of gold pillars of 100 nm hight on a 200 nm thick silicon substrate deposed on a thin gold film (200 nm).

In fig. 1.a one can observe the diagram of the investigated structure, meanwhile fig. 1.b shows absorption spectrums for three different geometrical parameters (diameters of 100 nm, 200 nm and 300 nm). These results where obtain by performing 3D-FDTD numerical investigations.

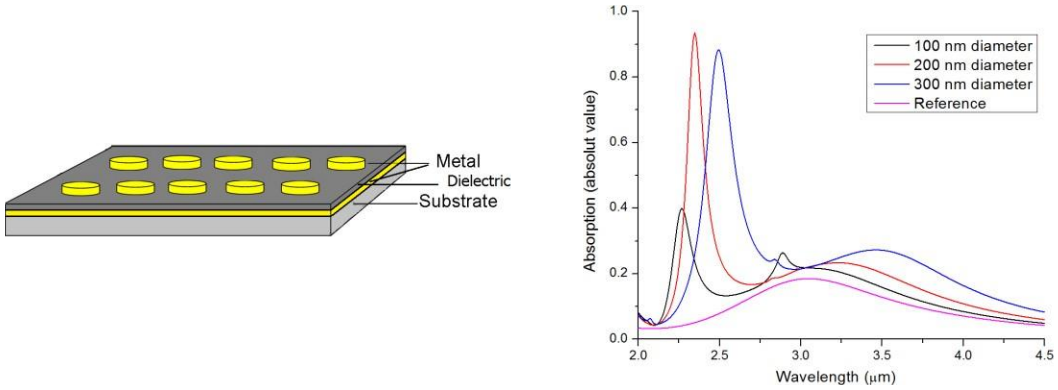

Figure. 1 Plasmonic metasurface a) Diagram of proposed structure; b) Absorption spectrum - incident wavelength centred at 3.15μm

From our results, we can conclude that the proposed plasmonic metasurface can improve the electromagnetic field absorption to almost unitary values for well-defined narrow wavelengths intervals.

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CARRIER CONCENTRATION VERIFICATION IN PLASMONIC WAVEGUIDE OF THE QUANTUM CASCADE LASERS BY USING FTIR SPECTROSCOPY

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One of the most important issues in the long process of the quantum cascade lasers (QCLs) growth is obtaining the proper concentration of electrons in different parts of the multilayer structure. It especially concerns the injector part, where electrons tunnel between the respective quantum wells but also the plasmonic waveguides responsible for proper light propagation along the whole structure. For doped plasmonic waveguides, one can use a direct correlation between the resonant plasmonic frequency and concentration of electrons in the given layer or material. Determining the latter, even post-growth, is crucial from several reasons. First, the carrier concentration has to be significantly high to get a good refractive index contrast between the resonator material and the waveguides. Second, depending on the emitted wavelength it has to fit to the proper plasmon frequency to allow efficient internal reflection for the given wavelengths. Finally, the concentration has to be high enough to satisfy the two mentioned points, but at the same time, the free carrier related losses should be minimized.

There exist several methods to determine the carrier concentration in semiconductors e.g. Hall and capacitance-voltage measurements. They are very useful from the point of view setup calibration, however require quite precise contacts preparation (which makes them destructive) and, or application of the external magnetic field.

In this communication, we present a different concept, namely fast differential reflectance technique (FDR)[1] based on Fourier transformed infrared (FTIR) spectroscopy, which is an non-destructive optical method, which allows to learn about the carriers' density, also in the buried waveguide layers of a QCL. Depending on the semiconductor, the effective mass of the electrons changes, and for high concentrations ($\sim 10^{18}$) allows to get significant electron - phonon interaction and further absorption minimum related to the plasmonic frequency, which can be observed in mid, and long wavelength infrared range [2]. The measurement sensitivity might be improved being realized in function of light polarization, which allows emphasizing such absorption in respect to polarization selection rules (Berreman effect). We present such measurements applied to differently doped semiconductors layers, e.g. InAs, InGaAs, InAlAs and InP, which can be considered for plasmonic waveguides of the quantum cascade lasers emitting in the mid and long wavelength infrared range.

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DETERMINATION OF NONLINEAR OPTICAL PROPERTIES OF ND-DOPED PHOSPHATE GLASS: A STUDY OF THE SATURATION INTENSITY ON THE DOPANT ION CONCENTRATION

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The effect of ion concentration on the saturation intensity, Is, was investigated and its effect on the evaluation of nonlinear optical properties was discussed. The calculation of the saturation intensity was done in two different ways: from the measurements of the lifetime at low concentration and low intensity regimes, $\tau_{0,0}$, and by adjusting the behavior of the inverse of the lifetime as a function of the incident intensity. Both approaches led to equivalent values of Is. This leads us to conclude that the saturation intensity should not be alculated directly from the experimental lifetime of the sample, as is usually done. But the correct approach is to use $\tau_{0,0}$. Here, the value of Is in the limit of low concentration and low incident intensity was obtained as (266□14) KW/cm^2 at 514nm.

The value of Is is important because it impacts the determination of several different optical parameters such as the formation and the contrast of population gratings in rare-earth doped fibers as well as the two-wave mixing in these systems [1–3]. In particular, in ion doped materials (Cr^{3+} and Nd^{3+} specially) it is well known that the nonlinear refractive index depends on a nonresonant contribution due to the polarizability difference, □□, between the excited and ground states and on the saturation intensity Is as $n'_2 \propto \Delta\alpha / I_s$ [4,5]. Through time resolved Z-scan the nonlinear refractive index, n_2, of Nd-doped phosphate glass could be evaluated for different Nd concentrations. Finally, using the values of n_2 as a function of the optical absorption coefficient, it was possible to demonstrate that $\Delta\alpha$ is independent of the concentration of dopant ions in the matrix. The n_2 and Is values were used to determine the polarizability difference between ground and excited states as □□ = (2.6 □ 0.2)x10^{-26} cm^3, for Nd^{3+} ions in this glass matrix.

We hope that these results contribute to a more precise determination of nonlinear optical parameters in active ion-doped materials, thus leading to a gain in their performance.

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GAMMA RADIATION EFFECTS ON LUMINESCENCE PROPERTIES OF DIFFERENT SIZE Eu- DOPED $(Y_{0.7}Gd_{0.3})_2O_3$ PARTICLES

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Eu^{3+} activated $(Y_{1-x}Ln_x)_2O_3$ (Ln=Y, Gd, Lu) phosphors are widely used as commercialized scintillators in medical and industrial scanning applications, with high performance and attractive properties. In this work, effects of high-energy radiation on luminescence properties of $(Y_{1-x}Gd_x)_2O_3:Eu^{3+}$ powders with different particle sizes in the nanometric range are analyzed. Powders were prepared by polymer complex solution route, followed by annealing. Particles were obtained with an average size between 20 and 120 nm according to annealing conditions (time and temperature). Samples were exposed to gamma-irradiation (doses up to 4 MGy) on a commercial gamma-irradiation plant. The effect of irradiation on different particle size is followed by XRD, TEM and monitoring their luminescence properties. No change was observed in structure, morphology and steady-state emission. On the opposite, after irradiation excited-state lifetimes and quantum efficiency values are particle size dependent.

PERSISTENT LUMINESCENCE WAVELENGTH SHIFT IN HEXAGONAL $Sr_{1-x/2}Al_{2-x}Si_xO_4$:$Eu^{2+}$, Dy^{3+} COMPOUNDS

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Rare earth doped aluminates, such as $SrAl_2O_4$:Eu^{2+},Dy^{3+} and $CaAl_2O_4$:Eu^{2+},Nd^{3+}, are among the best known materials for persistent luminescence or afterglow emission [1]. Numerous studies have been carried out on this strontium aluminate to find different elaboration ways and to elucidate its persistent luminescence mechanism (see for instance [2]). It recently appeared that its hexagonal phase polymorph could have promising properties. A recently efficient way to elaborate the hexagonal $Sr_{1-x/2}Al_{1-x}Si_xO_4$:Eu^{2+},Dy^{3+} phases has been developed by glass crystallization. We report here the optical features of Eu^{2+}, Dy^{3+} co-doped $Sr_{1-x/2}Al_{1-x}Si_xO_4$ ($0 \leq x \leq 0.6$) powders elaborated by this method. The experimental results show that the photoluminescence as well as the afterglow emissions shift from green to white/blue range as x increases (see Fig. 1-left). It seems that this color change toward the white color is due to two effects: the blue shift of Eu^{2+} broad emission and the appearance of Dy^{3+} emission. Advanced optical properties such as radiance decay, thermoluminescence and 2D afterglow excitation/emission (see Fig. 1-right) measurements have been performed in order to learn more about the influence of the Si content on the optical properties.

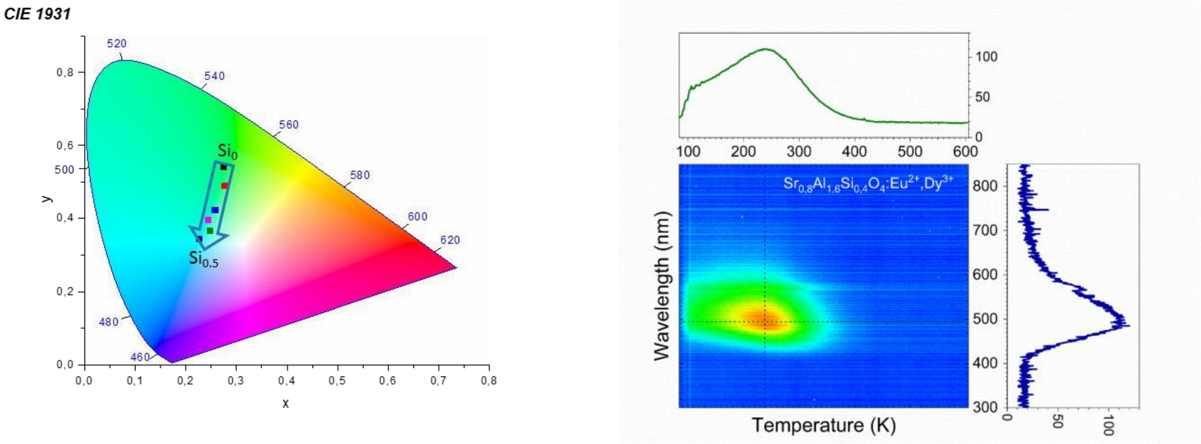

Figure 1. (left) CIE coordinates of SASO afterglow emissions. (right) 2D TL plot of SASO 0.5.

The authors acknowledge the ANR (PEPSI project) for funding and colleagues from Kyoto University, Kyoto, Japan.

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GREEN SYNTHESIZED SILVER NANOPARTICLES FOR OPTICAL CYSTEINE DETECTION

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A simple, fast and non-costly method for selective cysteine (Cys) detection, based on optical changes of silver colloids, is developed. For that purpose, stable colloids consisting of silver nanoparticles (Ag NPs) coated with polysaccharide dextran (Dex), isolated from bacterium species *Leuconostoc mesenteroides* T3, were prepared. The synthesized samples were thoroughly characterized including absorption and FTIR spectroscopy, as well as transmission electron microscopy and X-ray diffraction analysis. The silver colloids display high sensitivity and selectivity towards Cys detection in aqueous solutions. The Ag NPs coated with Dex provide possibility to detect Cys among a dozen amino acids and its detection limit was found to be 12 μM. The sensing mechanism – red shift of optical absorption – is discussed in terms of the agglomeration of Ag NPs due to formation of hydrogen bonds between Cys molecules attached to different Ag NPs.

OPTICAL AND THERMAL MODELING OF AN OPTRODE MICRODEVICE FOR INFRARED NEURAL STIMULATION

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Infrared neural stimulation (INS) is a promising medical technique using pulsed infrared light for generating temperature controlled firing of neurons. A combined optical and thermal model of a stimulating microtool – so called optrode – has been developed to investigate the amount, the spatial distribution and the temporal behavior of the thermal excitation [1]. A photo from the chip-scale silicon optrode is shown on Fig. 1. Infrared light is coupled into the device through an optical fiber placed to the tunnel denoted by c). Excitation is transmitted to the brain tissue through the shaft denoted by a). Temperature sensor can be found on the tip of the shaft.

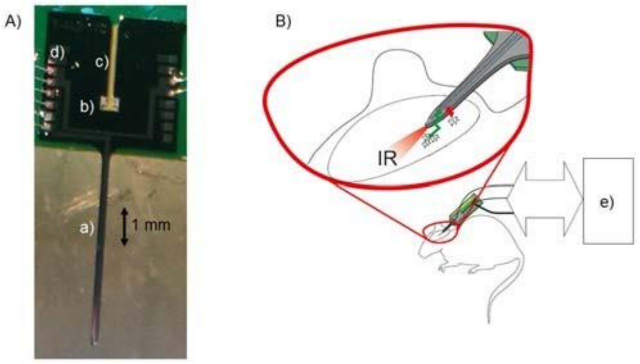

Figure 1. A) Photo of the chip-scale optrode a) shaft b) focusing lens c) place of the fiber d) printed circuit board B) A schematic figure of the application e) external optical/electrical interface

Ray tracing and Fourier optics were used to describe the propagation and scattering of light in the optrode, and finite element method (FEM) was applied to model heat transfer. The scattered intensity distribution profiles were calculated based on measured surface roughness of the surface of the device and were integrated into the ray optics model. As a validation of the optical model, the simulated and measured values of the light efficiency of the microoptical system have been compared, and showed a very good agreement. The temperature rise of the brain tissue during the infrared stimulation was estimated using the combined model. Using 30 mW total power and a single 100 ms pulse, the excitation resulted in a temperature rise of 3 °C of the brain tissue. The spatial and temporal distribution of the stimulation show characteristic patterns that are discussed in the presentation. The proposed combined model is an efficient tool for the investigation and the optimization of the stimulation process and for the further development of the optrode configuration.

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EFFICIENCY OF INTERFACIAL CHARGE TRANSFER COMPLEX BETWEEN TiO_2 NANOPARTICLES AND CAFFEIC ACID AGAINST DNA DAMAGE *IN VITRO*

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The genotoxic and antigenotoxic properties of surface-modified TiO_2 nanoparticles (NPs) with caffeic acid (CA) and their synergic effect were discussed in this study. TiO_2 colloid solution consisting of the anatase crystal structure was prepared by acidic hydrolysis of $TiCl_4$. The interfacial charge transfer (ICT) complex formation between surface Ti atoms and CA is indicated by immediate appearance of red color. Composition and stability constants of ICT complex were determined using Job’s method and Banesi-Hildebrand analysis, respectively. The experimental data were supported with quantum chemical calculations based on density functional theory (DFT). The genotoxic and antigenotoxic potential of ICT complex was evaluated in leukocytes of whole blood cells *in vitro* by comet assay method. Post-treatment of damage DNA by ICT complex formed between CA and TiO_2 consequently was shown antigenotoxic effect in lower concentration range. It seems that surface-modified TiO_2 NPs with CA and/or similar compounds can be used to maintain its beneficial activities.

THE ROLE OF Sb ON OPTICAL PROPERTIES OF Ga MODIFIED As–Se GLASSES

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The state of the art in the modern IR photonic devices permits to say that an applicatory field of chalcogenide glasses (ChG) produced by classic melt–quench procedure is authentically large-scale due to their exceptional properties in the IR region and relatively low manufacturing cost [1]. Recent progress in this branch of advanced IR optical materials is concentrated, among the others, on enhancement of solubility of rare earth (RE) ions in ChG matrices for the development of effective remote sources of light [2-3].

It was shown, that Ga constituent introduced into chalcogenide glass has positive impact on RE distribution [2-3]. In contrary to affirmative effects of Ga-doping, the eventual possibilities of minimization of negative outcome of Ga-addition (decrease in glass stability) has to be comprehensively studied.

In this work, effect of Sb addition on physical properties of Ga-doped As_2Se_3 alloys within $Ga_x(Sb_yAs_{0.4-y}Se_{0.6})_{100-x}$ system (x = 2, y = 0; x = 2, y = 0.12; x = 5, y = 0.12) is examined for further development of efficient matrix hosts for RE ions. The synthesized $Ga_x(Sb_{0.12}As_{0.28}Se_{0.6})_{100-x}$ alloys with 2 and 5 at.% of Ga showed good homogeneity and optical properties. No crystallization processes were observed in Sb-modified glass even in case of 5 at. % of Ga.

JS acknowledges financial support from "CampusFrance Pologne" via "Cotutelle Joint-PhD" scholarship programme.

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FLUORESCENCE NANOSCOPY OF SINGLE QUANTUM DOT PAIRS

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Semiconductor colloidal nanocrystals (quantum dots, QD) are artificial luminophores with size-dependent spectral properties. Quantum dots are promising objects for laser gain media, single photon sources, single fluorescent labels and for development of effective light emitting diodes, solar cells, QD-lasers, etc.

Optical properties of QDs have been investigated since early 1980-s. At single particle level the research has been carried since the pioneer work in 1996 [1]. Many intriguing effects have been discovered for single QDs. They include stochastical switching between emitting and dark states (fluorescence blinking or intermittency) and spectral diffusion (see review [2] and reference therein). The nature of blinking is still the matter of discussion [3].

Supper resolution fluorescence microscopy with single point-like emitters (fluorescence nanoscopy) is a set of techniques which provides the means to overcome diffraction limit associated with conventional optical far-field microscopy [4]. Localization accuracy for single emitters (coordinates determination accuracy) can be as small as several Angstroms and usually limited by a single emitter photostability, its quantum yield and by small dynamical range of highly sensitive 2-dimential detectors (EMCCD).

Implementation of fluorescence nanoscopy for single QDs and small QD clusters create a range of opportunity for investigation of underlying processes, which determine fluorescence and spectral properties of such artificial “atoms” and “molecules”. Reconstruction of emitters’ spatial coordinates with nanometer accuracy in such a cluster is an essential step in this type of experimental studies.

In the present work we consider the case when the cluster is represented by a two closely-spaced QD (inside a diffraction limited volume) with different fluorescent blinking behaviors. The distance between dots was varied in the range from 20 nm to 120 nm. The task was numerically simulated and errors were estimated in different blinking dynamics cases for developed processing algorithm based on statistical study of sub-diffraction coordinate distributions. The developed technique allows us to estimate distances between single emitters in pairs in real experiment with CdSe/ZnS colloidal QDs embedded inside a thin polymer film.

The study was supported by Russian Science Foundation (№ 17-72-20266).

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PHOTOLUMINESCENCE OF SILVER AND COPPER COMPLEXES IN ORGANIC SOLUTIONS

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In present paper we report the spectral properties of organic solutions activated with Ag^+ or Cu^+ ions.

The absorption, photoluminescence and photoluminescence excitation spectra of organic ($C_3H_8O_3$, C_2H_5OH, CH_3OH) aqueous solutions with impurity (10^{-5} – 10^{-1} mol/l) of Ag^+ or Cu^+ ions have been investigated in the temperature range of 77 – 290 K. The solutions involved do not luminesce at room temperature, but at 150 – 180 K they strongly emit under UV irradiation.

The organic solutions activated with Ag^+ or Cu^+ ions are characterized by groups of three bands in both the absorption (excitation) and emission spectra. The observed spectra are conditioned by electron transitions between the energy levels of Ag^+ or Cu^+ ion which are deformed due to the interaction with environment.

It is found that the temperature shifts of emission bands of solution with silver or copper complexes are closely bound with a quantum yield of emission.

A deforming effect of polar solvents on absorption spectra of involved systems with Ag^+ (or Cu^+) ions is studied.

Analyzing the spectral characteristics of Ag^+ and Cu^+ ions in the organic solutions confirms the validity of the ionic model of absorption (emission) centers in the systems presented.

LUMENESCENCE AND CHARACTERIZATION OF ZnO NANOSTRUCTURES CAPPED WITH SODIUM DODECYL BENZENE SULFONATE SYNTHESIZED BY CHEMICAL BATH DEPOSITION

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This investigation describes the effect of sodium dodecyl benzene sulfonate (SDS) on optical and luminescence properties of ZnO nanostructures. The X-ray diffraction (XRD) spectra of the un-capped and capped ZnO nanostructures correspond to the various planes of a single hexagonal ZnO phase [1]. The estimated crystalline grain size was calculated using the XRD spectra and was found to be in the order of 51± 1 nm and dependent on the SDS. It was also observed that the hexagonal ZnO structure transformed to $Zn(OH)_2$ at high mol% of SDS as shown in Fig. 1(a). The surface morphology study revealed the flower-like for un-capped ZnO. There was change in morphology with an increase in the amount of SDS. The UV analysis showed that there was blue shift at high mol% of SDS. The PL results showed that the luminescence intensity decreased with an increase in the amount of SDS in yellowish region but at high mol% of SDS luminescence band shift to lower wavelength as shown in Fig. 1(b).

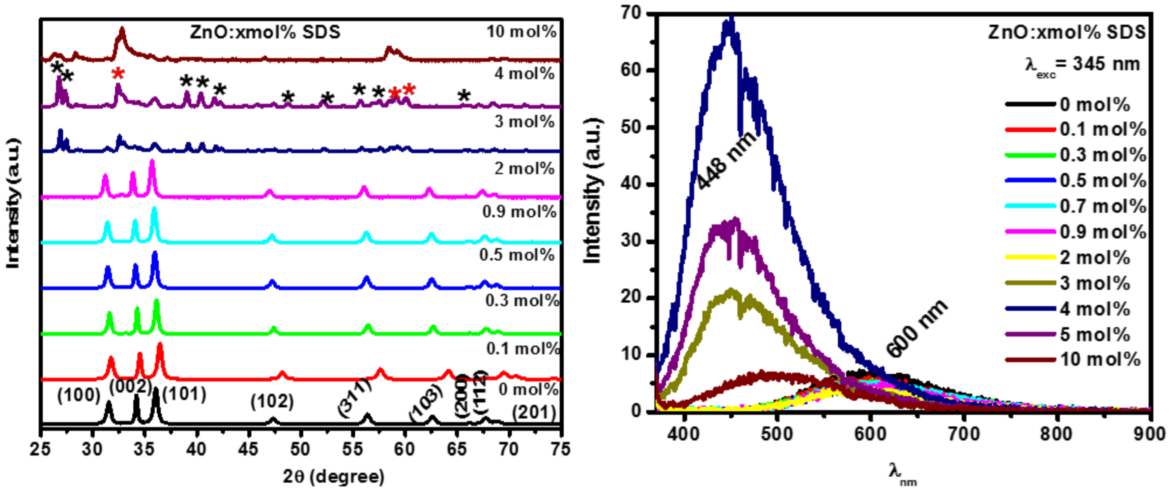

Figure 1. (a) XRD (b) PL spectra for un-capped and SDS-capped ZnO nanostructures with different amounts of SDS.

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DISSOLVED ORGANIC MATTER (DOM) IN DANUBE RIVER IDENTIFIED USING EEM FLUORESCENCE AND PARAFAC: BEFORE AND AFTER GAMMA IRRADIATION

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Dissolved organic matter (DOM) is present in all fresh waters and can originate from different sources such as surrounding landscapes, wastewaters, microbial activity in the water etc. Human activity is often a great source of DOM, e.g. direct discharges of waste into the water, and has a big influence on water ecosystem. For that reason it is crucial to monitor DOM in fresh waters and to understand it's influence on the carbon cycle. In recent years, fluorescence spectroscopy has been successfully used as a practical tool for characterization of organic materials in water. In our research, water samples were taken from February to October 2017 at 6 locations around Belgrade on Danube river (50 km of waterway in total). Fluorescence EEM and absorbance were measured using Horiba Jobin-Yvon Fluorolog-3 FL3-221 and Shimadzu UV-2600, respectively. Fluorescence measurements were carried out with 270-450 nm excitation and 300-500 nm emission range. Additionaly, water samples were irradiated with gamma irradiation at 5 kGy in order to compare DOM concentration before and after irradiation treatment. PARAFAC analysis was used to decompose EEM spectra and to identify fluorescent compounds present in water samples. After the modeling, three PARAFAC components were found. First component was identified as tryptophan-like substance, the second as terrestrial humic-like subsutance and the third corresponds to UVA humic-like component. The biggest difference between sampling locations could be seen in first component concentration where the concentration was significantly higher for locations near wastewater discharge. After gamma irradiation, the concentration of DOM in all samples decreased to almost zero (concentration range was between 0 and 1). This research investigates the DOM concentration in Danube river near Belgrade, the impact of wastewaster discharged into the Danube and the influence of gamma irradiation on the organic materials in water samples.

SYNTHESIS, STRUCTURAL AND OPTICAL PROPERTIES OF NANOPHOSPHORS $Y_{2-x}Eu_xSn_2O_7$ OBTAINED VIA CLEAN CO-PRECIPITATION METHOD

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The $Y_{2-x}EuxSn_2O_7$ nanophosphors were successfully synthesized via easy and green co-precipitation method, in wide doping concentration range ($0 \leq x \leq 0.6$) of Eu^{3+} ions. In dependence of group of symmetries (space group Fm-3m, 225 or space group Fd-3m, 227), the $Y_2Sn_2O_7$ could be crystalized in defect-fluorite or pyrochlore structure [1, 2, 3]. In order to solve dilemma of symmetry, XRD patterns of synthesized $Y_{2-x}Eu_xSn_2O_7$ ($0 \leq x \leq 0.6$) samples are compared with standard data of two different referent cards for pyrochlore or defect-fluorite structures. Crystal lattice parameters are calculated for all examined samples. TEM analysis for undoped $Y_2Sn_2O_7$ and for three doped samples are showed particles in average diameter 40-30 nm. Luminescence properties are also investigated. Excitation into $^5D_2$ level of Eu^{3+} led to formation of bands at 580 nm ($^5D_0 \rightarrow {}^7F_0$), 593 nm ($^5D_0 \rightarrow {}^7F_1$), 612 nm ($^5D_0 \rightarrow {}^7F_2$), 628 nm ($^5D_0 \rightarrow {}^7F_2$), 653 nm ($^5D_0 \rightarrow {}^7F_3$) and 709 nm ($^5D_0 \rightarrow {}^7F_4$). The most intensive band was at 612 nm. The CIE coordinates of $Y_{2-x}Eu_xSn_2O_7$ nanophosphors are closer to the standard red color coordinates (0.670, 0.330) [4].

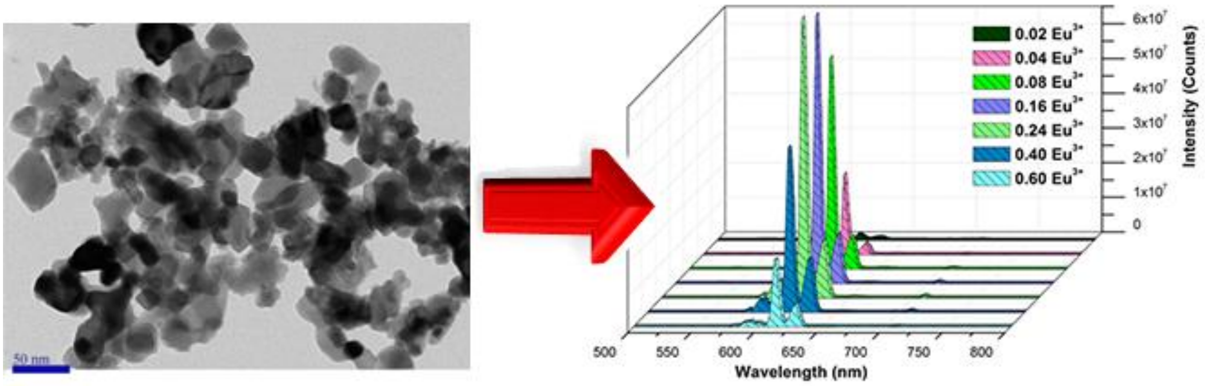

Figure 1. TEM nanoparticles vs emission spectra of $Y_{2-x}Eu_xSn_2O_7$

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LUMINESCENCE PROPERTIES OF Dy^{2+} and Ho^{2+}

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Work on the optical properties of divalent lanthanides focused mostly upon Eu^{2+}, Sm^{2+}, Yb^{2+}, occasionally Tm^{2+}. Only few publications exists which are treating the luminescence properties of Ho^{2+} and Dy^{2+} mostly in alkaline earth fluorides [1-5]

The luminescence properties of Ho^{2+} have been investigated for the first time by direct doping of H_5Cl_{11} into the host lattices SrCl and SrFCl. At around 5465 cm^{-1}, a sharp emission band was observed in both host lattices. This band corresponds to the parity forbidden f-f- transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$. In the lattice SrFCl, an additional sharp band at 8650 cm^{-1} was detected at room temperature as well as at 10 K and can be assigned to the transition $^4I_{11/2} \rightarrow {}^4I_{15/2}$. The low-energy band ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) is more dominant at room temperature, whereby the high-energy band ($^4I_{11/2} \rightarrow {}^4I_{15/2}$) is more intensive at low temperature (fig. 1). In addition, lifetime measurements were carried out. For the high-energy band, the lifetime was determined at room temperature with 4µs, which is unusual short for a parity forbidden transition.

The optical properties of MCl_2 (M = Ca, Sr, Ba) and MFCl (M = Ca, Sr, Ba) compounds doped with $DyCl_2$ have been studied at both room temperature and 10 K. For the room temperature measurements, a narrow emission at 7050 cm^{-1} (1420 nm) was detected in all compounds. However, for the low temperature measurements in the MFCl compounds an additional emission band at 9200 cm^{-1} (1090 nm) was observed. The emission bands at 7050 cm^{-1} and 9200 cm^{-1} both correspond to the parity-forbidden $^5I_6 \rightarrow {}^5I_8$ and $^5I_5 \rightarrow {}^5I_8$ transitions of Dy^{2+}. The lifetime of the $^5I_6$ level for MFCl:Dy^{2+} (M = Ca, Sr, Ba) was measured and a three exponential decay was observed. However, the determined lifetimes ranging from 8 µs to 323 µs are also very short for a parity-forbidden transition.

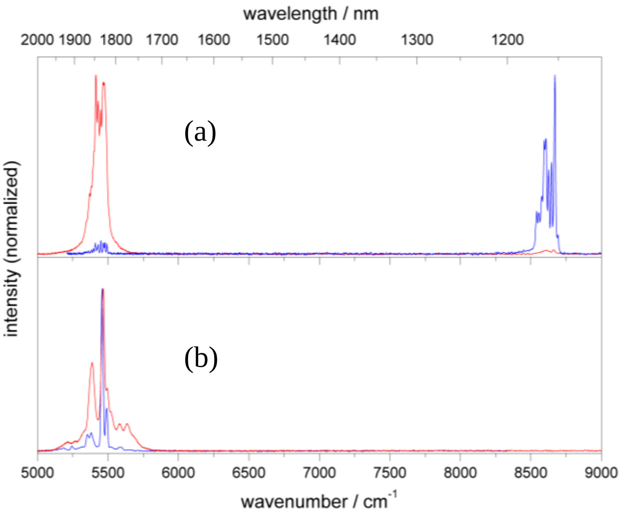

Figure 1. Emission spectra of Ho^{2+} doped in a) SrFCl and b) $SrCl_2$ at room temperature (red) and 10 K (blue)

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LESS MATERIAL-MORE ENERGY – NOVEL NANO PHOSPHORS

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Due to the continuous miniaturization of electronic and optical devices, the importance of functionalized nanoparticles (NPs) has drastically increased in the past few years. In contradiction to the analogous bulk samples, lanthanide doped luminescent NPs present several advantages as high packing density, low light scattering effects, energy saving synthesis (with shorter preparation time and lower sintering temperatures) and are easily suspendable in liquid media [1-3]. Due to the small size, nanophosphors are able to build thinner films simply by printing e.g. on the surface of light emitting diodes (LEDs) and are less subjected to concentration quenching effects, in comparison to doped micron-sized phosphors. Moreover, core-shell NPs can be functionalized on their surface and are therefore suitable as biological sensors or medical markers [3].

In this presentation, we present several different lanthanide doped NPs and their optical properties. Above all, Eu^{2+} containing NPs are very interesting in this context, which are most important for all respective applications [4]. However, the common preparation methods using water as solvent in general do not work due to the oxidation behavior of Eu^{2+} ions. Therefore, we developed novel synthesis methods, e.g. in ionic liquids as solvent. By the usage of fluoride containing ionic liquids it is also possible to prepare fluoridic NPs which are not available by common melting methods. In detail, we were successful preparing phase pure samples of several flouridic Eu^{2+} doped materials with small sizes and low size distributions (30-40 nm) with extremely high luminescence quantum yields for the first time. Finally, some applications in biological and medical fields (e.g. medical sensors, Fig 2) and also multifunctional magnetic, afterglow NPs (Fig. 1, right) are presented, showing their large benefits compared to common materials due to their higher stability at extremely low toxicity. Especially afterglow nanoparticles overcome the problem of absorption of visible radiation of biological tissue because it can be exited before injection.

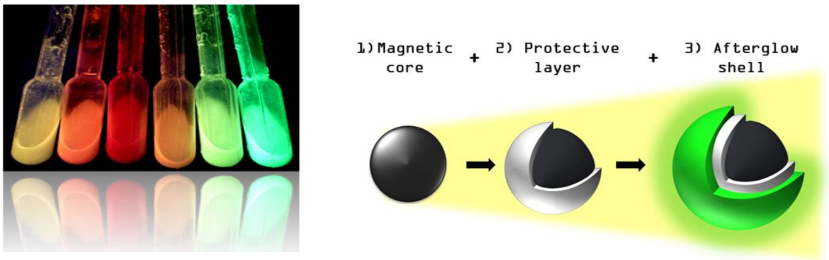
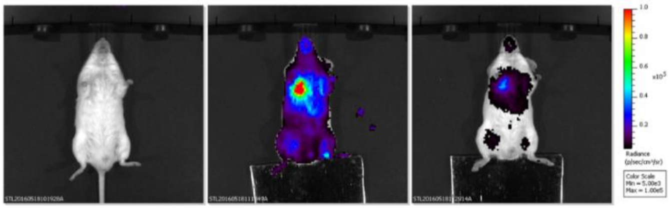


Figure 1. Left: emission of several Eu^{2+} containing nanoparticles suspended in water, right: sketch of magnetic, afterglow NPs.

Figure 2. Eu^{2+} containing afterglow nanoparticles injected in mice, with excitation of the



luminescence before emission.

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SOL–GEL SILICA GLASSES FOR RADIATION DOSIMETRY[*]

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In the field of new techniques for radiotherapy, also in harsh environment such as in nuclear facilities or in space industry, ionizing radiation dosimetry requires monitoring over long distances and/or with high space resolution of the measurement. For these applications, fibered solutions seem particularly adapted, but in this domain, new sensitive materials, able to be drawn into fibers, are needed. Indeed, scintillating fibers already exist, generally made of tissue-equivalent organic materials, which are particularly interesting to remotely measure real-time X-ray doses in radiotherapy applications. However, these plastic optical fibers exhibit rather poor guiding properties and could suffer from radiation in hostile environment. Thereby, increased attenuation losses and degradation of the scintillating dopant may occur in those devices when exposed to high dose rates, which is a problem in nuclear industry where radiation hardening of the safety or radioprotection devices is a crucial point. Inorganic radio-sensitive optical elements, like doped silicate glasses, can overcome these drawbacks. Moreover, compared to their crystalline counterpart, the glassy scintillators show higher mechanical and thermal stabilities, facilitating their shaping as optical fibers. Hence, this presentation will focus on the potentialities of doped sol-gel silica glasses for *in-vivo* / *in-situ* or high dose rate remote measurements.

This work deals with the spectroscopic and optical properties of a bulk cerium-doped sol–gel vitreous glass, obtained by densification either in air or in helium atmosphere. In comparison with the glass densified under air atmosphere, the one obtained after sintering the xerogel under helium gas presents improved optical properties, with an enhancement of the photoluminescence quantum yield up to 33 %, which is attributed to a higher Ce^{3+} ions concentration. The second kind of samples are sol-gel silica glasses activated with various concentrations of Cu^{+} ions. Here again, we show that the densification atmosphere has a decisive impact on the visible luminescence performance of the glass. The exposition of these Cu-doped samples to high doses of X-ray or γ-radiation induces point defects, a visible darkening and a strong reduction of their photoluminescence quantum yield. However, the materials remain optically active and can be used in a dosimetry setup.

Such glassy cylindrical samples have been drawn at high temperature into thin canes, pieces of which have been used as active materials in fibered remote X-ray radiation dosimeters. The samples exhibited a reversible linear radioluminescence intensity response versus the dose rate up to 50 Gy s^{-1}. The optically stimulated luminescence properties of these doped silica rods have also been investigated using the same fibered setup. These results confirm the potentialities of such materials for *in- vivo* / *in-situ* or high dose rate remote dosimetry measurements.

[*] Operation supported by Andra within the French government “Investissements d’Avenir” program: Surfin Project

STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF NEW CUBIC Nd^{3+} -DOPED Y_6MoO_{12} POLYCRYSTALLINE POWDERS FOR OPTICAL MATERIALS

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Tungstates and molybdates are excellent host lattices activated by rare earth (RE) ions. They found many applications in the optical field as laser materials, phosphors or scintillators. However, the knowledge about the structure and spectroscopic properties of these materials crystallizing in the cubic structure is very limited. So, there is therefore a great need to deepen and complete characterizations. Especially, there is also a huge challenge to fabricate new RE-doped transparent ceramics for application in optics.

We are first interested in the most known Nd^{3+} laser dopant. Our research is focused on synthesis, investigation of morphology and spectroscopic properties of Nd^{3+}-doped cubic Y_6MoO_{12} molybdate solid solutions with various concentration of Nd^{3+} optical activator (0.1–50 mol%) in the form of nanocrystalline powders. Nano-powders were obtained by the combustion method at 600°C/3h, which is a wet synthesis route leading to formation of grains of the order of few nanometers (5-10 nm). The nano-powders were additionally calcined at 800°C/5h (grain size 90 nm) and 1050°C/5h (grain size 120 nm). Obtained samples were compared with micro-powders synthesized by high-temperature solid state reaction at 1550ºC (grain size was up to 10 μm). The detailed analysis of phase transformation with the temperature have been performed. XRD analysis shows that nano-crystalline Nd^{3+}-doped Y_6MoO_{12} molybdate obtained by combustion method crystallize in a low temperature body centered cubic defect fluorite structure, space group $Fm\bar{3}m$ (no. 225). At temperature above 1100 °C, the metastable cubic phase transformed into the rhombohedral one crystallizing in the space group $R\bar{3}$. Subsequently, at 1500ºC the cubic phase is observed again, this time the high temperature face centered cubic bixbyite structure type, space group $Ia\bar{3}$ (no. 206).

In turn, when using high-temperature solid state reaction pure high temperature face centered cubic structure space group $Ia\bar{3}$ was obtained only at 1550ºC, without any presence of low temperature body centered cubic variety. SEM analysis confirmed the presence of only one phase both for nano and micro-crystalline powders. The powders are homogeneous, porous and if temperature increases, grains tend to agglomerate. Main spectroscopic results will be presented in relationship with the average size of grains and the multisite effect observed by site selective and time-resolved spectroscopies on Nd^{3+} ions.

Acknowledgements

We would like to thank the French Embassy in Warsaw for BGF Master 2 scholarships for Magdalena and Piotr Sobota, as well as the National Science Center of Poland for the grant HARMONIA 8 No UMO-2016/22/M/ST5/00546.

$ZnGa_2Se_4$: A CRYSTAL FOR NONLINEAR LASER APPLICATIONS WITH A WIDE MID INFRARED TRANSPARENCY AND A HIGH THERMOMECHANICAL RESISTANCE

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The need of high power laser sources in the mid infrared and especially covering the band III (8-12 micrometers) has been increasing for the last ten years and no industrial solution is proposed. Indeed, OPO systems requiring non-linear crystals are one of the best solutions. Nevertheless, the crystal which is the core of the system must have adequate optical and thermomechanical properties. Selenides are interesting compounds because they are almost the only ones transparent in the band III, compared to sulfides [1] and phosphides. However, their thermomechanical properties are not suitable for high power applications. Only $LiInSe_2$ or $LiGaSe_2$ have thermal conductivities higher than 2 $W.m^{-1}.K^{-1}$ [2] but their crystal growth present difficult problems and they have a medium transparency range. We proposed in this work an innovative compound never studied for non-linear optical applications, $ZnGa_2Se_4$ (ZGSe), cumulating a transparency from 0.55 µm (suitable for 1 or 2 µm pumps) up to 17 µm and a strong thermal shock resistance compared with other materials suitable for application in the band III of the mid infrared. At this time we can only present characterization of the polycrystals as the single crystals process is in progress.

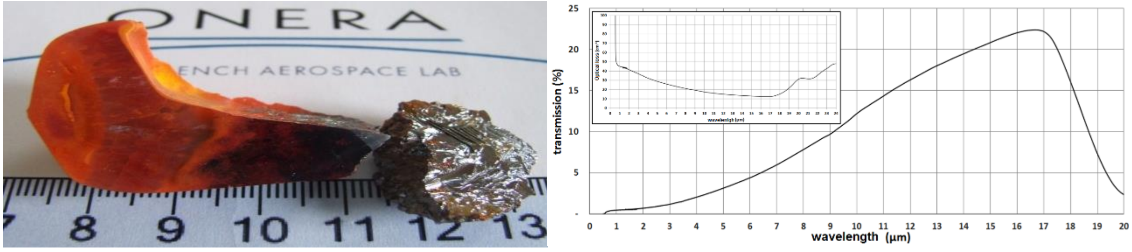

Figure 1. Left : Picture of polycrystalline ingot (50%mol of Ga_2Se_3) and right: transmission and optical absorption of ZGSe 2mm thick ingot

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LUMINESCENCE AND SCINTILLATION PROPERTIES OF Ce-DOPED $GdBO_3$ NANOPHOSPHOR SYNTHESIZED BY AQUEOUS SOL-GEL METHOD

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$GdBO_3:Ce^{3+}$ emitting phosphors as nanopowders were prepared using aqueous sol-gel method. The photoluminescence (PL) and scintillation properties were analyzed as function of the pH value of precursor suspension (pH=2, 5 and 8) and the nominal Ce^{3+} concentration at different annealing temperatures (600, 700, 800, 900, 1000, 1100 and 1200) °C. The crystal structures of the as-prepared materials were cheeked using several techniques such as: XRD, IR. All the samples of $GdBO_3:Ce^{3+}$ present pure phases which crystallize in the vaterite form. The highest PL intensity, corresponding to the 5d-4f transition of Ce^{3+}, as well as the scintillation light yield is obtained for the sample containing Ce^{3+} 0.5 mol.% prepared at pH=8 annealed at 800°C during 4 h. The scintillation yield has been deduced under X-ray excitation by comparison with the standard x-ray phosphor $Gd_2O_2S:Tb^{3+}$ or Eu^{3+} (Gadox). These results, including scintillation decays and afterglows were discussed as a function of the synthesis parameters.

Keywords: Ce^{3+}; $GdBO_3$; aqueous sol-gel, luminescence and scintillation

OPTICAL AND SCINTILLATION PROPERTIES OF Ce-DOPED BaBrI CRYSTALS

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BaBrI doped with Eu^{2+} ions was discovered as a prospective scintillator [1]. It exhibits high light yield and gamma-ray energy resolution. The vacuum refereed binding energy (VRBE) diagram of lanthanide ions doped BaBrI crystal was given in [2, 3]. In these articles a possibility of 5d-4f emission of Ce^{3+} ions was proposed. However, there has not yet been an spectroscopic study of Ce^{3+} ions in BaBrI crystals. Despite the fact that Ce-doped crystal has a number of indisputable advantages over the Eu-doped one due to faster decay time and temperature stability of light yield. Therefore, Ce-doped BaBrI crystals will be important high-performance scintillator with applications in homeland security, medicine, and well logging. In this paper we present the results of study Ce-doped BaBrI crystals.

The stable phase of BaBrI crystal at room temperature has the orthorhombic PbCl2 structure with space group D2h, Pnma [1, 2]. The elementary cell has a centre of inversion, the local symmetry of all cation and anion sites corresponds only to the point group CS with a single symmetry plane parallel to the *bc*-plane. Ce^{3+} ions substitute Ba^{2+} ions and can be O^{2-} compensated interstitial anions or oxygen ions. Photoluminescence measurements performed at 300 K in BaBrI:Ce^{3+} show a resolved luminescence doublet peaking at 363 and 391 nm, and a second band with an unresolved peak at 480 nm. These can be assigned to two Ce^{3+} luminescent sites. In excitation spectra several peaks in 230-340 nm region were found. The doublet photoluminescence peaked at 363 and 391 nm may be assigned to Ce^{3+} ions on the unperturbed Ba^{2+} sites. The unresolved peak at 480 nm could be attributed to Ce^{3+}-O^{2-} complexes. The decay time constant of Ce^{3+}-related emission was estimated at about 30 ns. Photostimulated and thermostimualted luminescence, and temperature dependence of photo- and x-ray excited luminescence measurements were performed.

In this paper we estimate U(6,A) parameter of VRBE model based on the experimental data and discuss possible nergy transfer mechanism to Ce^{3+}-realated centers. The scintillation properties of Ce-doped BaBrI crystals are also measured.

The research was supported by grant of Russian Science Foundation RSF 17-72-10084

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INVESTIGATION OF CRYSTAL STRUCTURE AND PHOTOLUMINESCENCE PROPERTIES OF NEW Tb (III) COMPOUND AS GREEN LIGHT EMITTING DIODE LAYER

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Over the last twenty years, materials produced with lanthanide-based compounds have taken up a number of technological areas such as OLED layer, gas storage/separation, bio-marking, luminescence probes, solid-state lasers, molecular magnetism and photoluminescence [1,2].
In this study, a new 2D TbIII coordination polymer, formulated as {[TbIII(2-stp)(H2O)3]. 2(4,4'-bipy).5(H2O)}, (**1**) (4,4'-bipy = 4,4'-bipyridine and 2-stp = 2-sulfoterephthalate) has been hydrothermally synthesized and characterized by FT-IR and UV-Vis spectroscopy, elemental analysis, single crystal and powder crystal X-ray diffractions and Field emission scanning electron microscopy. Solid State Photoluminescence properties were also studied.
The luminescent behavior indicates that complex **1** exhibit several characteristic emissions of the TbIII ion in the UV-Visible region and emits strong green light with CIE chromaticity coordinates (0.185, 0.632) which is attributed to the 5D4□7F5 electronic transition. Thus, complex **1** can be a candidate for the luminescent materials and green light emitting diodes (LEDs), owing to its strong luminescent emission.

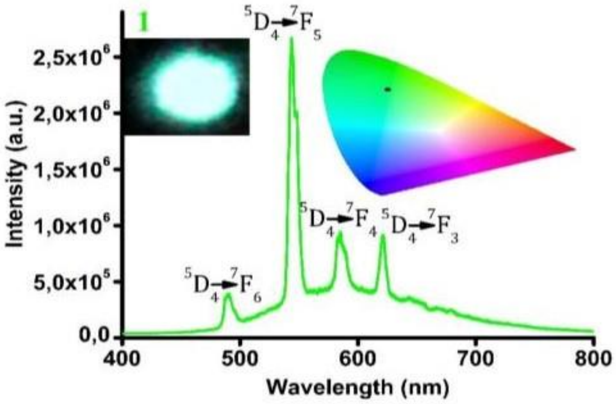

Figure 1. The solid-state luminescence spectrum of the 1. (Upper-left photo is a photoluminescent image and the right photo is CIE chromaticity diagram of **1**).

Acknowledgment: This work was supported by BAP 2018/006 (Research Funds of Muğla Sıtkı Koçman University).

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LOW-VALENT OXIDATION STATES OF URANIUM WITH OXOANIONIC SULFUR LIGANDS

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In contrast to the well characterised uranium compounds containing the uranyl cation, UO_2^{2+}, low valent uranium chemistry is less developed. Herein we present our previous and ongoing research towards low oxidation state uranium compounds with redox innocent ligands, focussing on the oxoanions of sulfur. Sulfate complexes of hexavalent uranium have been investigated both computationally[1] and spectroscopically in aqueous solution[2,3]. Their relative stability may be dependent on the water activity, and they may form different isomers with different coordination numbers. Here, we have reinvestigated sulfate complexes of uranium in non-aqueous, highly oxidizing media. Using concentrated H_2SO_4, oleum, SO_3 and CH_3SO_3H we have identified a range of new uranium complexes, and we will present the formation of low-valent uranium complexes from these solvents. In particular, we will present the synthesis and spectroscopic data of $U(SO_4)_2$,[4] two modifications of $U(CH_3SO_3)_4$ and the mixed-valent sulfonate $(UO_2)U(CH_3SO_3)_6{\cdot}CH_3SO_3H$ with special regard to its excitation and emission spectra. The spectra are strongly influenced by the presence of the UO_2^{2+} ion in the compound. Not only the electronic transitions are seen but also the vibronic structure of these transitions could be identified and show the presence of both uranium(IV) and uranyl(VI) within the compound.

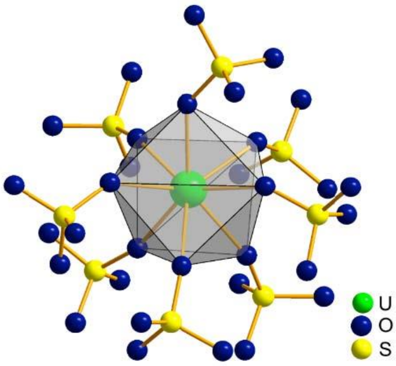

Figure 1. The U^{4+} cation in $U(SO_4)_2$ is coordinated by eight monodentate sulfate ligands forming a slightly distorted square antiprism. The distances U–O range between 231 and 240 pm for $U(SO_4)_2$.[4]

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COLLOIDAL EuVO$_4$ AND GdVO$_4$:Eu^{3+} NANOPARTICLES AS FLUORESCENT PROBES FOR PESTICIDE DETECTION

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Aim. In the past few decades, the use of pesticides has drastically increased; applied pesticides can be found in drinking water or food products. It is very important to study the harmful impact of pesticides on human health and the environment and there is a need for new, simple techniques to detect them. In this work, we report possible application of vanadate based colloidal nanoparticles (NPs) as fluorescent probes for pesticide detection using fluorescence techniques.

Synthesis. Synthesis of colloidal solutions of EuVO$_4$ and Eu^{3+}-doped GdVO$_4$ (the fraction of Eu^{3+} was 25 mol %) NPs was performed by precipitation of the Gd^{3+}(Eu^{3+})-citrate complex which was then converted to the respective vanadate by dialysis. TEM image and particle size distribution show that nanoparticles are about 2 nm in diameter which is in accordance with the crystallite size evaluated from the XRD measurements.

Photoluminescence (PL) measurements. Quenching effect of the widely used pesticides (2,4-D acid, MCPA and glyphosate) on the emission intensity of Eu^{3+} ions was studied using colloidal EuVO$_4$ and GdVO$_4$:25mol%Eu^{3+} NPs as fluorescent probes in TRIS buffer (50 mM, pH=7.4). Different concentrations (0-1.22 mM) of the pesticides solutions were added to the dispersion of NPs in TRIS. The emission spectra were obtained under 393 nm excitation wavelength. Figure 1 shows emission spectra of EuVO$_4$ colloidal NPs after the addition of different mM concentrations of the one of the studied quenchers-2,4-D pesticide. It can be observed that PL intensity of Eu^{3+} ions decreases with the increase of pesticide concentration in the measured solution. Stern-Volmer equation, $A_0/A = 1+K_{SV}[Q]$, was used to establish the nature of the PL quenching. There is no deviation from the linear fit of the curve which indicates only dynamic quenching is occurring.

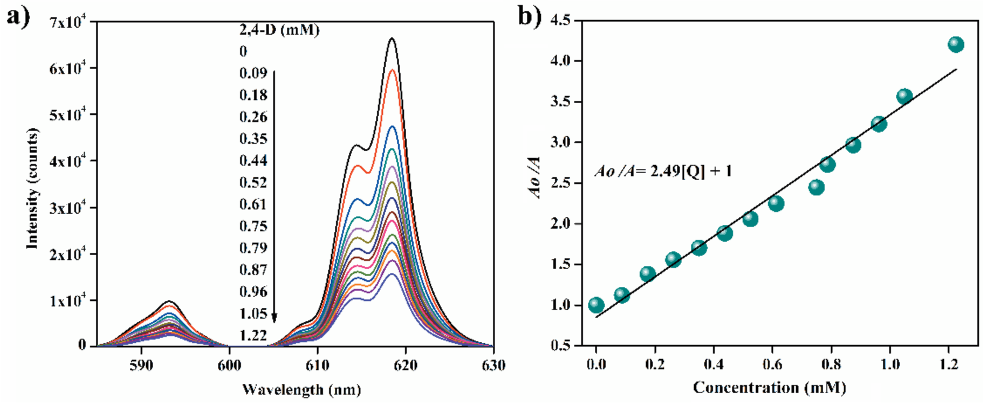

Figure 1. a) Quenching of emission of EuVO$_4$ NPS in the presence of 2,4-D pesticide and b) Stern-Volmer plot

Conclusion. We have used simple colloidal synthesis to obtain fluorescent probes based on the EuVO$_4$ and Eu^{3+}-doped GdVO$_4$ NPs for pesticide detection. These colloidal nanoparticles could potentially find application as sensing materials in environmental science.

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LUMINESCENT EUROPIUM(III) COMPLEXES IMMOBILIZED ON A GOLD NANOPARTICLE SURFACE

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Photofunctional nanohybrides are very promising materials for many different applications not only due to their unique surface properties. In contrast to other luminescent materials, lanthanide compounds show long lifetimes and narrow emission bands. Especially the optical properties of Eu^{3+} and Tb^{3+} have been intensively investigated because of their intense emission at visible wavelengths.[1] These unique properties can be tuned by forming nanohybrides containing gold nanoparticles (AuNP).

Here we present our ongoing research towards the linking of Eu^{3+} complex on a gold nanoparticle surface. Lanthanide complexes are well-suited for decorating the AuNP due to their low concentration quenching and the luminescence even in aqueous solution. The high coordination number of Eu^{3+} complexes allows a broad range of linker attachment. Therefore, donor atoms like oxygen or nitrogen are common.[2] Thus, we use carboxylates or bipyridine functionalities for bidentate coordination to the Eu^{3+} center by ligand exchange.

Forming a composite containing gold nanoparticles as the inorganic part and a Eu^{3+} complex with organic components an influence of the lifetime is expected due to interaction between the plasmonic resonance and the emitted light. This plasmonic resonance coupling is well known for a variety of luminescent materials including for Eu^{3+}. The distance between the gold core and the emitter is the key parameter determining whether the luminescence is enhaced or quenched.[3] It can be designed by the shell thickness of core shell nanoparticles or different chain length of the linker (see figure 1). Particles with different SiO2 shell thickness can be attached to a bifunctional linker containing a silane functionality. In another approach no SiO2 shell is formed and thiol linkers are directly attach to the gold surface. There are a lot of variation possibilities of the nanohybride systems to adjust their properties, for example changing the ligands, the nanoparticle size or the oxidation state of the europium complex.

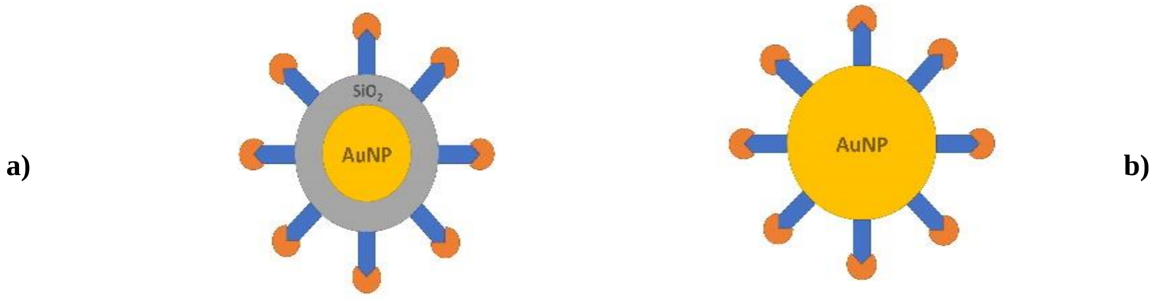

Figure 1. Gold nanoparticle (yellow), SiO_2 layer (grey), bifuctional linker (blue) and Eu^{3+} complex (red). Two diffenrent linking approches are presented a) SiO_2 core shell nanoparticle and b) thiol

OPTICAL AND THERMAL PROPERTIES OF ARYLAZO DYES BASED ON 6-HYDROXY-4-METHYL-2-OXO-1,2-DIHYDROPYRIDINE-3-CARBOXAMIDE

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Arylazo dyes represent a large class of compounds with wide industrial applications such as optical data storage, dye-sensitized solar cells, laser technology, non-linear optics and biological systems. New azo dyes based on 6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carboxamide were synthesized in order to examine their optical and thermal properties. All synthesized compounds were characterized by melting point, FTIR, ^{1}H and ^{13}C NMR spectroscopy, XRD analysis and UV/Vis spectroscopy. Optical properties have been analyzed on the basis of solid-state dyes reflection and excitation spectra. Also, absorption and fluorescence spectra of the studied dyes were recorded in different polarity solvents. The effects of electron-donor and electron-acceptor substituents on the absorption and fluorescence spectra have been assessed using Hammet equation. Thermal degradation processes of arylazo dyes were investigated with thermogravimetric analysis (TGA), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The kinetic experiments were performed at different heating rates (2.5, 5, 10 and 20 °C). Kinetic parameters, such as activation energy (E_a) and frequency factor (A), were estimated using Kissinger and Ozawa methods.

TEMPERATURE AND CONCENTRATION QUENCHING OF Mn^{4+} EMISSION IN Li_2TiO_3

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Red-emission phosphors have an important role in displays, fluorescence sensors, probes in the first biological window, and are more often used to achieve nature-like light in white light-emitting diodes (W-LEDs). Depending on the crystal field, Mn^{4+} can emit in 620–720 nm spectral range. [1] In oxide materials, octahedral coordination was found to be the most optimal for stabilizing manganese in 4+ ion state, with $3d^3$ electron configuration. Broad emission in the red region originates from spin forbidden $^2E \rightarrow {}^4A_2$ transition superimposed the spin allowed $^4T_2 \rightarrow {}^4A_2$ transition.

Using environmentally safe precursors, a low temperature solid-state reaction was optimized to synthesize $Li_2Ti_{1-x}Mn_xO_3$ phosphor powders. To obtain optimal concentration of the dopant, emission and lifetime of several manganese concentrations (x= 0.1–2.0) were investigated. It was observed that quenching of the Mn^{4+} ions occurs for the concentrations above x=0.5.

Temperature-dependent measurements for Li_2TiO_3:Mn^{4+} (in 10–350 K temperature range) of emission intensity and lifetime suggest that thermal quenching is caused by thermally activated crossover via the $Mn^{4+} \rightarrow {}^4T_2$ excited state. Temperature sensitivity was calculated using fitting methods. [2, 3]

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SYNTHESIS AND LUMINESCENCE PROPERTIES OF BARIUM ZIRCONATE DOPED WITH EUROPIUM PHOSPHOR POWDERS

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Zirconates with perovskite-type structure $AZrO_3$ (A = Ba, Ca, Sr) are prosperous phosphors for display and sensing applications [1]. Recently, research has been focused on the luminescent properties of rare earth ion-doped zirconates because they are very stable and can steadily work in various environments, which is a merit for the phosphors' application.

$BaZr_{1-x}Eu_xO_3$ phosphors with x = 0.01, 0.05, 0.01, 0.15, were synthesized by the solid-state reaction technique [2]. The powders crystalize in cubic Pm-3m (221) symmetry. Due to increased lattice defect and disorder formation induced by the doping, crystallite size decreases from 30 nm to 20 nm, and band gap shifts to lower values.

Photoluminescence properties were observed by emission, excitation and lifetime measurements in the temperature range 10K–300K. The highest intensity in the europium characteristic orange-red emission region from $^5D_0 \rightarrow {}^7F_2$ emission (around 612 nm) was found to be for the x = 0.05 sample. The sharpest spectral features were found to be for the x = 0.01 sample, and high-resolution spectra and lifetime kinetic were investigated for that sample in the low-temperature range.

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BRAGG REFLECTION IN A HETEROSTRUCTURE BASED ON MULTIPLE QUANTUM WELLS OF GaAs/AlGaAs UNDER THE EFFECT OF HYDROSTATIC PRESSURE

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In the present work, we studied the reflection in a heterostructure composed of N multiple quantum wells. The supercellular structure is formed of a GaAs-based quantum well (QW) sandwiched by relatively thin AlxGa1-xAs barriers with a raised content at x = 74% of Al. In our study, we evaluated the effect of quantum well number modification on reflection, and calculated the theoretical transition energies for different excitons in the sample. The multiple quantum well structure used in this work consists of 60 GaAs quantum wells separated by AlGaAs barriers. The bragg resonance has been granted and satisfied for a normal incidence of light, with a photon energy equal to the energy of the heavy-hole excitons at the second level of quantum confinement in the quantum wells.

Our results show that, due to interference with light reflected from the bottom, the resonant part is slightly deformed of the Lorentzian form. When increasing the number of wells N, the resonant part is obviously different from the Lorentzian form. Since the resonance, levels of the different QWs are electronically isolated. This spectral evolution is entirely caused by the dependence of the radiative correction, which becomes more and more important as N increases. Under the effect of pressure, the reflection coefficient moves towards the high frequencies. We have shown its effect on interband transitions. These optical properties also depend on the dopant concentration ratio and the quantum well width.

Keywords: Bragg reflection, quantum well, Reflectance.

LUMINESCENCE NANOTHERMOMETRY USING ANOMALOUS EMISSION QUENCHING OF INTRINSIC BiFeO$_3$ NANOWIRES

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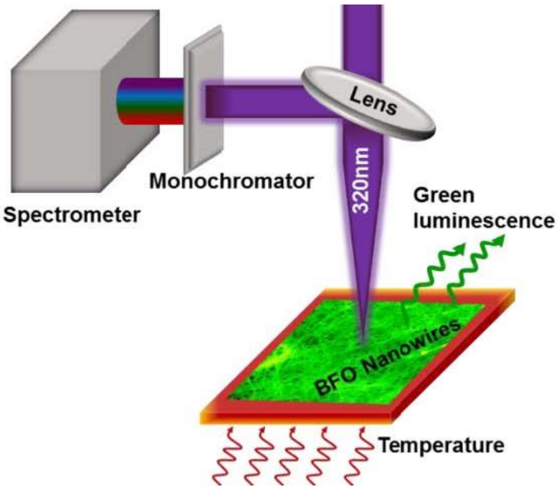
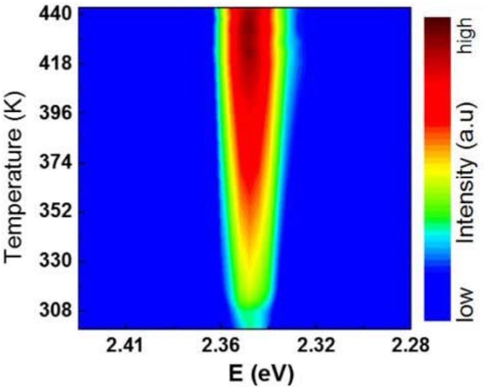
Wide-bandgap semiconductor nanowires with surface defect emission centers have the potential to be used as sensitive nanothermometers and optical probes. Here, we show that the luminescence of an intrinsic BiFeO$_3$ (BFO) nanowires shows negative thermal quenching (NTQ) of emission. The release of charge carriers from localized surface states is suggested as a possible mechanism for the increased green luminescence and the constant emission lifetime which was experimentally observed at elevated temperatures. The absolute thermal sensitivity of this radiometric thermometry is $\sim 10\times10^{-3}$ K^{-1} over the 300 K– 438 K temperature range, while the relative sensitivity is 0.75 % K^{-1} at 300 K.

Unlike conventional optical thermometry, where increasing the temperature quenches the emission intensity of materials and limits their applications at elevated temperatures, negative thermal quenching of nanowires provides a new strategy for optical nanothermometry at higher temperatures.





QUANTITATIVE STOCHASTIC ANALYSIS OF COOPERATIVE UPCONVERSION AMONG YTTERBIUM IONS AND ENERGY-TRANSFER PROCESSES AMONG THULIUM IONS

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Spectroscopy is an important tool to understand the population processes in actively doped materials. In situations where energy-transfer processes take place among the active species, e.g., among neighboring rare-earth ions, the actual distribution of these ions becomes important. The commonly applied models of energy-transfer processes treat all ions spectroscopically equally, i.e., they assume a homogeneous ion distribution. However, already a statistical distribution drastically changes the spectroscopy of the material.

Here we apply a stochastic model [1], which takes the statistical distribution of ions into account and treats single ions and ions with active neighbors by different sets of rate equations, to the spectroscopy of Tm^{3+} and Yb^{3+} in planar waveguides of amorphous aluminum oxide reactively co-sputtered onto thermally oxidized silicon wafers [2]. In Al_2O_3:Tm^{3+}, we confirm spectroscopically the concentration-dependent fraction of single ions [Fig. 1(a)] and determine the microscopic and macroscopic parameters of cross relaxation and energy-transfer upconversion. In Al_2O_3:Yb^{3+}, we relate quantitatively the fraction of quenched ions [3] detected in pump-transmission measurements [Fig. 1(b)] to the fraction of ions participating in cooperative upconversion between two neighboring Yb^{3+} ions.

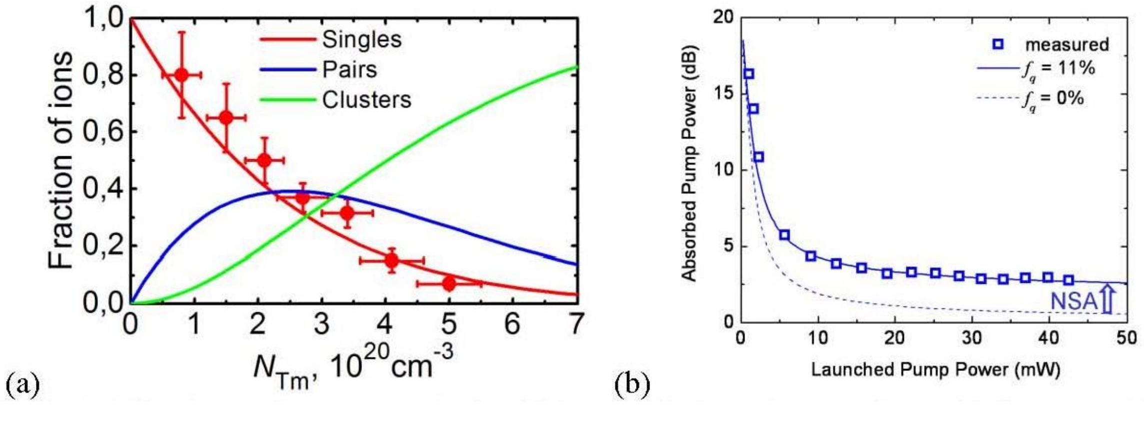

Fig. 1. (a) Fractions of spectroscopically distinct Tm^{3+} ions in amorphous Al2O3 versus Tm^{3+} concentration [1]. *Symbols*: experimental data for single ions determined from the luminescence decay. *Curves:* stochastically calculated data for single ions and ions with neighbors (pairs, clusters).
(b) Absorbed versus launched pump power for an Al2O3 channel waveguide with an Yb^{3+} concentration of 5.8 10^{20} cm^{-3} and a length of 0.7 cm [3]. *Squares*: measured data. *Solid line*: fit assuming a fraction *fq* = 11% of quenched ions. *Dashed line*: calculation assuming the absence of quenched ions (*fq* = 0%). *Arrow*: non-saturable absorption (NSA) induced by quenched ions.

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NON-QUADRATIC RELATION BETWEEN INTRINSIC AND UPCONVERSION LUMINESCENCE

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Grant’s rate-equation model [1] assumes that migration of excitation among neighboring ions is infinitely fast, establishing a “sea” of excitation. It implies that the rate R_{ETU} of an energy-transfer upconversion (ETU) processes involving two ions in the same level i scales quadratically with the level population density N_i, R_{ETU} □ N_i^2. More sophisticated models [2□5] imply somewhat more complex relationships. Nevertheless, all these models treat active ions spectroscopically equally, thereby assuming a homogeneous ion distribution, such that the upconversion luminescence follows a relationship with the intrinsic luminescence, as given by the model.

Here we demonstrate a fundamentally important spectroscopic effect that is directly related to the usually non-homogeneous distribution of ions in a host material. At reasonably low dopant concentrations some ions are isolated, hence do not participate in ETU, whereas other ions have neighbors and can, in principle, participate in ETU. The measured intrinsic luminescence is the sum of both classes of ions, whereas the upconversion luminescence is emitted only by ions from the second class. This de-correlates the two luminescences from each other, thereby leading to a fundamental deviation from the assumed law of upconversion (Fig. 1), e.g. the quadratic dependence mentioned above. Our theoretical considerations have been verified experimentally by measuring intrinsic infrared decay and yellow upconversion decay of Nd^{3+} ions in two host materials with various dopant concentrations and modelling the luminescence decays by a stochastic model for the ion distribution [6].

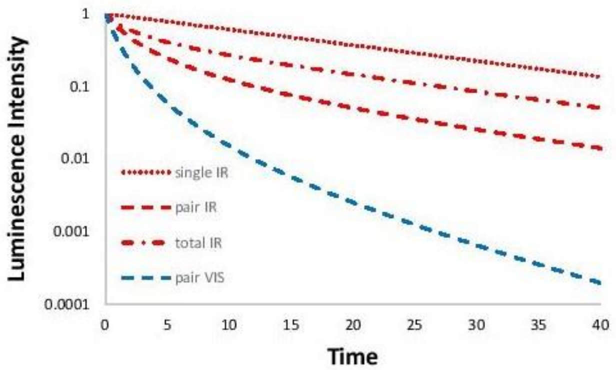

Fig. 1. Intrinsic infrared (red lines) and visible upconversion (blue line) luminescence decay. *Dotted red line*: intrinsic decay from single ions. *Dashed red line*: intrinsic decay from ions with neighbors. *Dashed-dotted red line*: total intrinsic decay when assuming 30% of single ions. *Dashed green line*: upconversion decay from ions with neighbors.

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PHOTONIC CRYSTAL FIBER INTERFEROMETER pH SENSOR BASED ON GOLD AND SILVER NANOPARTICLES COATING

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In this paper, the pH sensor that utilized a photonic crystal fiber (PCF) interferometer is proposed and experimentally demonstrated. The pH sensor operates in the reflection mode, which is fabricated by splicing the LMA-10 PCF with single mode fiber (SMF) from one side while another side is cleaved and polished to be reflection surface like a mirror. Furthermore, to increase the sensitivity of pH sensor, the polished end of the PCF is coated by either gold or silver nanoparticles. The proposed pH sensor is experimentally tested over a pH range of 2-13. The experimental results show that the sensitivity of proposed is highest when the silver-nanoparticles are used. With uncoated pH sensor that utilizes LMA-10 PCF with length of 1.6 cm, the sensitivity is 139 nm/RIU while the sensitivity is raised with coating polished end by gold and silver nanoparticles to 156 nm/RIU and 395 nm/RIU; respectively.

PHOTONIC CRYSTAL FIBER SENSOR FOR Fe ELEMENT CONCENTRATION IN LIQUID

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Photonic crystal fiber interferometers have unique properties so that they are widely used for sensing applications. In this work PCFs solid core(LMA-10) based on Mach-Zehnder modal interferometer for sensing Fe element constriction in water is presented. The general structure of the sensor was applied by fusion splice PCF of different length between two SMF-25,at the fusion splice region where the air holes were fully collapsed,so that the core and cladding mode could couple and recombine. the sensor immersed in a solutions at different concentration (2%,5%,10%,15%and 20%) which leads to different refractive indices in the range of (1.3428-1.3439), in the PCF (LMA-10) of 0.4 cm length the sensitivity was 85nm/RIU whereas, in 1.4 cm length the sensitivity was 914 nm/RIU and ,in 2.7 cm length, the sensitivity was180 nm/RIU.

PHOTOCATALYTIC PROPERTIES OF CARBONIZED PANI/TNTs NANOCOMPOSITES

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A simple method for the preparation of novel and very efficient photocatalytic nanocomposite system based on carbonized form of polyaniline (PANI) and titania nanotubes (TNTs) is reported. TNTs were synthesized according to modified procedure of Kasuga et al. [1]. The carbonized PANI/TNTs nanocomposites were synthesized in a two-step procedure. Noncarbonized PANI/TNTs nanocomposites were synthesized by chemical oxidative polymerization of aniline by oxidant (APS) in the presence of TNTs [2], at room temperature. Initial mole ratios were 50, 100, and 150. In the second step, following the polymerization process, the carbonization of PANI/TNTs nanocomposites was performed by thermal treatment in an inert atmosphere at 650◦C. The morphological and structural properties of the carbonized nanocomposites were studied using transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). The appearance of anatase and rutile crystal forms in TNTs upon carbonization, with mass ratio depending on the initial [ANI]/[TNTs] molar ratio was revealed by XRD measurements. TEM analysis confirmed the complete change in morphology of TNTs after carbonization. The optical properties of synthesized powdered nanocomposite samples was carried out by UV-Vis spectroscopy in reflection mode. Increase of absorbance in the visible part of the spectra of nanocomposites is in accordance with the increase of initial [ANI]/[TNTs] mole ratio. It is known that incorporation of the carbon phase into the TiO_2 matrix led to an increase in absorbance in visible spectral region, which is proportional to carbon content in composite [3]. The photocatalytic activities of carbonized PANI/TNTs nanocomposites were evaluated following the photocatalytic degradation processes of model molecule such as Rhodamine B. Carbonized PANI/TNTs nanocomposites showed significantly higher photocatalytic efficacy compared to bare TNTs, as well as noncarbonized PANI/TNTs nanocomposites.

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LASER-INDUCED BREAKDOWN SPECTROSCOPY AS AN EFFECTIVE APPROACH FOR DISTINGUISHING OF DIAMONDS

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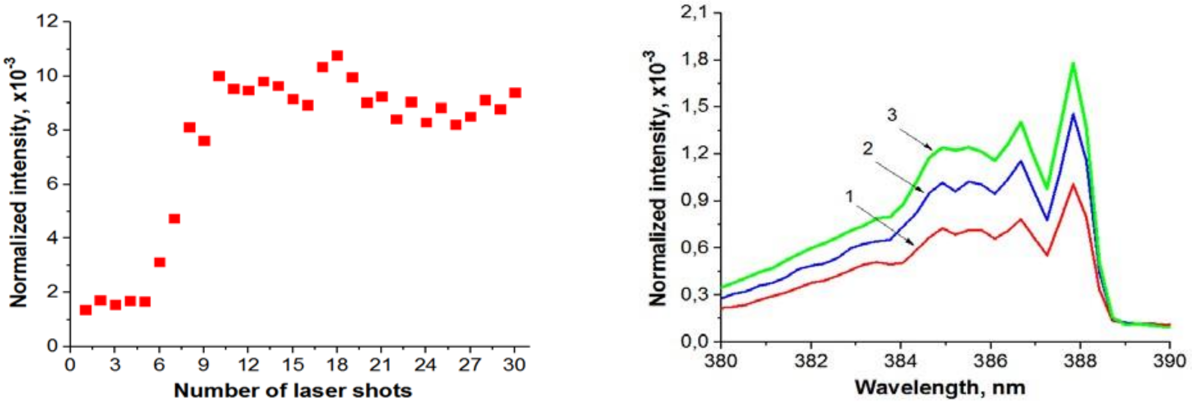
At present, large high-quality single crystal synthetic diamonds for photonics can be grown by HPHT-method. LIBS is a suitable express spectral technique for multi-elemental analysis.

Single- and multi-sectoral plates of the yellow synthetic single-crystal diamonds with dimensions 5x5 mm^2 were studied. A Q-switched Nd^{3+}:YAG laser with a repetition rate of the frequency 2 Hz, the pulse duration 17 ns and the pulse energy 230 mJ was used. The plasma spectra of diamonds were recorded in argon atmosphere by the AvaSpec-ULS2048L-USB2 spectrometer using our own software [1]. The Raman spectra of the initial and irradiated diamond plates were measured using a micro-Raman system (InVia, Renishaw).



a)

b)

Figure 1. a) Normalized intensity of C_2 emission band vs number of laser shot; b) Normalized intensities of CN emission band averaged for: 1 - 1-5th shots, 2 – 6-10th, 3 – 14-30th.

The rapid graphitization of the sample surfaces and the steady-state plasma emission were observed after 10-12 laser shots (Fig. 1a). The Raman spectrum of graphitized surface consisted of the wide diamond D-band (1332 cm^{-1}) and G-band (1600 cm^{-1}) which characterizes sp^2 hybridized carbon atoms. The sharp increase in the number of C=C double bonds led to increase of the C_2 Swan bands emission intensity up to five times. A weaker rise of the CN emission intensity also was observed (Fig. 1b). Changes of intensities of C_2 and CN emission bands are related to changes in bonding structure of the atoms [2] and have been observed for the different samples and the different sectors of each diamond plate. The changes in the intensity of the plasma emission have been increased significantly by the surface graphitization of diamonds.

As a result, the laser-induced graphitization is a suitable process, which leads to an increase in the LIBS technique sensitivity for the recognition of diamonds. This sensitivity varies with other impurities due to selective evaporation in laser ablation.

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AB INITIO MOLECULAR DYNAMICS STUDY OF SELF-TRAPPED EXCITON IN BaF$_2$ CRYSTAL

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In this work we present the results of *ab initio* molecular dynamics (MD) study of localization and transformation mechanism of self-trapped exciton (STE) in BaF2 crystal. The calculations have been carried using PBESol density functional theory in DFT+U approximation with U = 11 and J = 3 values adjusted. MD simulation is performed for temperature linearly increasing from 70 to 350 K.

During molecular dynamics simulation we found only two configurations of self-trapped exciton in BaF$_2$ out of four configurations proposed by Song [1]. These configurations are represented by fluorine ions 1a, 1b, 1c and 2a, 2b, 2c respectively (fig. 1). We plotted the temperature dependence of the probability of transformation event within the first configuration and the transfer from the first configuration to second one (fig. 2).

The activation energy for transformation within the first configuration (0.035 eV) is relatively small, compared to the energy for transformation from the first to the second configuration (0.076 eV). So transformation within the first configuration occurs within the MD simulation at lower temperatures (at a temperature of about 76 K) than transformation from the first to the second configuration (at a temperature of about 190 K).

In our MD simulation of self-trapped exciton in CaF2 crystals the transformation within the first configuration is realized too and has similar values of activation energy (0.03 eV).

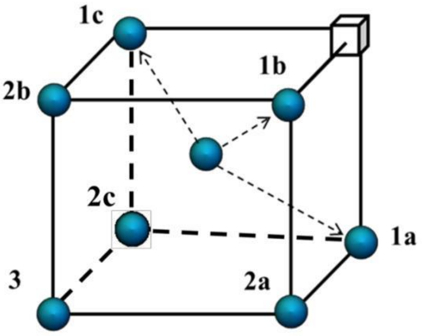

Figure. 1 Possible configuration of self-trapped events exciton in BaF$_2$ crystal

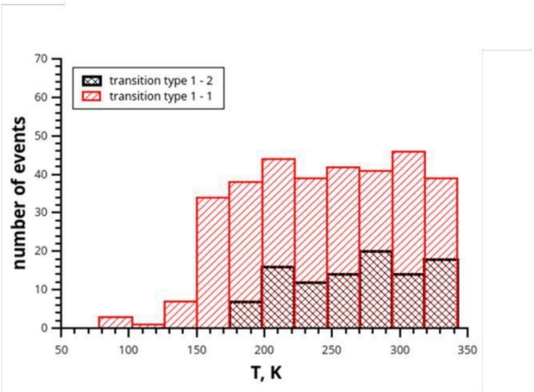

Figure. 2 Temperature dependence of diffusion probability

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PHONONICS OF PHONON ASSISTED ENERGY TRANSFER IN Yb^{3+} AIDED UPCONVERSION LUMINESCENCE OF Tm^{3+} AND Ho^{3+} IN SOLIDS

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The theory of phonon assisted energy transfer (PAET) in a solid, is based on the concept that even in the case, when the donor and acceptor energy levels are energetically far apart, the donor ion by sacrifising part of its emission energy to its coupled host-phonons may become energetically matching with the energy of the excited state of the acceptor and hence can make energy transfer from the donor to acceptor possible. However to accomplish such energy sacrifice by the donor emission to the host phonons, the former requires to stay in the system for a sufficient time to interact with the host. This is possible only when the donor's emission is a resonant emission which repeatedly gets absorbed by the ground state ions.

In recent literature there has been a number of reports where the PAET has been used to explain Yb^{3+} aided enhanced NIR emission/ upconversion (UC) emission of various rare earth ions in Yb^{3+} co-doped different solids. The reported phonon dynamics in most of the cases, are however, incomplete and erroneous.

To have a clear understanding of such PAET dynamics, in the present work, we have studied Yb^{3+} aided UC- luminescence of Tm^{3+} and Ho^{3+} in two high barium tellurite glasses co-doped respectively with (Yb^{3+}/Tm^{3+}) and (Yb^{3+}/Ho^{3+}). We have first determined the emission cross- section of the resonant component of the Yb^{3+} emission and then obtained the phonon assisted energy transfer probability in each case at the overlapping region of donor's emission and the acceptor's absorption [Fig.1] by using the Dexter's equation. The scheme clearly explain the phonon dynamics of the UC-emissions of Tm^{3+} and Ho^{3+} of the two present systems. It is also found to be equally valid when applied to similar other systems.

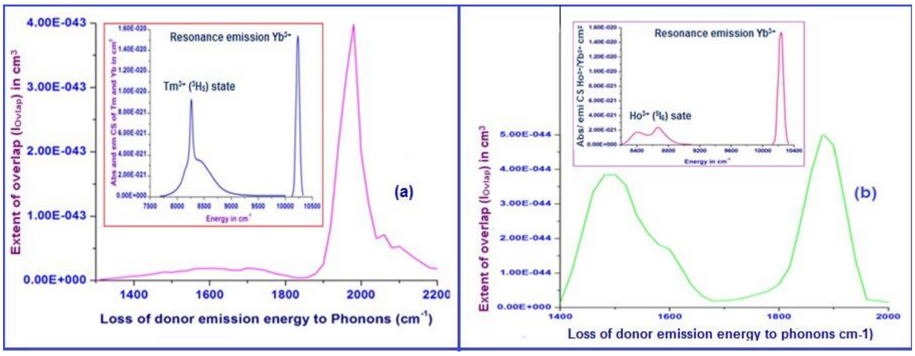

Figure 1. Phonon assisted energy transfer probability of (a): [Yb^{3+}/Tm^{3+}] and (b): [Yb^{3+}/Ho^{3+}] co-doped systems as a function of loss in donor's emission energy to the host's phonons.

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CONCENTRATION QUENCHING IN UPCONVERSION NANOCRYSTALS

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Upconversion luminescence is an active field of research since the pioneering work by Auzel. The past two decades the discovery of upconversion nanocrystals has triggered renewed interest, also because of the potential applications in bio-imaging, solar cells, sensor and security. The Yb^{3+}-Er^{3+} ion couple is one of the most efficient systems of upconversion and is widely used for infrared (1000 nm) to green upconversion. However, the upconversion efficiency, especially in nanocrystals, is still quite low, typically below a few percent, even with approaches aimed at enhancing the efficiency, including core-shell architectures, sensitization with dye-antennas, photonic and plasmonic enhancement. It is of prime importance to understand the underlying reason why the upconversion process is intrinsically inefficient.

A major loss mechanism is related to the high concentrations of rare earths ions like Yb^{3+} and Er^{3+} in upconversion materials. Upconversion relies on multi-step energy transfer. For this reason high dopant concentrations are crucial to realize efficient transfer between lanthanide neighbors. On the other hand, the high dopant concentrations give rise to energy migration and cross-relaxation quenching. The trade-off between efficiency loss by concentration quenching and efficiency gain by energy transfer upconversion determines the maximum upconversion quantum yield but is not well understood. Here we present a systematic investigation on the concentration dependence of luminescence quenching for Er^{3+} and Yb^{3+} in $NaYF_4$ nanocrystals, the upconversion model system. Yb^{3+} and Er^{3+} concentrations are varied between 1 and 60% for core and core-shell nanocrystals where an undoped isocrystalline shell is grown around the lanthanide doped core. Luminescence spectra and luminescence lifetime measurements, by both indirect and direct excitations, are reported and analyzed. The results show that the concentration quenching is strongly reduced in core-shell geometries. For Yb^{3+} concentration quenching is limited up to the highest concentration of 60%. For Er^{3+} concentration quenching varies for different emitting levels. The strongest quenching occurs for the $^4I_{11/2}$ level which is an important intermediate state in the IR to green upconversion process. Variation of the solvent reveals that a major loss mechanism is multi-phonon relaxation due to coupling with high-energy vibrations of the coordinating ligands and solvent. These results give more insight of decay dynamics and concentration quenching for lanthanide ions involved in upconversion process. The results can serve to optimize the upconversion efficiency by careful tuning of concentrations and core-shell design and thus boost the application of upconversion nanomaterials.

GRAPHENE BASED PLATFORMS FOR SENSING AND IMAGING

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We are pursuing two different approaches to develop two kinds of sensors based on graphene with possible applications for ultra-sensitive detection and quantification of molecules and biomarkers as well as for optical imaging of any 2D or quasi 2D material.

The first one is based on the covalent functionalization of graphene by adding carboxyl acid groups which allow successive binding with different biologically active molecules for antigen sensing applications. We present a new approach for specific surface functionalization of graphene during its CVD growth which differ from the graphene oxide derived materials commonly used for these applications. With this method it is possible to obtain highly conductive COOH functionalized either monolayer or few-layer graphene films on copper substrates. The homogeneity and functionalization degree are evaluated combining micro-Raman and XPS spectroscopies. The COOH content is around 5 %, which corresponds to an average inter-spacing < 1nm, adequate to accommodate antibodies. The usual drawbacks of the graphene oxide derived platforms regarding the massive presence of other functional groups or the low conductivity are overcome to a great degree. The relative concentrations of the other functional groups are optimized and the electronic transport characteristics (sheet resistance and mobility) are very adequate for sensing using the change in conductivity induced by antigen anchoring. The bio-molecules detection is carried out through the immobilization of antibodies (IgG1– with a green fluorophore) by the carbodiimide method, which allows the formation of a strong amide bond. The anchoring is demonstrated to be effective by comparing bare and functionalized graphene fluorescence images.

The second kind focuses on enhancing the analyte Raman signal. Raman spectroscopy is a non destructive easy to use specific technique but with low sensitivity. Here we present how interference enhanced Raman scattering (IERS) [1] in adequately designed ordered porous alumina structures provide interesting amplification factors We have designed and fabricated, according to the calculations, Al_2O_3 membranes from Al where the Al_2O_3 layer at the pore base has been reduced down to < 5nm. Transferred graphene on top of these membranes is used here to reveal the amplification power of the tested platform and as the appropriate substrate for the deposition of organic molecules. The overall IERS amplification is > 400 and, optimized membranes for IERS combined with metallic nanoparticles can lead to IERS + SERS combined effects with excellent amplification values.

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