The 6<sup>th</sup> International Conference on the Physics of Optical Materials and Devices &

The 5<sup>th</sup> International Workshop of Persistent and Photostimulable Phosphors

**BOOK OF ABSTRACTS** 

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# ICOM&IWPPP 2022

The 6<sup>th</sup> International Conference on the Physics of Optical Materials and Devices

&

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Belgrade, Serbia, 29<sup>th</sup> of August to 2<sup>nd</sup> of September 2022

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 AND the International Workshop of Persistent and Photostimulable Phosphors – ICOM&IWPPP 2022. The conference is organized by the Society for science development of Serbia (Serbia), l'Institut de Recherches de Chimie Paris (France), the CEMHTI University Orléans (France). 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, Bečići, Montenegro in 2015 and Igalo in 2018. The last editions of IWPPP were organized in 2011, (Ghent, Belgium), 2013 (Guangzhou, China), 2015 (Arlington, USA), 2018 (Beijing, China).

The ICOM&IWPPP 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 5 plenary, 9 keynote, 21 invited lectures, 38 oral and 72 poster presentations will be presented in the following sections: Light for sensing, Thin Films and Composites, Exploring Luminescent Systems, Persistent Luminescence Materials, Persistent Luminescence Mechanisms, Tools and Applications of Persistent Phosphors, Design of Optical Thermometers, Phosphors for bio-applications, New Optical Phenomena, Optical Thermometry, Applications of Rare Earth Emissions, Tuning Optical Properties.

We hope that ICOM&IWPPP 2022 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&IWPPP 2022 wish you a nice time during the conference in Belgrade!

Conference Chairpersons:

Prof. Dr. Miroslav D. Dramićanin, Prof. Dr. Bruno Viana, Prof. Dr. Mathieu Allix

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### PL - 1

#### Non-radiative transitions: our dark foe ...and friend

#### Andries Meijerink

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The knowledge on radiative transitions has increased in the past century to a level where we can with great accuracy calculate radiative decay rates (using Fermi's Golden rule) and understand the influence of the (photonic) environment [1]. Non-radiative decay is less well understood and is generally considered as our dark foe: in applications of light emitting materials for energy efficient lighting and displays thermal quenching of luminescence is bad as it turns our phosphors dark. However, for other applications non-radiative transitions are crucial and faster non-radiative processes can improve the performance, making non-radiative decay our friend. In this presentation a basic (and hopefully insightful) overview of known luminescence quenching processes will be followed by a discussion on how we can increase our understanding of luminescence quenching using new experimental and theoretical capabilities that may help to acquire new insights [2-4]. Implications for applications where non-radiative transitions are considered as foe (e.g. LED lighting) and where they are our friend (e.g. luminescence thermometry) will illustrate how better insight can help in the design of superior luminescent materials for these applications [5,6].



Figure 1 - Compilation of figures in which non-radiative transitions serve as friend or foe or both

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## Traps for persistence or/and photochromism; can they be AND?

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There exist many kinds of inorganic/organic materials that show photochromism. Formation of the color centers is often caused by uv irradiation, resulting in some kind of electron trap centers. By heating or IR irradiations, many of them show bleaching of colors, depending on the trap depth. When the supplier of the electron acts as luminescent center, the photochromic material may behave as a persistent phosphor or photo-stimulated phosphor. When the electron trap of a storage phosphor can have excited states for optical



Fig.1. (left) Illumination time evolution of reflectance spectra of Basilicate GC sample:Eu<sup>2+</sup> by 660nm-light illumination and (right) Dependence on the temperature of heat treatment (1 min)[1].

absorption in visible range, then we can observe interesting phenomena. Some persistent phosphors show photochromism and their bleaching can often be correlated with thermoluminescence.

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Fig.2. Photochromism and blue persistent luminescence in CaAl<sub>2</sub>O<sub>4</sub>: Eu,Nd ceramics[2].

# PL - 3

## THE FUTURE OF BRAIN THERMOMETRY: THE ERA OF NANO

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Minimally invasive monitoring of brain activity is essential not only to gain understanding on the working principles of brain, but also for the development of new diagnostic tools. In this talk I will describe how brain thermometry could be an alternative to conventional methods (e.g., magnetic resonance or nuclear medicine) for the acquisition of thermal images of the brain with enough spatial and temperature resolution to track brain activity in minimally perturbed animals. I will focus on the latest advances in transcranial luminescence thermometry introducing a critical discussion on its advantages and shortcomings. I will also show how polymeric nanoparticles and nanoparticles with structural phase transitions in the physiological temperature range can be used for thermal tomography in brain. The talk also includes a critical discussion about the main challenges that the application of optical nanoparticles for brain thermometry will face in next years.

### Luminescent Nanoparticles: A Wonderful Toolbox for Imaging and Assistive Technologies

#### Xiaogang Liu

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**Abstract:** Lanthanide-doped nanoparticles exhibit unique luminescence properties, including massive Stokes shift, sharp emission bandwidth, high resistance to optical blinking, and photobleaching. They are also unique in converting long-wavelength stimulation into short-wavelength emission. These attributes offer the possibility of developing alternative luminescent labels for organic fluorophores and quantum dots. In recent years, researchers have demonstrated spectral-conversion nanocrystals for many biological applications, such as highly sensitive molecular detection and autofluorescence-free cell imaging. With significant progress over the past decade, we can now design and fabricate nanoparticles that display tailorable optical properties. In particular, by controlling different combinations of dopants and dopant concentrations, we can generate a plethora of colors under excitation with a single wavelength. By incorporating a set of lanthanide ions in defined concentrations into different layers of a core-shell structure, we have expanded the emission spectra of the particles to cover almost the entire visible region, which is not possible with conventional bulk phosphors. This talk will highlight recent advances in the broad utility of lanthanide-based nanocrystals and perovskite nanomaterials for multimodal imaging, bio-detection, therapy, X-ray scintillation, and assistive technology.

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#### **PL - 5**

# LUMINESCENT THERMOMETERS AS NEW TOYS IN THE BLOCK. ALL YOU NEED IS LIGHT

#### Luís D. Carlos

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The emergence of luminescent nanothermometry during the last decade opened the possibility of measuring thermal flows at spatial scales below 10  $\mu$ m, unreachable by conventional electrical methods. Diverse phosphors capable of providing a contactless thermal reading through their light emission properties have been examined, e.g., polymers, DNA or protein conjugated systems, organic dyes, quantum dots, and trivalent lanthanide (Ln<sup>3+</sup>) ions incorporated in organic-inorganic hybrids, multifunctional heater-thermometer nanoplatforms, upconverting, downconverting and downshifting nanoparticles.<sup>1</sup>

In the last couple of years, the focus of luminescence thermometry has gradually shifted from the fabrication of more sensitive nanoarchitectures towards the use of the technique as a tool for thermal bioimaging and the unveiling of properties of the thermometers themselves and their local surroundings, as, for instance, the instantaneous ballistic velocity of Brownian nanocrystals suspended in both aqueous and organic solvents.<sup>2</sup>

The lecture will give a general perspective of the work done on luminescence nanothermometry since the explosion of the field one decade ago, illustrating the potential of the technology with recent examples of thermal bioimaging<sup>3</sup> and the unveiling of the anomalous properties of liquid water.<sup>4</sup>

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# K - 1

# **CRYSTAL FIELD AND FIRST-PRINCIPLES CALCULATIONS OF OPTICAL PROPERTIES OF THE Mn<sup>4+</sup>-DOPED PHOSPHORS**

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The red phosphors doped with the  $Mn^{4+}$  ions are nowadays essential components of the white light emitting diodes (LED) used for lighting and horticultural applications. Analysis of the spectroscopic properties of a large number of such materials allowed to establish the main factors that are responsible for the energy of the  $Mn^{4+} {}^2E \rightarrow {}^4A_2$  emission transition [1] and intensity of its zero-phonon line [2].

In this presentation, the main emphasis is placed on the use of the crystal field theory and first-principles calculations when analyzing the structural, electronic, and optical properties of crystalline solids doped with the  $Mn^{4+}$  ions. It is shown how systematic applications of these methods can give a deeper insight into the relations between the spectroscopic properties of the  $Mn^{4+}$  dopant and the host's structure. Consistent calculations of the crystal field parameters for the  $Mn^{4+}$  ions and crystal field splittings of its energy levels allowed to reveal the relations between the local symmetry of the  $Mn^{4+}$  crystal lattice sites and its spectroscopic features [3-4].

Applications of the first-principles methods resulted in determination of the  $Mn^{4+}$  ground state position in the band gap, variation of the crystal field splittings versus pressure and energy formation of various substitutional defects, which is of paramount importance for identification of the most preferable position occupied by a dopant when several substitutional sites are potentially available [5-7].

Importance of theoretical analysis of the Mn<sup>4+</sup> spectra in solids is emphasized by numerous examples and explanation of relevant experimental spectroscopic results.

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# QUASI-2D HALIDE PEROVSKITE LIGHT EMITTING MATERIALS AND DEVICES

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Quasi-2D perovskites, with a formula  $C_z A_{n-1} B_n X_{3n+1}$  where C is monovalent (z=2) or divalent (z=1) bulky spacer cation, A is a small organic monovalent cation or Cs<sup>+</sup>, B is a divalent metal cation (commonly  $Pb^{2+}$ ), X is a halide anion, and n is the number of 3D perovskite layers which are separated from each other by spacer cations, are of significant interest for light emitting applications due to their tunable bandgap, bright emission, and improved stability compared to 3D perovskites with a formula ABX<sub>3</sub>. As the emission wavelength in quasi-2D perovskites can be tuned by adjusting the number of octahedral layers n, they allow for more flexibility in material choice compared to 3D perovskite where halide alloving is used to tune the emission wavelength (which can lead to emission shifts during operation). However, spincoated films typically contain multiple n phases, which affects the emission colour and emission efficiency, since the electroluminescence typically occurs from the highest *n* (lowest bandgap) phase, while the efficiency of this emission is dependent on the efficiency of funneling from higher bandgap (lower n) to lower bandgap (higher n) phases. To achieve efficient and stable emission, it is necessary to control the crystallization of quasi-2D perovskites. This can be achieved by multiple methods. Here we will discuss two different approaches, one is by controlling the film morphology (which can be achieved by different methods to obtain nanocrystals-in-amorphous-matrix morphology)<sup>[1,2]</sup> and the other is controlling the crystallization by tailoring the spacer cations, either by mixing different spacers<sup>[3,4]</sup> or by adjusting the spacer structure.<sup>[5]</sup> We will discuss the relationship between perovskite composition, preparation method (including the application of antisolvent and solvent annealing), obtained structure, and the resulting device performance in green and/or blue light emitting diodes with quasi-2D halide perovskite emitters.

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# NEW STRATEGIES OF ENHANCING THE PERFORMANCE OF LANTHANIDE BASED LUMINESCENCE THERMOMETERS

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The aim to increase the reliability of remote temperature readout using luminescent thermometry based on the emission of lanthanide ions  $(Ln^{3+})$  doped materials necessitates the search for new approaches enabling to enhance both the relative sensitivity of the thermometer and the brightness of its emission[1,2]. In response to these requirements, large-scale researches related to the optimization of the chemical composition of the matrix and the selection of appropriate dopant ions are being carried out. However, the not always satisfactory results of these investigations prompt a shift of the paradigm in the research being conducted. Therefore, during this lecture, two approaches to increase both the sensitivity of luminescent thermometers and the brightness of their emission will be proposed.

The first proposed approach exploits the sensitization of  $Ln^{3+}$  luminescence by transition metal ions (TM)[3]. As will be shown, the TM absorption cross section far exceeding that observed for  $Ln^{3+}$  and the spectrally broad nature of the 3d-3d absorption bands will contribute to a significant increase in the sensitivity of such thermometers and a broadening of the spectral range of the useful excitation wavelength. In addition, the nonresonant character of the TM $\rightarrow$ Ln<sup>3+</sup> energy transfer allows for enhanced sensitivity of such thermometers.

The second proposed approach is based on the employment in luminescent thermometry of materials exhibiting temperature-induced first-order phase transitions[4,5]. The change in the point symmetry of the crystallographic position occupied by  $Ln^{3+}$  accompanying such a phase transition affects the splitting strength of the *4f-4f* bands into Stark components. Hence, this solution enables the development of a luminescent thermometer with very high relative sensitivity, in which the high sensitivity is not associated with luminescence thermal quenching. It will be demonstrated how, by optimizing the stoichiometry of the matrix, it is possible to design such thermometers depending on the requirements of a specific application.

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# MOVING PERSISTENT PHOSPHORS BEYOND AFTERGLOW: A PLATFORM FOR SENSING

# <u>Philippe F. Smet</u><sup>a,b</sup>, Robin Petit<sup>a</sup>, Ang Feng<sup>a</sup>, Simon E. Michels<sup>a</sup>, David Van der Heggen<sup>a</sup> <sup>a</sup>LumiLab, Ghent University, Ghent, Belgium, <sup>b</sup>philippe.smet@ugent.be

The emission behavior of a persistent or afterglow phosphor can in principle be modeled by a fairly simple system of a luminescent center and a charge trapping defect. Boosting the performance of such a phosphor would then simply imply the creation of as many traps as possible, characterized by a suitable trap depth. In reality, however, the situation is far more complex as several loss mechanisms and interactions need to be accounted for [1]. Consequently, the optimization of the total light output of persistent phosphors is partially driven by a finetuning of synthesis parameters.

Nevertheless, by painstakingly studying the influence of compositional and synthesis conditions and by application of advanced analysis techniques [2], the research community has made good progress in identifying some of the key trapping and detrapping routes in persistent phosphors, including retrapping and optically driven detrapping [3,4].

In this work, we start from those recent insights to turn persistent phosphors into a sensing platform for mechanical pressure [5,6], ultrasound [7], temperature [8] and optical dosimetry [9]. For each application, the relevant trapping and detrapping mechanisms are highlighted. Despite great sensing potential, the drawbacks and remaining hurdles are discussed as well.

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# Can we control luminescent thermometers? – From the application to a fundamental understanding of non-radiative rates

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Luminescent (nano)thermometers have emerged as promising new candidates for remote and non-invasive temperature sensors especially at the micro- and nanoscale [1]. Potential application areas could range from *in situ* monitoring of temperature changes in chemical reactions [2], over *in vivo* bioimaging [3], thermal imaging [4] to the investigation of fundamental thermodynamic phenomena at the nanoscale [5]. A particularly simple way of luminescence thermometry employs an ensemble of non-interacting luminescent centers with two thermally coupled and radiatively emitting states from the same electron configuration. In that case, the luminescence intensity ratio follows Boltzmann's law. Trivalent lanthanoids with their narrow line  $4f^n$ - $4f^n$  luminescence doped into crystalline powders are among the primary candidates for this type of thermometry. The ultimate desire to tailor such thermometers for the application of interest with highest possible measurement precision requires, however, a careful understanding of both thermodynamic and kinetic concepts of their performance [6].

In this lecture, a general overview over the foundations of these so-called Boltzmann-type thermometers will be given. It will be demonstrated that every luminescent Boltzmann thermometer can be used for precise temperature measurements in only a small temperature window and what thermodynamic tricks can be exploited to overcome this apparent obstacle [7]. In the second part, the relevance of excited state kinetics will be highlighted. It will be shown how decisive the doping fraction and choice of the surrounding host compound for the lanthanoid ions can be to control the dynamic working range of luminescent thermometers [8]. These questions offer a change in the interpretation of non-radiative transition rates in general and indicate that there is more than just the energy gap law [9].

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# Bismuth for luminescence and charge carrier storage in inorganic compounds

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Bismuth combined with lanthanides as dopants in inorganic compounds is gaining momentum for afterglow and storage phosphor research and development. The location of the divalent and trivalent lanthanide levels in the bandgap of inorganic compounds are today well-established, and one may engineer the electron trapping and hole-trapping depths by the choice of lanthanide or/and by the choice of host compound. Like for the lanthanides, methods have been developed to establish the location of the Bi<sup>3+</sup> and Bi<sup>2+</sup> levels in the band gap [1]. Whereas lanthanides either can trap an electron or a hole or neither, it appears that Bi<sup>3+</sup> may trap an electron but it also may trap a hole. Combining this dual role of Bi<sup>3+</sup> with a suitably chosen divalent or trivalent lanthanide then provides large trap depth engineering potential.

In this work we will review the role and functioning of bismuth and how it can be combined with lanthanides to engineer and develop new afterglow and storage phosphor materials. We will start with how to locate the Bi<sup>3+</sup> and Bi<sup>2+</sup> ground states in the bandgap. These locations are also known as the Bi<sup>3+/4+</sup> and Bi<sup>2+/3+</sup> charge transition levels. For that the concept of vacuum referred binding energy (VRBE) as obtained with the (refined) chemical shift model (RCS) [2] will be used. Very recently, first papers have appeared on the VRBE of Bi charge transition levels obtained by computational methods [3,4]. They agree encouraging well with the RCS methods. Next we will demonstrate how Bi can be combined with lanthanides to engineer the hole trap, the electron trap and the recombination center.

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# "Real-time intracellular temperature imaging and monitoring. Application to local magnetic hyperthermia therapy."

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Exogenous and endogenous heat generation inside cells is a subject of intense debate in recent times. In particular, the generation of temperature gradients on nanoparticles heated externally by a magnetic field is of crucial importance in the magnetic hyperthermia therapy of cancer. In the absence of reliable direct measurements of the local temperature on cell-internalized nanoheaters, a controversy has been established between those who theoretically predict that it is not physically possible to reach substantial temperature increments on the heat source, and those who measured temperature gradients up to tens of degree. We present a system for real-time intracellular temperature imaging based on  $\text{Sm}^{3+}/\text{Eu}^{3+}$  ratiometric luminescent thermometer probes<sup>1</sup> in combination with a microscope detection instrument (Fig. 1). Using this system, we were able to monitor the local temperature of magnetic nanoparticles and non-magnetic micelles in cell cultures,<sup>2</sup> and we were able to follow the variation of the temperature at different intracellular and extracellular locations when an AMF was applied. Even for moderate magnetic fields, temperature increments of around 11°C were measured at the nanoheaters surface without any appreciable increment of the temperature on the cell membrane. These local temperature increments are sufficient to produce noticeable cell apoptosis, which is much enhanced as the magnetic field intensity is increased to the maximum level tolerated for human use.



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# Luminescence thermometry of Eu-Tb mixed metal-organic frameworks: some ways to tune the thermometric performances

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Since the discovery of the first ratiometric Eu-Tb-mixed MOF luminescent thermometer in 2012, the number of potential luminescent thermometers increases drastically, notably because of the inexhaustible choice of suitable organic ligands, and consequently the infinity of potential materials. Since then, the research on Eu-Tb mixed MOFs was summarized on the investigation of on single material with a specific lanthanide composition. Thus, as solid-state chemist, we have attempted for few years to identify the structural parameters which can govern or guide the thermometric performances, such as the use temperature range or the relative thermal sensitivity. Our objectives are to rationalize the research on Eu-Tb mixed MOFs for thermometry to design highly performant materials which could be proposed as an alternative of the well-recognized inorganic compounds.

In Eu-Tb mixed MOFs, the organic ligand plays the role of structuring agent for the network but also of sensitizer for lanthanide emission (antenna effect). Thus, we decided to start our approach by investigating a series of MOFs built upon the same organic ligand but exhibiting different topologies of the  $Ln^{3+}$  polyhedra network (planes, chains, dimers...). We highlighted the important effect of the Eu/Tb ratio on the relative thermal sensitivity, but also the necessity to control the Tb-to-Eu energy transfer by using Gd<sup>3+</sup> as diluting agent. This first results enabled us to design more sensitive luminescent thermometers in a controlled way. Finally, our first results have also evidenced the impact of the topology on the temperature sensing.

# RARE-EARTH MOLECULAR CRYSTALS FOR PHOTONIC QUANTUM TECHNOLOGIES

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A promising perspective of using rare-earth ions to build quantum light-matter interfaces relies on nano-fabricating crystalline host materials preserving the rare-earths quantum properties while enabling integration into nanophotonic devices. Molecular chemistry is very attractive in this respect, offering unmatched flexibility in terms of material composition fine structural tuning together with integration capabilities.



Figure 1: **a**- X-ray crystal structure of the  $Eu^{3+}$  complex. Color code: grey, carbon; white, hydrogen; pink, europium; red, oxygen. **b** -Two pulse photon echo decay from the molecular europium crystal yielding a linewidth of 30.2 kHz.

Here, we report europium molecular crystals exhibiting linewidths in the 10s of kHz range (Figure 1), several orders of magnitude narrower than other molecular centers [1]. We harness this property to demonstrate efficient optical spin initialization, coherent storage of light using an atomic frequency comb, and optical control of ion-ion interactions towards implementation of quantum gates [2]. These results open the way to using rare-earth molecular crystals as a new platform for photonic quantum technologies.

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# LUMIMESCENCE OF d<sup>5</sup> TRANSITION-METAL IONS UNDER HIGH-PRESSURES

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 $Mn^{2+}$  ions in solids exhibit luminescence in the spectral regions between green and far red, depending on the local environment and distances between central ion and ligands. The basic optical properties of this dopant are well described by the crystal field theory for d<sup>5</sup> electronic configuration, i.e. by the Tanabe-Sugano diagram. According to this theory, all optical transitions at ambient conditions occur between the <sup>6</sup>A<sub>1</sub> ground state and higher energy excited states with a different spin, thus being strongly spinforbidden, having very small transition probability and long decay times of luminescence. Fe<sup>3+</sup> ions with the same d<sup>5</sup> electronic configuration as Mn<sup>2+</sup> ions show very similar optical properties. Usually, the optical transitions, especially between the ground and the first excited level are also strongly coupled with the lattice, thus both absorption and luminescence spectra are broad, often without 0-phonon lines, even at very low temperatures. An externally applied pressure may strongly influence the spectral position of luminescence as well the luminescence decay kinetics of the ions with a d<sup>5</sup> electronic structure.

High hydrostatic pressure application increases the strength of the crystal field experienced by central ions due to compression of the examined materials. Thus, following the Tanabe-Sugano diagram, the luminescence spectrum of  $d^5$  ions is shifted towards longer wavelengths since the separation between the first excited  ${}^{4}T_{1}$  and the ground level decreases. The spectral shift is accompanied by a decrease of luminescence efficiency and a strong reduction in the radiative decay rates. The most probable reason for the decrease of the luminescence efficiency is the crossing between the  ${}^{4}T_{1}$  and  ${}^{2}T_{2}$  levels. The  ${}^{2}T_{2}$  level is even much stronger coupled to the lattice than the former one, which results in nonradiative quenching of the luminescence.

Analysis of these effects has to take into account several processes in addition to the crossing between the  ${}^{4}T_{1}$  and  ${}^{2}T_{2}$  levels, such as pressure-induced phase transitions of the examined compounds, or pressure-induced increase of the electron-phonon coupling. On the other hand, the d<sup>5</sup> electronic configuration is somehow unique since the energy level scheme is the same in the octahedral and tetrahedral symmetry.

Results of pressure-induced luminescence quenching for different compounds such as NaScSi<sub>2</sub>O<sub>6</sub>:Mn<sup>2+</sup> clinopyroxene [1] and Gd(Zn,Mg)B<sub>5</sub>O<sub>10</sub>:Mn<sup>2+</sup>pentaborate [2], LiGaO<sub>2</sub>:Fe<sup>3+</sup> and others [3] will be presented. A comparison with previously obtained results for ZnS:Mn<sup>2+</sup> [4], i.e. d<sup>5</sup> ion in tetrahedral coordination, will be considered. Finally, certain consequences for the possibility of observing d<sup>5</sup> ions emission in the infrared region will be shown.

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# OPTIMIZATION OF DOPED SPINEL OXIDES AND SILVER SULFIDE FOR OPTICAL IMAGING AND TEMPERATURE SENSING. SOME EXAMPLES OF TEMPERATURE MEASUREMENTS.

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Luminescent nanoparticles have gained particular attention these last years since many applications of such materials in structural and functional *in vivo* imaging (early diagnosis of tumors, cell's biodistribution) as well as in the development of new devices for the energy transition (photovoltaic, LED lighting and display). Among the possible applications, bioimaging has been successfully established with persistent luminescent nanoparticles, which emit in the region of partial transparency of living tissues in the red/near infrared range. Their use has a clear advantage as the irradiation step to create optical excited states, can be performed before injection, avoiding tissue stress and other autofluorescence phenomena<sup>1</sup>. Luminescent particles are also used as local optical temperature probes in the nanoscale. The emergence of luminescence nanothermometry is based on the very strong dependence of radiative phenomena on temperature and the remarkable sensitivity of luminescent probes<sup>2</sup>.

We will present synthesis strategies used for the creation of architectured luminescent nanoparticles allowing to adjust luminescent parameters, namely, intensity, spectral position, lifetime, brightness, thermal sensitivity and stability. We will develop recent advances on thermosensitive probe emitting in the first and second NIR windows and that are relevant to perform in real-time local temperature readings<sup>3</sup>. We will demonstrated that such optical nanoprobes has now reached sufficient maturity to focus on the demonstration of nanothermometry applications and the expected benefits of nanothermometry for safer biological hyperthermia treatment and for the development of sustainable catalysis.

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# Mid-Infrared Luminescent Materials: Overview and Structure–Property Relationship

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The range of high spectral transparency for chalcogenide or halide crystals [1], glasses [2] or ceramics [3] (from about 500 nm to several dozen micrometres) is unique and do not available for oxygen containing materials. In addition, these materials with low energy of the phonon system are predestined for use as active elements, e.g., for lasers operating in the mid-infrared range. Therefore, chalcogenides and halides are, from formal point of view, an excellent matrix for long-wave luminescence. However, the embedding of rare earth ions in chalcogenide/halide structures is not an easy experimental undertaking.

The mid-IR wavelength region is attractive for performing laser remote sensing for several reasons. Most small organic and inorganic molecules have their fundamental absorption features in the mid-IR wavelength regions from  $1,5 \,\mu\text{m}$  to  $5 \,\mu\text{m}$ . Therefore, strong emitting sources in mid-IR spectral range will be extremely useful in the construction of lidar allowing remote detection of gases (including hazardous gases), which is important for health and environmental protection, chemical rescue, the mining industry or military applications.

Thereat halide-based matrices containing rare earths and exhibiting longwave luminescence [1-3] (as well as semiconductor lasers based on them) can be an alternative to e.g., troublesome and unwieldy in operating (mobile applications) CO<sub>2</sub> lasers operating through non-linear optical effects SHG, THG in this spectral range.

It is expected that the result of the analysis of the available experimental data give opportunity to establish "structure-property" and "property-property" relations for the system matrices-(luminescence center) and should have great significance for searching new, efficient sources emitting in mid-IR spectral range.

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#### X-ray Induced Photodynamic Therapy: Deeper and Better

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Despite these advantages, Photodynamic therapy (PDT) has one major drawback: penetration depth. This limits the use of conventional PDT methods to skin (surface) tumors only and are not effective for deep tumors. There are four possible solutions for the light delivery of deep tumor treatment: particles activated by near-infrared (NIR) light, upconversion nanoparticles that absorb NIR light and emit visible light for other photosensitizers, fiber optics and ionizing X-rays. Of these options, the best is X-rays. Near-infrared light can penetrate only 5 mm in tissue while retaining enough energy to activate PSs. The use of fiber optics is neither convenient nor efficient as it cannot effectively and evenly activate the photosensitizers. It is also almost impossible for the treatment of metastatic sites or lymph nodes involved with this disease, unless they are located in the region where light delivery is feasible. In contrast with the other methods, X-rays can easily penetrate as deeply as necessary into patients, and are convenient as they are commonly used in cancer therapy.

The use of novel Copper Cysteamine (Cu-Cy) nanoparticles is a good solution for overcoming these issues because Cu-Cy nanoparticles can be effectively activated by X-rays to produce singlet oxygen, which makes it very efficient for deep cancer treatment. Here I will discuss the use of copper cysteamine nanoparticles to enhance radiation therapy in combination with PDT and targeting therapies.

# COUPLING PERSISTENT LUMINESCENCE MATERIALS FOR INCREASED APPLICABILITY: THIN FILMS AND UPCONVERSION ENERGY TRANSFER

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The rise of modern research on persistent luminescence (PersL) materials in the late 90s – early 2000s led to the discovery of many new persistent phosphors. In the already vast literature one can find persistent materials of several colors, different excitation wavelengths, and several smart and new applications. However, there are still some drawbacks on the design of intelligent materials like: i) the absence of transparent and flexible materials and ii) the lack of PersL materials with efficient excitation in the infrared region.

This presentation will deal with methodologies coupling persistent materials to overcome the mentioned situations in two case studies. On the first, the use of cellulose-ether polymers as composite matrix coupled with persistent nanoparticles proved to be a good route on the design of translucent persistent films [1]. These micrometric persistent films proved to conserve good transparency even with 10 g/m<sup>2</sup> of Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>.

The second case study shows that coupling persistent nanomaterials with upconversion nanoparticles via dry impregnation can lead to persistent luminescence via NIR irradiation [2]. The pair  $\beta$ -NaGdF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup>/Zn<sub>1.33</sub>Ga<sub>1.33</sub>Sn<sub>0.33</sub>O<sub>4</sub>:Cr<sup>3+</sup> showed to be a good candidate for this proof of concept due to the intense green upconversion of fluoride combined to the gallate PersL efficient excitation in the green region.

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# CAN THEORITICAL CALCULATIONS MEET EXPERIMENTS AND EXPLAIN LUMINESCENCE PROPERTIES?

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Electronic structure calculations can be regarded as a very useful tool to complete collected experimental data and to help in the understanding of the structure–property relationships in solids. It is particularly true when physical properties are closely related a chemical element in low amount and possibly undetectable. A case in point is the optical properties of phosphors that originate from dopants with very low concentration. Here we will discuss the luminescent properties in S doped Na<sub>4</sub>Al<sub>3</sub>Si<sub>9</sub>O<sub>24</sub>Cl [1], O or S doped KX (X= Cl, Br) [2], Ti doped ZrO<sub>2</sub> [3] and Ti doped BaZrO<sub>3</sub>. Namely, based on simulations, the yellow-orange fluorescence of scapolite is definitely assigned to (S<sub>2</sub>)<sup>-</sup> activators trapped in [Na<sub>4</sub>] square, the stability of superoxide (O<sub>2</sub>)<sup>-</sup> and supersulfide (S<sub>2</sub>)<sup>-</sup> anions in potassium halides is evidenced, and the origin of the luminescence in m-ZrO<sub>2</sub>:Ti and BaZrO<sub>3</sub>:Ti can be related to Ti/O charge transfers rather than on site *d-d* trantisions at Ti site or oxygen vacancies. The determination of the position in energy of intrinsic and extrinsic defects may also open discussion concerning the nature of traps when luminescence is delayed.

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### Lanthanide Ions: from Visible to Mid-Infrared Emission

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Rare earth-doped crystals and nanocrystals have long been studied in the UV and VIS spectral regions, but near (NIR) and mid (MIR) infrared emission of lanthanide ions can have important developments for applications in several fields like biomedical imaging and therapy [1,2], metrology, sensor technology [3], forensics, and anticounterfeiting [4]. Experimental investigation of lanthanide doped materials for mid infrared emission has mainly been focused to bulk materials for laser applications and very few reports of mid infrared emission from nanoparticles can be found in the literature. Efficient NIR emission requires judicious choice of both the host material and the lanthanide ion, moreover, NIR and MIR emissions are particularly sensitive to various sources of vibrational deactivation, for this reason, a good control of the lanthanide ion environment is required. Within the NIR and MIR spectral windows, the most interesting ions are  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Ho^{3+}$ , and  $Er^{3+}$ . In this talk I will review the importance of studying the NIR and MIR emissions of lanthanide ions for various applications and I will present the latest results in the field.

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# CHEMICAL TUNING OF Mn<sup>4+</sup> PHOTOLUMINESCENCE IN Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> ALLOYS

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Photoluminescence properties of  $Mn^{4+}$  ions in the Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> solid solutions have been studied in details in the temperature range from 4.4 to 500 K. For this purpose, a series of samples with nominal composition (Al<sub>1-x</sub>Ga<sub>x</sub>)<sub>2</sub>O<sub>3</sub>: Mn(0.05at.%), Mg(0.05at.%) with x = 0; 0.05; 0.10; 0.15; 0.2; 0.25; 0.5; 0.75 and 1.0, were obtained by the sol-gel citrate method and afterward calcined at temperatures up to 1500°C. The phase composition and crystal structure of the studied materials and their evolution with calcination temperature from 900 to 1500°C have been analyzed in detail using corresponding powder XRD data.

Main attention is paid to the temperature behavior of the Mn<sup>4+</sup> emission and their evolution with the Al/Ga ratio in the Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> alloys. Depending on chemical composition of the host, three different types of Mn<sup>4+</sup> centers have been revealed in the studied compounds. The first one, Mn( $\alpha$ ), ( $\lambda_{ZPL}$  = 676.3 nm at *T* = 4.4 K), coinciding with the known Mn<sup>4+</sup> emission in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, is observed in the corundum phase hosts (*x* = 0...0.15). Another one, marked by us as Mn<sub>I</sub>( $\beta$ ), ( $\lambda_{ZPL}$  = 652.1...659.9 nm) is observed in the monoclinic-type hosts with *x* = 0.2...0.75, while the third one, Mn<sub>II</sub>( $\beta$ ), ( $\lambda_{ZPL}$  = 709.7 nm) was revealed only in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (*x* = 1.0) of the same type of the monoclinic structure. Nature of the Mn<sup>4+</sup> emission in the studied compounds and their evolution with the Al/Ga ratio will be discussed.

Obtained results confirm wide opportunities for the chemical tuning of  $Mn^{4+}$  emission in the studied Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> alloys. Prospects for use of the studied phosphors for low-temperature luminescence thermometry will also be discussed.

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# LumTHools - software for analysis of phosphors' luminescence temperature dependence

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From semiconductors to phosphors on LEDs, quantum dots, and nanoparticles to bulk luminescent materials, temperature greatly affects the spectral characteristics of the emission, leaving no optical device unperturbed by its change. Temperature causes changes in intensity or spectral shape, energy, broadening, rise-time, or the lifetime of emission. Those phenomena are modelled by equations that vary in their mathematical complexity and number of fitting parameters (2 to 6), and often require manual adjustment, which is not easily achievable with the currently available fitting software. We have built LumTHools (Figure 1), an interactive software capable of fitting the experimental data to 32 different theoretical models. The graphs change in real-time as the user adjusts the parameters via sliders, and fitting parameters can be fixed to a certain value. The graphs can be exported as high-resolution images. The program also creates interactive graphs of sensitivities and temperature resolutions for the phenomena that can be used for luminescence thermometry. LumTHools is freely available at <a href="https://www.omasgroup.org/lumthools/">https://www.omasgroup.org/lumthools/</a>. It was designed to make data fitting easier and faster, and we hope that other researchers interested in Luminescence thermometry or temperature effects on luminescence in general will find it useful for research or educational purposes.



Figure 1. LumTHools GUI with experimental data of lifetime of Sm<sup>2+</sup> (taken from Ref. [1]) loaded and fitted to one of the appropriate models.

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# Nanophosphor-based Photonic Materials provide fine control over the emission properties of rare-earth nanocrystals

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Rare earth (RE) emitters are central for applications related to the generation of light since these nanomaterials feature exceptional thermal and chemical stability. However, such stability entails an intrinsic complexity to alter their emission properties. Herein, we show that the integration of RE nanocrystals or nanophosphors in devised optical environments allows a fine control over the features of the emitted light, without modifying their chemical composition or compromising their efficiency. Key to the achievements herein reported is the careful analysis of the structural and optical properties of thin nanophosphor layers with the processing temperature to achieve bright, transparent and efficient light-emitting films that are suitable for the photonic integration.[1-3] In one of the examples we discuss, the integration of a thin nanophosphor film in the middle of a photonic multilayer renders a onlydielectric optical cavity. Following a precise computational design, the cavity resonances were devised to match selected emission peaks of the nanophosphors at targeted directions, hence tuning the spectral content of the emitted light.[4,5] Also, the nanoimprint of color-converting layers made of nanophosphors provide periodic surface textures, which enables brighter emission.[6] On another example, the integration of nanophosphors in the vicinity of the interface of a periodic multilayer and a metal film, which sustain optical Tamm Plasmons, enables the enhanced out-coupling of the nanophosphor emission in well-defined directions.[7] From a different perspective, the incorporation of Mie resonators in a nanophosphor-based matrix allows enhancing the fraction of light emitted by the nanophosphors that is efficiently out-coupled in flexible materials.[8] The combination of nanophosphors and photonic architectures opens the door to develop versatile and costeffective conversion layers, which connects with the growing interest of our society for the development of light sources with expanded functionalities.[9, 10]

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# ADVANCED CRYOGENIC THERMALLY STIMULATED EMISSION SPECTROSCOPY- A NEW TOOL FOR ASSESSING OPTICAL MATERIALS

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Electron/hole traps alter the optical properties of materials by creating additional recombination pathways, trapping or providing charge carriers and modifying exciton dynamics. Understanding the defect/trap dynamics and measuring their activation energies are crucial to control the properties of optical materials. A new highly sensitive cryogenic thermally stimulated emission spectrometer (C-TSeS) for the low temperature regime of 9–325 K was developed to detect and characterize shallow traps in optical and bandgap materials with enhanced sensitivity (Journal of Applied Physics 130, 033104 (2021)).

The performance of the spectrometer was tested on Ce doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> single crystals. Then, its capabilities were further demonstrated by detecting low density shallow levels created in Ga<sub>2</sub>O<sub>3</sub> by H-diffusion [Fig.1], and by characterizing ultra-thin films of Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, and their alloys. Additionally, the spectrometer was employed to monitoring radiation induced defects in optical materials and clearly revealed how radiation modulate trap levels and strongly modify the electronic and optical properties of materials.

This technique provides a unique tool for studying exciton dynamics in photonic materials and measuring donor/acceptor ionization energies and densities in luminescent materials. It can advance material characterization and development for a wide range of applications including lasers, electronic and illumination devices, and detectors for medical diagnostic.



Fig.1. (a)C-TSeS glow curve of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> before and after H-diffusion. The glow curve was measured up to room temperature; however, no peaks were shown beyond the region in the graph. (b) Trap level calculation in H annealed Ga<sub>2</sub>O<sub>3</sub> using the initial rise method [2].

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# **DIVALENT LANTHANIDE TRIFLATES**

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Even if low-valent lanthanides are no longer a curiosity, the number of comprehensively studied compounds is still limited. This is especially true for the salts of simple oxoacids, e.g sulfates and nitrates. In fact, the long known EuSO<sub>4</sub> is the only known binary Eu(II)sulfate so far.<sup>[1]</sup> It is apparent that the possibility of preparing divalent oxoanionic lanthanide compounds correlates with the oxidation power of the respective acid. Thus, the preparation of divalent rare earth sulfates, besides of EuSO<sub>4</sub>, is certainly a challenge. However, there are suitable derivatives of sulfuric acid that are much weaker oxidizers, for example triflic acid, CF<sub>3</sub>SO<sub>3</sub>H. Indeed, some reports on divalent lanthanide triflates occurred in literature,<sup>[2,3]</sup> and even a study on a Tm(II)triflate has been published five years ago.<sup>[4]</sup>

We have now studied in a more systematic the preparation of divalent lanthanide triflates and their properties. The triflates could be obtained as crystalline solids from reactions of Ln(III)-triflates with the respective metals in various solvents. As metals we have used Eu, Sm, and Yb. Furthermore, we prepared the respective compounds of the alkaline earth metals Sr and Ca as host lattices for doping experiments. Fig. 1 shows crystals of Sm(OTf)<sub>2</sub>(CH<sub>3</sub>CN) and the structure of the compound.



Fig. 1 Single crystals of Sm(OTf)<sub>2</sub>(CH<sub>3</sub>CN) (left) and crystal structure of the compound (right)

In the presentation, details of the synthesis and of the crystal structures will be discussed. Moreover, the luminescence and the magnetism of selected compounds, in particular containing  $Eu^{2+}$  and  $Sm^{2+}$ , will be shown.

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# Laser Cooling of Sapphire on an Electric-Dipole Transition

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A major factor that has limited the rate of laser cooling by anti-Stokes fluorescence (ASF) is the forbidden nature of the optical transitions used to implement refrigeration. While forbidden transitions avoid configuration relaxation which would otherwise generate significant heating and quench laser cooling, the rate of cooling is limited by the long lifetime of the excited state on such transitions. Here the first observation of laser cooling of a solid on an electric-dipole (ED) allowed transition is reported in  $Ti^{3+}$ -doped sapphire. Cooling took place at optical phonon-assisted resonances at a rate enhanced by three orders of magnitude over that of typical forbidden transitions. This finding should promote cryo-cooling of imaging sensor arrays grown on sapphire for space applications and Raman cooling of solids.

Thermal lens spectroscopy was performed for  $\pi$ - and  $\sigma$ -polarized excitation in a high-quality crystal of 0.02% Ti<sup>3+</sup>:Al<sub>2</sub>O<sub>3</sub> (Figure of Merit FOM=800). Samples were irradiated with a tunable, single-mode Ti:sapphire laser tuned to wavelengths longer than the mean fluorescence wavelength for each polarization. At photon energies lower than the average Stokes shift, configuration relaxation was prohibited despite the ED nature of the transition and a total of twenty-five narrow, discrete cooling resonances were observed as dips in the TLS signal for both polarizations (An example spectrum is shown in Fig.1).



Figure 1. Example of cooling resonances observed via TLS in a Ti<sup>3+</sup>:Al<sub>2</sub>O<sub>3</sub> crystal in  $\pi$ -polarization.

To assign these resonances, the inhomogeneous distribution of  $Ti^{3+}$  ions in sapphire was assumed to be dominated by four sites that have local modes only slightly perturbed from the optic modes of the host. Differences between calculated and observed wavenumbers were then found to be less than 0.01% on average for  $\pi$ -polarized resonances. All 25 resonances were well accounted for by purely electronic transitions between known  $Ti^{3+}$  sublevels [1] or optical phonon sidebands [2]. Doped sapphire crystals with low FOM did not show cooling.

These results open the door to future advances in (i) optical refrigerators capable of cooling larger payloads more rapidly than those operating on forbidden transitions, (ii) Raman cooling [3] to reach *l*-He temperatures, and (iii) electronic sensors for use in space.

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# Polarization control in chirowaveguides: towards integrated chiral sensors

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The transverse polarizations propagating in integrated photonic devices are the two well-known transverse electric and transverse magnetic (TE and TM) linear polarizations. As a consequence, any application requiring other polarizations, especially the circular one, such as chiral sensing, 3D-display, quantum optics..., cannot take the full advantage of integrated optics. However, chiral materials, through their optical rotation, can overcome the geometrical properties of the waveguides to allow eigenmodes propagation of any polarization from linear to circular. These are chirowaveguides [1, 2].

Chirowaveguides fabrication requires techniques which are able to conserve the chirality and thus, the film's chiroptical properties. In this talk, we will give an overview on the requirements to build chirowaveguides. We will then present our last results concerning the coating of thin films of high optical rotation based on different chiral organic molecules and their microstructuration to perform chanel-chirowaveguides. Two deposition techniques are investigated and compared: Pulsed Laser Deposition of purely organic chiral thin films and dip coating of hybrid Binaphtyl-Silica material (ORMOSIL) [3-6].

Using these materials, we demonstrate that the eigenmodes polarization can be tailored from linear to nearly circular in symmetric planar waveguides with optimized refractive index contrast [7] and in channel chirowaveguides with optimized geometries [8]. Optical characterisations of these chirowaveguides in term of losses, mode propagation and state of polarization will be presented. These new chirowaveguides can give rise to novel integrated photonic devices based on the propagation of eigenmodes with circular polarization, such as integrated chiral sensors.

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# TRANSPARENT PERSISTENT LUMINESCENCE FILMS: FROM DESIGN TO GLOWING PERSPECTIVES

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Persistent luminescence (PersL) materials, generally transition metal- or rare earth- doped insulators, are phosphors that feature unique delayed and long-lasting luminescence coming from a temporary storage of optical energy at defects. PersL phosphors, are now typically being commercially used as microsized powders dispersed in resins or inks for applications ranging from design to night security. Also, several relevant scientific fields such as anticounterfeitings, illumination or imaging would clearly benefit from the development of low scattering PersL coatings.[1] However, the relatively low storage capacity of PersL phosphors hurdles their potential use for emerging applications, being the development of transparent PersL materials that enable efficient energy storage highly demanded. In this context, we develop transparent films featuring PersL using two synthesis and processing strategies.

First, we demonstrate that wet deposition of colloidally stable ZnGa<sub>2</sub>O<sub>4</sub>:Cr<sup>3+</sup> nanoparticles, elaborated using a micro-wave assisted hydrothermal method,[2] allows obtaining transparent layers ranging from few hundreds of nanometers to several microns in thickness. Controlled thermal annealing enables obtaining sufficient crystalline quality as to demonstrate red PersL with limited particles sintering, harmful for layers transparency.

In the second one we develop few nanometer-thick nanostructured garnet-based films following a "one-pot" monolithic sol-gel route.[3] After reaction, deposition and controlled thermal annealing, we demonstrate transparent garnet films featuring efficient green emission and afterglow. We prove the versatility of our method by changing the garnet composition to reach films with distinct PersL kinetics and chromaticity.

Finally, we demonstrate that the transparency and dimension that our layers feature allow exploring novel ways to tune PersL properties and to go beyond limits set by phosphor composition.

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# Metastable states in persistent phosphors: A spectroscopic game of hide-and-seek

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Persistent phosphors are luminescent materials that emit light long after the excitation has ended. These materials are widely applied in safety signage and gadgets but hold the potential to be used in far more promising applications including pressure and light sensing or bioimaging.<sup>[1-3]</sup> In order for a phosphor to exhibit persistent luminescence it must contain specific defects that can act as charge trapping centres. Quite often a trivalent lanthanide codopant is added which can act as a trap was recently shown for the blue-emitting  $Sr_4Al_{14}O_{25}$ :Eu,Dy.<sup>[4]</sup>

The charge transfer that is induced between the activator and the trap upon excitation of the phosphor will inevitably change the absorption spectrum of the material which can have important consequences for the phosphor's performance. For example, if the absorption of the filled traps overlaps with the excitation spectrum of the activator additional losses due to optically stimulated luminescence can arise when trying to fill the traps in the phosphor.<sup>[5]</sup> It is hence vital that the absorption spectrum of these trapping defects is properly characterized. Here we will discuss the spectral characteristics of the metastable trapping defects in SrAl<sub>2</sub>O<sub>4</sub>:Eu codoped with trivalent lanthanides and emphasize how important these are when engineering new persistent phosphors.

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# MULTI-BAND PERSISTENT LUMINESCENCE EMISSION IN GARNET CRYSTALS (YAGG) AND GARNET NANOPARTICLES WITH MAGNETIC RESPONSES (GAGG)

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Persistent luminescence (Pers. Lum.) materials are related to the trapping of charge carriers in electronic defects and their slow release upon time and/or temperature.<sup>1-2</sup> Here we present  $Ce^{3+}$ ,  $Cr^{3+}$ -doped YAGG single crystals that provide Pers. Lum. in the VIS, deep-red and NIR ranges. Our objective is twofold:

-First, we intend to shed light onto the Pers. Lum. mechanism taking advantage of the lack of surface defects in comparison with powder samples. Defects could be beneficial or detrimental depending on their trap depths, so one cannot make an a-priory general statement on whether the lack of surface defects enhances the performance. However, the crystallinity of the sample and a volume effect<sup>3</sup> where the whole material can be excited is expected to potentially modify some charging and/or discharging properties. Indeed, afterglow intensity and duration improvement are observed in big crystals in regard to powders. A precise control and study of the composition, including defects, is reported (Figure 1).

-On the other hand, Pers. Lum. based on YAGG have been proposed for bioimaging at micro-<sup>4-7</sup> and nanoscale<sup>8-9</sup> In the present work, we focus on the elaboration of core-shell magnetic and Pers. Lum. NPs for bimodal imaging thanks to the incorporation of Gd, Fe, Ni or Co for MRI (magnetic resonance imaging) and Er, Nd or Tm for Pers. Lum. in the NIR II/III biological windows. Furthermore, these NPs can be combined with spin crossover NPs for which the high-spin state is MRI active whereas the low-spin state is magnetically mute.



**Figure 1.** Absorption spectrum of the crystals collecting the f-d transitions of  $Ce^{3+}$  (left) and f-f transitions of  $Cr^{3+}$  (middle), and image of a transparent YAGG crystal (right).

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# INORGANIC PHOSPHORS: STRUCTURAL CHARACTERISATION ACROSS THE LENGTH SCALES

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Optical properties and performance of luminescent materials are inherently linked to their structure in a broad sense: from local structure (first coordination sphere,  $\sim$ Å) to microstructure (grains and defects,  $\sim \mu$ ). Between these two lies the all-important crystal structure of the host material, which determines the phosphor properties in multiple ways. The crystallographic sites available for dopants, their coordination environment and site symmetry determine which ions can be used effectively as activators and sensitisers and influence emission, while the connectivity and rigidity of the host structure affect temperature-dependent behaviour related to thermal quenching.

This talk will focus primarily on the characterisation of crystal structure of luminescence mixed metal oxides by diffraction techniques and state-of-the-art methods for analysis of diffraction data. The use of complementary methods, such as solid state nuclear magnetic resonance and total scattering/pair distribution function analysis for elucidation of local structure will also be addressed.
## Luminescence of Mixed Valent Compounds -Essential Unexplored

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Mixed valent compounds are known since a few hundred years due to their bright colors; a famous example is Prussian blue ( $[KFe(CN)_6Fe]$ ), which was used as ink by ancient romans due to its intense blue color. In fact, mixed valent compounds with identical or at least comparable coordination spheres of the cations with different oxidations states (Robin-Day classes II or III) cause a so called intervalence charge transfer (IVCT) excited state, which is the origin of the deep colors due to the allowed absorption starting from the ground state (Fig. 1). While absorption bands ending at these IVCT states are already described, emission starting from IVCT states are never been observed.

Therefore, mixed valent lanthanide ions containing compounds are very promising materials to investigate their  $Ln^{2+}-Ln^{3+}$  interactions. In this context, the UCL<sub>3</sub>-type structure compounds, namely NaEu<sub>2</sub>Cl<sub>6</sub> and KEu<sub>2</sub>Cl<sub>6</sub> are very exciting candidates with an intense blue color, and also NaEuSmCl<sub>6</sub>, and NaSm<sub>2</sub>Cl<sub>6</sub> showing a deep red color.

To investigate the respective luminescent properties, isostructural host lattices with alkaline and alkaline earth cations, like NaBaLaCl<sub>6</sub>, are suitable candidates, because they provide suitable sites for divalent as well as for trivalent lanthanides. In this talk, the optical properties of mixed valent lanthanide containing materials will be presented as well as the hosts doped with divalent and trivalent lanthanides as well as their interaction like energy transfer processes.



Fig. 1: Absorption spectra of KEu<sub>2</sub>Cl<sub>6</sub> (left), Crystals of NaSrLaCl<sub>6</sub>:Sm<sup>2+</sup> under day light (above) and the red emission of NaSrLaCl<sub>6</sub>:Sm<sup>2+</sup> under UV light (below) [2]

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## 2D luminescence thermometry using dual low power LED excitation and

## single-band emission

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Luminescence thermometry using inorganic phosphor particles, or phosphor thermometry is a robust technique to monitor thermal gradients in a variety of engineering processes. For 2D measurements, the widely employed methods are the emission ratiometric or spectral method based on a ratio of emission intensity in two separate wavelength regions, and the emission decay time approach, which extracts the luminescence decay time from multiple exposures following a single excitation pulse. The spectral method requires two detectors with respective spectral filters, and accurate image mapping between the two recorded images. The decay time approach on the other hand requires a high-speed detector or interline transfer CCDs and the signal is limited by the short measurement window necessary to resolve the decay time.

Here, we present an alternative approach for 2D temperature imaging which exploits temperature-dependent features in the excitation spectrum of some luminescence thermometers. Two LEDs emitting in different spectral regions are subsequently pulsed to excite the phosphor, and a single low frame rate camera records each luminescence emission pulse. The ratio of the luminescence emissions corresponding to the two LEDs provides a two-dimensional temperature map after calibration.

This method is demonstrated using YVO4:Eu<sup>3+</sup>, which excitation spectrum shifts towards the visible region with increasing temperature [1]. A plate is coated with a 30-micron thin phosphor coating and two low power (<1mW) LEDs are used to exploit this thermometric response, peaking at 270 and 340 nm, respectively. The resulting ratio has a temperature sensitivity around 1%/K from 20 to 70 °C. Measurements are performed on the phosphor plate when subject to transient heating by a flame to demonstrate the ability of this approach to resolve the spatio-temporal dynamics of this thermal process.

Despite an excitation power density below  $0.3 \text{ mW/cm}^2$ , this simple low-cost approach yielded a single pixel precision of  $1.5^{\circ}$ C at a resolution of 160 micron over a 25 x 25 mm region. This is due to the excellent photon budget of the approach, which combines long excitation pulse durations (50 ms), and the collection of the entire emission band and decay.

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# ALL DIMENSIONS WITHIN SOLE CATION: STRUCTURE AND OPTICAL PROPERTIES OF LOW-DIMENSIONAL HALIDE PEROVSKITES WITH FORMAMIDINIUM

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Hybrid halide perovskites (HHPs) are a growing class of semiconductors, attracting great and increasing attention of the world scientific community owing to their unique set of optical and electronic properties, such as direct band gaps, high optical absorption coefficients, long charge carrier lifetime, and remarkable tolerance to defects, making them almost ideal materials for photovoltaics and optoelectronics. Another unique feature of the halide perovskite family is the unprecedented structural flexibility expressed in the ability to adopt dimensionally reduced structures across the full range of 3D to 0D inorganic frameworks.

The majority of structural design strategies for hybrid compounds are based on the concept of achieving the desired dimensionality by introducing bulk organic cations that act as a template for the structure. In this research we show alternative concept of dimensionality reduction through successive "cleavage" of the anionic framework of the parent perovskite compound FAPbI<sub>3</sub> (FA<sup>+</sup> = formamidinium) by addition of FAI salt to form a child low-D compounds with formula  $A_nPbX_{x+n}$ . Particularly, we isolated and characterized for the first time three new formamidinium-based low-D perovskites (LDPs): the 1D FA<sub>3</sub>PbI<sub>5</sub>, the 2D FA<sub>2</sub>PbI<sub>4</sub> (110) layered perovskite and the "hollow" perovskite (A<sub>1.5</sub>PbI<sub>3.5</sub>) with intermediate dimensionality between 3D and 2D. DFT calculations predict a monotonic reduction of the electronic dimensionality with decreasing of structural dimensionality: the bandgap of the phases follow the trend 3D < "Hollow" < 2D < 1D, the VBM and CBM becomes less dispersive for low-dimensional phases. The experimentally determined optical bandgap, photoluminescence maximum, and exciton binding of the LDPs also consistently increase with lowering the structural dimensionality.



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### **O** - 3

# Bulk crystal growth of Ce:GAGG and Ce:La-GPS single crystal from the melt using precious metal crucible-free OCCC Method

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#### 1. Introduction

At past few years Ce-doped Gd<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub> single crystals (Ce:GAGG) and Ce-doped (La,)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (Ce:La-GPS) were found as one of the most prospective scintillator materials. Our group has already reported the use of the Czochralski technique to successfully grow Ce-GAGG crystals up to 4 inch in diameter [1] for GAGG and up to 2 inch in diameter for La-GPS [2]. Both Ce:GAGG and Ce:La-GPS as many other high melting temperature oxides, iridium is used as a crucible material for the crystal growth. Iridium is more resistant to oxidation than other high-melting-point metals such as tungsten and molybdenum, and can be used to increase the oxygen partial pressure of growth atmosphere up to about 2%. However, many oxide crystals have oxygen deficiency due to melt growth under this oxygen partial pressure. Since oxygen deficiency in scintillator crystals causes afterglow and other problems [3]. Co-doping has been investigated to reduce the slow component [4], but it would be ideal if melt growth under high oxygen partial pressures could be realized and this problem effectively eliminated.

During many years cold crucible technique (other name "Scull-melting technique") is known as simple and effective way to produce high melting temperature oxide single crystals without necessity to use any crucible [5]. In traditional Scull-melting technique water-cooled Cu container with a melt moves slowly down through the RF coil and crystals grow spontaneously from the melt [5]. However, just few materials with unique set of physical properties (F.e. ZrO<sub>2</sub>, HfO<sub>2</sub>) can be grown as big single crystals using such technique. In this work, we report the growing results of Ce:GAGG and Ce:La-GPS single crystalline scintillators by pulling on seed using cold container with a melt under high oxygen partial pressure without use of precious metal crucible. This is a fusion of the skull-melting method and Czochralski (CZ) methods, which we call the Oxide Crystal growth from Cold Crucible (OCCC) method.

#### 2. Experimental & Results

The OCCC equipment consists of a high-frequency oscillation coil, a Cu basket cooled by water flowing in it, a pull-up shaft equipped with a rotation structure, and a hot zone. As in the traditional Skull

technique, the sintered material has been places into the Cu basket. As in the CZ method, the seed crystal is attached to the lower part of the pull-up shaft, touches the melt from above, and is pulled up while being rotated to grow a single crystal.

Figure 1 shows a) the obtained Ce:GAGG crystal and b) Ce:La-GPS crystal. A single crystal region were obtained in both crystals, although there are few cracks.



Fig.1 Ce:GAGG crystal and b) Ce:La-GPS crystal

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# Coating ZGO nanoparticles for in vivo imaging

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Persistent luminescence nanoparticles (PLNPs) are useful tools for biological applications.<sup>[1,2]</sup> This is mainly due to their optical properties that allow *in vivo* imaging without autofluorescence background.

However, once injected *in vivo*, naked PLNPs (no coating) are rapidly captured by reticuloendothelial cells mainly localized in liver and spleen, as can be seen in Figure 1, left. This may be a limitation for some applications.

To avoid this phenomenon, different options can be considered to coat the surface of PLNPs with hydrophilic molecules in order to increase their residence time in the blood.

Several strategies developed in our lab will be presented and applied to the coating of Cr<sup>3+</sup> doped zinc gallate (ZGO) nanoparticles in order to get stealth PLNPs, as shown in Figure 1 right.<sup>[3,4]</sup>



Figure 1. Effect of surface coating on the biodistribution of ZGO nanoparticles

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#### **O** - 5

## Crucible free growth and scintillation properties of $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals

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 $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is well known as a semiconductor material for power devices, and so on. Recently  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has also been reported as a scintillator with light yields of ~8400 ph./MeV scintillation decay time of <1 µs, and density of 6.44 g/cm<sup>3</sup> [1].  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals are industrially grown by the edge-defined, film-fed growth (EFG) and the Czochralski (Cz) method using iridium crucibles and die [2]. In recent years, the price jump of Ir metal has become a major issue in producing these oxide crystals. Iridium crucibles and dies must be used under low oxygen partial pressure atmosphere during the growth to prevent the oxidation and loss of the iridium materials. Evaporation of gallium oxide becomes more pronounced under low oxygen partial pressure and is a problem in crystal fabrication. It has been reported that this evaporation causes various crystal defects and degrades semiconductor performance [3]. It is also known that  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has luminescence at 400 nm, which is derived from host defects.

In this study, 1-inch diameter  $\beta$  -Ga<sub>2</sub>O<sub>3</sub> single crystals were grown by the oxide crystal growth from cold crucible (OCCC) method under high oxygen partial pressure. In the OCCC method, as in the cold crucible method, high frequency is applied directly to the oxide material, which is heated and melted, and the outermost solid material itself is used as a crucible to hold the melt by water-cooling with a copper hearth. In the OCCC method, crystal growth is performed while rotating the seed crystal, as in the Choklarsky method, to expand the crystal diameter. Photographs of the grown crystal and polished 1 mm thick plate samples are shown in Figure 1. The higher the oxygen partial pressure during growth, the more the blue coloration was reduced. Absorption in the wavelength above 500 nm was also reduced. Light yield of ~4000 ph./MeV and scintillation decay time of 12.2 ns (16.9%), 164 ns (83.1%) were confirmed in the O<sub>2</sub> 100% atmosphere sample under 662keV gannma-ary eradiation. Details of the growth method, crystal quality, and radiation responses will be reported in the presentation.





Fig. 2 An example photograph of the grown  $\beta$  -Ga<sub>2</sub>O<sub>3</sub> (left) and polished plates (right) References

Fig. 1 Decay curves of the  $\beta$  -Ga<sub>2</sub>O<sub>3</sub> samples

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## Crystal Growth of Ce-doped (Gd,Y)ScO<sub>3</sub> Scintillators by Micro-Pulling-Down Method and Their Optical Properties

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**1. Introduction** Ce-doped perovskite-type crystals, such as Ce-doped YAIO<sub>3</sub> and LuAIO<sub>3</sub>, have attracted attention as scintillation crystals with excellent properties [1,2]. In this study, we focused on GdScO<sub>3</sub> for to develop other promising perovskite-type scintillators. GdScO<sub>3</sub> with 10 mol% Ce as the luminescent center has been developed and reported to have a relatively short decay time (~ several ns), however low light output has been a problem [3]. This can be attributed to the relatively small band gap energy of GdScO<sub>3</sub> and also the relatively small energy difference between the Ce<sup>3+</sup> 5d<sub>1</sub> level and the bottom of the conduction band. Here, the energy position of the Ce<sup>3+</sup> 5d levels strongly depend on the crystal structure of the host crystal, as the Ce<sup>3+</sup> 5d orbitals are not shielded by outer electrons. Therefore, we considered that the light output could be improved by substituting rare-earth ions at the Gd<sup>3+</sup> site.

**2. Materials and Methods** The crystal growth was performed using micro-pulling-down ( $\mu$ -PD) method [4] utilizing tungsten as crucible and afterheater material. After weighing Sc<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and Gd<sub>2</sub>O<sub>3</sub> in a stoichiometric composition of (Ce<sub>0.002</sub> Gd<sub>0.998-x</sub> Y<sub>x</sub>)ScO<sub>3</sub> (x = 0.000, 0.400, 0.600), the powders were sintered at 1600°C for 24 hours in air. The sintered compacts were introduced into the W crucible, and the crystals were grown on <110>- oriented seeds prepared from a Czochralski-grown Ce-doped GdScO<sub>3</sub> single crystal [5] or metal W rod as seed crystal at a pulling down rate of 0.03 mm/min. The structure of the grown crystals was estimated by the powder X-ray diffraction analysis. In addition, the photoluminescence (PL) excitation and emission spectra were measured to evaluate the effect of Y<sup>3+</sup> substitution on the Ce<sup>3+</sup> luminescence.

**3. Results** The grown crystals by  $\mu$ -PD method with the W crucible are shown in Figure 1. We succeeded in growing transparent and translucent (Ce<sub>0.002</sub> Gd<sub>0.998-x</sub> Y<sub>x</sub>)ScO<sub>3</sub> (x = 0.000, 0.400, 0.600) crystals. PL excitation and emission spectra were measured for mirror polished sample with a thickness of 1 mm, . From the PL emission spectra, the typical broad emission spectra associated with the Ce<sup>3+</sup> 5d<sub>1</sub>-4f transitions were observed in all crystals. The emission shifts to longer wavelengths with increasing Y<sup>3+</sup> substitution. Details of the crystal structure and the optical properties of Ce-doped (Gd,Y)ScO<sub>3</sub> crystals will be presented.



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## Development of novel eutectic scintillators for thermal neutron detections and their material design

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**[Introduction]** <sup>3</sup>He gas proprotional counters have been mainly used as thermal neutron detectors. However, due to the recent shortage of <sup>3</sup>He, there is an urgent need to develop a neutron detector that does not require <sup>3</sup>He. Scintillators containing elements such as <sup>3</sup>He, <sup>6</sup>Li, <sup>10</sup>B, and <sup>157</sup>Gd, which have large reaction cross sections with thermal neutrons, can be used to detect thermal neutrons. Currently, the use of Li-containing solid scintillators such as LiCaAlF<sub>6</sub> (LiCAF)[1] and Cs<sub>2</sub>LiYCl<sub>6</sub> (CLYC) [2], which shows high light yield to thermal neutrons, has been reported to be promising. On the other hand, our group has focused on eutectics that increase the <sup>6</sup>Li content conmaring to solid single crystal scintillators, where the Li concent must be limited by the crystal composition. Up to now, LiF/LiGdF<sub>4</sub>, Li<sub>3</sub>AlF<sub>6</sub>/Eu:CaF<sub>2</sub>, LiF/CaF<sub>2</sub>/LiBaF<sub>3</sub>, and so on were reported[3,4]. In order to develop a <sup>6</sup>Li containing scintillators with higher light yield and better neutron and gamma-ray discrimination performance, we have designed a new eutectic scintillator that combines a chloride or bromide scintillator phase with high light yield and a <sup>6</sup>Li-containing neutron capture phases with refractive indexs close to each other.

**[Results]**In this research, binary eutectic combinations of LiBr/(BaBr<sub>2</sub>, LaBr<sub>3</sub>, CeBr<sub>3</sub>), LiCl/(BaCl<sub>2</sub>, SrCl<sub>2</sub>) and a ternary eutectic of LiCl/SrCl<sub>2</sub>/LaCl<sub>3</sub> were investigated. Each powder material was sealed in a quartz tube with an inner diameter of 4 mm, and eutectics were prepared by the vertical Bridgman method at a pull-down rate of 0.1-0.2 mm/min. Figure 1 shows photographs, backscattered electron images (BEIs) and refractive index values of each eutectics. It can be seen that the transparency of the wafer changes due to the difference in refractive indices of the each crystal phase in each eutectic. Among of them, <sup>6</sup>LiBr/Ce:LaBr and LiCl/SrCl<sub>2</sub>/Ce:LaCl<sub>3</sub> showed high light yields of 74,000 and 30,000 photons/neutron under <sup>252</sup>Cf neutron iradiation, respectively. The LiCl/SrCl<sub>2</sub>/Ce:LaCl<sub>3</sub> sample wafer showed transparency. The concept of material design and results of eutectic fabrication, and scintillator performance evaluation will be reported on the presentation.



Fig.1 The photographs, BEIs and refractive index values of the fabricated eutectics

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## DEVELOPMENT OF RARE EARTH-FREE ALUMINIUM BORATE-BASED PHOSPHORS AND COMPOSITE FILMS

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#### Abstract :

Solid-state white light sources using light-emitting diodes (LEDs) are a breakthrough technology in the lighting and display markets allowing a significant reduction of the energy consumption. Major part of current LED devices converting near-UV or blue excitation in white or coloured light contain rare earth (RE) elements. These critical materials are associated to environmental, economic and geopolitical issues. This context has led to the search for alternative LED phosphors materials. Here, based on previous works carried out at Néel Institute, RE-free aluminium borate (AB) matrices have been developed.[1] These innovative luminescent compounds generate a broad and adjustable emission band on the entire visible spectrum under commercial UV LED excitation (365 nm; 385 nm; 405 nm) (Fig. 1a) linked to organic emitting centres (polycyclic aromatic hydrocarbons molecules, PAHs).[2] The AB micron-sized powders are originally prepared by modified Pechini synthesis. This method allows to get a very homogeneous metal oxides matrix. The optimisation of this synthesis protocol by replacing the reflux heating step with autoclave assisted by microwave (MW) heating allows to save two days on the whole synthesis and improves the optical performances of the resulting powders. The latter were dispersed in a polymer matrix to elaborate luminescent composite films (Fig. 1b) to study the photometric properties on a remote-phosphor LED prototype. Morphological and optical properties of powders and coatings as well as their stability under thermal and/or photonic stresses were investigated and the results will be presented and discussed.



Figure 1: Emission spectra of aluminium borate powders synthesized by Pechini method (reflux) and microwave-assisted hydrothermal process (MW) and composite film preparation process

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## Dual-emission luminescence thermometry using LaGaO<sub>3</sub>:Cr<sup>3+</sup>, Nd<sup>3+</sup> phosphors

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The  $Cr^{3+}$ ,  $Nd^{3+}$  activator combination has attracted attention due to its excitation and emissions within the first biological window (650 – 950 nm).<sup>1</sup> This area of the NIR spectrum is significant due to being able to penetrate skin more effectively than shorter wavelengths.<sup>2</sup>

In this investigation, a series of La<sub>1-x</sub>Ga<sub>0.99</sub>O<sub>3</sub>: Cr<sub>0.01</sub>, Nd<sub>x</sub> phosphors (where x = 0.005, 0.01, 0.02) were synthesised by conventional solid-state methods and structurally characterised by Rietveld refinement of a structural model and powder diffraction data.<sup>3</sup>

Room temperature photoluminescence was undertaken with emission spectra showing both the  $Cr^{3+} {}^{2}E$  sharp peak at 729 nm, and the  $Nd^{3+} {}^{4}I_{3/2} \rightarrow {}^{4}I_{9/2}$  emission of  $Nd^{3+}$  *ca*. 890 nm. Excitation spectra of both the  $Cr^{3+}$  and the  $Nd^{3+}$  showed energy transfer to the other emission centre alongside showing the characteristic  $Cr^{3+}$  broadbands, and sharp  $Nd^{3+}$  line excitations.

Variable temperature thermometric analysis was undertaken, with the La<sub>1-x</sub>Ga<sub>0.99</sub>O<sub>3</sub>: Cr<sub>0.01</sub>, Nd<sub>x</sub> (x = 0.02) sample exhibiting the emissions from the Cr<sup>3+</sup> and Nd<sup>3+</sup> centres at comparable intensities. Monitoring by luminescence intensity ratio (LIR) showed Cr<sup>3+</sup> emission being quenched slower than Nd<sup>3+</sup> emission. The phosphor produced a relative sensitivity of ~2.0% K<sup>-1</sup> at 300 K, high absolute sensitivity, and a temperature resolution of 0.04 K at 300 K.



Figure 1: Variable temperature emissions (excitation = 473 nm) of  $La_{1-x}Ga_{0.99}O_3$ : Cr<sub>0.01</sub>, Nd<sub>x</sub> (x = 0.02) (left), Sensitives of the  $La_{1-x}Ga_{0.99}O_3$ : Cr<sub>0.01</sub>, Nd<sub>x</sub> (x = 0.02) phosphor (right).

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# Effect of silver (Ag) nanoparticles on the luminescence properties of Dy<sup>3+</sup> ions in borate glasses for solid state lighting applications

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In recent years, metallic nanoparticle doped glasses have been studied as promising candidates for various technological applications due to their ability to improve the luminescence properties of rare earth ions. In this study, Dy2O3 and Ag2O doped borate glasses were synthesized by conventional melt-quenching technique with glass matrix 74.5B<sub>2</sub>O<sub>3</sub>-10Al<sub>2</sub>O<sub>3</sub>- $15Na_2O-0.5Dy_2O_3/xAg_2O$  where, x=0, 0.5, 1, 2, 5 wt%, labeled BANDy-xAg). The amorphous nature of the glass systems was verified by the X-ray diffraction. Transmission electron microscope (TEM) images confirmed the presence of spherical Ag nanoparticles, whose average diameter is 7.60 nm, in the BANDy1.0Ag glass matrix. The optical and luminescence properties were investigated according to Ag nanoparticle concentrations. The negative value of the bonding parameters calculated from the absorption spectra indicates the ionic nature between the Dy<sup>3+</sup> ions and its surrounding ligands. In order to determine the nature of the Dy-O bond and the symmetry around the  $Dy^{3+}$  ion environment, Judd–Ofelt intensity parameters  $(\Omega_{\lambda}, \lambda=2, 4, 6)$  were obtained and the trend of these parameters was found as  $\Omega_2 > \Omega_6 > \Omega_4$ . The luminescence spectra were obtained under 350 nm excitation and exhibited four emission bands at 481 ( ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ ), 572 ( ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ ), 662 ( ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ ), and 750 ( ${}^{4}F_{9/2} \rightarrow {}^{6}H_{9/2}$ ) nm. The intensity of emission spectra increased with increasing of Ag<sub>2</sub>O content until 1.00 wt% in BANDy-xAg glasses and then this intensity decreased due to the back-energy transfer from  $Dy^{3+}$  ions to Ag<sub>2</sub>O. The various radiative properties were calculated by using Judd-Ofelt intensity parameters and emission spectra. It was found that the 572 nm emission band, located in the yellow region, has higher radiative parameters. As function of Ag concentration, the Y/B values, CIE chromaticity coordinates (x,y) and correlated color temperatures (CCT) were found using the excitation and emission spectra of BANDy-xAg glasses. The CIE chromaticity coordinates and CCT values of all glasses are located in the white light region. All these results indicate that  $Dy^{3+}$  and Ag doped borate glasses can be potential candidate for solid state lighting applications such as WLEDs.

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#### **Enormous photonic artefacts in luminescence nanothermometry**

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Nanocrystals with temperature-sensitive luminescence become increasingly popular as thermometers. Excitation and detection of the luminescence occurs remotely, which makes this a versatile and user-friendly thermometry technique. In principle, it only requires a fluorescence microscope to map the temperature of luminescent nanocrystals, embedded in a sample, with a diffraction-limited spatial resolution. However, photonic artefacts that may occur for the highest resolution mapping can distort the luminescence spectra, resulting in incorrect temperature readout.<sup>1</sup>

Here, we quantify these artefacts by analyzing the luminescence of nanothermometers that are deposited on a mirror coated with a spacer of variable thickness. These substrates allowed us to systematically vary the photonic environment, which resulted in errors in the read-out temperature of more than 100 K. We identify the experimental parameters that cause the photonic artefacts and provide strategies to minimize them. These findings are not only relevant for the application of temperature sensors but are also important for the development of other optical sensing methods.



Figure 1. (a) Schematic illustration of the substrate with controlled photonic environment. The alumina spacer ( $Al_2O_3$ ) systematically varies the distance between the Au mirror and a sub-monolayer of nanocrystals doped with lanthanide ions ( $Ln^{3+}$ ). (b) Read-out temperatures of the  $Er^{3+}$ -doped nanocrystals for various emitter–mirror distances measured at physical temperatures of 298 K (blue dots), 323 K (orange dots), and 373 dots (red dots). The colored solid lines are the read-out temperatures calculated using the averaged collected LDOS and the calibration based on the Boltzmann model.

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## ERBIUM DOPED MATERIALS AND CORRELATION OF PHOTOLUMINESCENCE, STRUCTURE AND SYMMETRY

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Research of lanthanides doped materials necessitate to complete the data on split energy levels of rare earth ions in solid hosts and their correlation with structure and symmetry [1]. During XRD-based structural analysis in some optical materials the color centers can be formed as radiation-induced defects which affect their optical properties [2-4]. Low cryogenic temperatures of 10 K are also necessarily for registration of spectroscopic data. Novel data-driven approaches can be proposed which can help in overcoming the abovementioned issues with a possibility to access spectroscopic data in a comprehensive database.

In this work we obtained and analyzed a series of erbium doped BaF<sub>2</sub>, CaF<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>/Y<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub> and MgAl<sub>2</sub>O<sub>4</sub> materials, performed a structural refinement and measured high resolution luminescent properties. We identified the Stark structure of Er<sup>3+</sup> energy levels at low and room temperatures and correlated the acquired data with hosts structure and local symmetry. All experimental data obtained were compared with literature and arranged in a potential database form. This approach could reduce necessity of exposure of materials to XRD and low, helium temperatures; only high resolution luminescence spectra of the lanthanides doped materials can be sufficient to identify their symmetry.

Future systematization of data of lanthanides doped materials in such database could reduce the time for analysis and understanding of optical, structural, symmetry and correlated properties and could allow further predictions, simulations and development of more efficient optical materials.

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## **O** - 13

# EUROPIUM DOPED BISMUTH BORATE GLASSES: FROM STRUCTURE TO LUMINESCENCE PROPERTIES

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Nowadays the design and development of rare earth ion doped glass materials have come into prominence due to important application areas such as solid-state lasers, optical detectors, light emitting diodes (LED), color displays and solar cells. There is a growing demand to develop materials which have optimum structural, optical and luminescence features for the advanced photonics technologies. Among the rare earth ion doped glasses europium doped ones are the most suitable materials for optical devices thanks to their simple energy level structure, narrow emission band, sensitive red emission, and longer decay times.

Herein, Eu<sup>3+</sup> doped B<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>O<sub>3</sub>-Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> glass system were synthesized via traditional melt quenching method. A synergistic quantitative analysis including X-ray diffraction, Fourier Transformed Infrared, optical absorption, photoluminescence (PL), and x-ray excited luminescence spectroscopy was carried out.

The structural modification of the borate network as a function of  $Eu_2O_3$  content was identified by the change in the ratio of  $[BO_3]$  and  $[BO_4]$  units. It is found that N<sub>4</sub> fraction is inversely proportional with europium doping which was also verified by the band gap calculations on the basis of absorption measurements.

Phonon side band in  $Eu^{3+}$  ions, associated with the  ${}^7F_0 \rightarrow {}^5D_2$  transition, was used to analyze the phonon energy, electron-phonon coupling strength and multiphonon relaxation of the glasses. The efficient energy transfer from Bi to Eu was verified by the improvement of  $Eu^{3+}$  emission with respect to decrement of Bi emission.

Tunable luminescence was achieved by adjusting the Eu<sup>3+</sup> content from bluish green to white and to red in the studied system. Based on Judd-Ofelt theory, radiative properties including transition probabilities, radiative decay times, branching ratio and emission cross section were calculated. In addition, photoluminescence quantum yield values were calculated for the title glasses. This study contributes to the fundamental understanding and design of tunable lightemitting Eu-doped borate glasses for photonic applications.

### **O** - 14

# GdAl<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> :Cr<sup>3+</sup> FOR LIGHT-INDUCED HEAT GENERATION

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The phenomenon of light absorption by nanoparticles, their heating, heat dissipation and exchange with the environment, are becoming intriguing research matters in nanotechnology [1]. Especially, when such nanoparticles could find application in targeted therapies like hyperthermia of tumors, photothermal induced drug release processes, etc. [2,3]. The effectiveness of light-induced heat generation process depends strongly on the type of involved photothermal agent. Currently, effective heat generation in doped nanomaterials was performed mainly with the use of lanthanide ions [4,5]. However, in this case emerge a limiting factor, which is the relatively low absorption cross-section of lanthanides with an +3oxidation state. Therefore, a new approach that involves the Cr<sup>3+</sup> ions as light-induced heat generators was presented in this research. The main motivation of this study was the fact that these ions possessing a larger absorption cross-section than lanthanide ions. This enables more quantity of energy to be absorbed, which could be then released in the form of heat as a result of nonradiative processes. Both the absorption spectral range of Cr<sup>3+</sup> ions and the probability of the nonradiative relaxation are strongly dependent on the dopant concentration and the host material stoichiometry, thus appropriate modification of these parameters will provide enhancement of the light induced temperature increase. Therefore, in this work the influence of Cr<sup>3+</sup> ions concentration on the effectiveness of light-induced temperature increase will be estimated.

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# Growth and scintillation properties of a novel K<sub>2</sub>CeCl<sub>5</sub>/LiCl eutectic for thermal neutron detection

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**[Introduction]** Scintillators were used in radiation detection applications such as medical imaging and security system. Scintillators for thermal neutron detection have been developed. Thermal neutron detection requires solid scintillators with a high thermal neutron cross-section and low background gamma-ray sensitivity to discriminate neutron and gamma-ray. In this decade, single crystal scintillators such LiCaAlF<sub>6</sub> (LiCAF)[1] and Cs<sub>2</sub>LiYCl<sub>6</sub> (CLYC) [2] have been reported. These scintillators have a function of the pulse shape discrimination between neutrons and gamma-rays. However, <sup>6</sup>Li content is limited by the chemical formula. Most recently, eutectic scintillators for thermal neutron detection such <sup>6</sup>LiBr/CeBr<sub>3</sub>[3] and <sup>6-</sup>LiBr/LaBr<sub>3</sub>[4] were developed. These eutectics consist of a <sup>6</sup>Li-containing phases and scintillator phases, and can contain a higher concentration of <sup>6</sup>Li than single crystals.

**[Results]** K<sub>2</sub>CeCl<sub>5</sub>/LiCl eutectic was fabricated by the vertical Bridgeman method. K<sub>2</sub>CeCl<sub>5</sub> was selected as scintillator phase to obtain enough scintillation light (30,000photon/MeV) [5]. LiCl, KCl, and CeCl<sub>3</sub> powders (4N purity) enriched by <sup>6</sup>Li were mixed according to the eutectic composition of K<sub>2</sub>CeCl<sub>5</sub>/LiCl. The molar ratio of KCl:LiCl:CeCl<sub>3</sub>=48.4:27.5:24.1 mol% was employed. Fig.1 shows the photographs of eutectic crystal and fig.2 shows the polished wafer with 1mm thickness. Fig.3 shows the BSE of the eutectic. K<sub>2</sub>CeCl<sub>5</sub> and LiCl phases were confirmed by powder XRD and BSE analysis. The light yield of the sample was about 27,000 photon/neutron. In our presentation, growth condition, eutectic structure and scintillation properties will be discussed. Neutron response will be also demonstrated.



Fig.1 The fabricated eutectic crystal





Fig.3 The BSE of K<sub>2</sub>CeCl<sub>5</sub>/LiCl

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eutectic crystal

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Fig.2 The polished wafer of

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# Growth of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> Single Crystals with High Melting Point by Novel Growth Method and their Luminescent Properties

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Inorganic optical single crystals have been grown by various growth methods using a metal crucible such as Czochralski and Bridgman methods. In general, Iridium, Platinum and their alloys crucibles are used for the crystal growth because of the stability at high temperature. By the conventional growth methods, various luminescent single crystals have been developed as represented by the garnet-type and perovskite-type oxide materials. However, single crystals with higher melting point (m.p.) than ~2100°C couldn't be grown by the conventional methods due to the usage limitation of Ir (m.p. 2446°C) and Pt (m.p. 1768°C). Therefore, we developed a novel growth method to grow single crystals with high m.p. The method uses a tungsten (m.p. 3422°C) crucible and insulators are deoxygenated because the W is easy to oxidize by surrounding oxygen. In this study, La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> [LZO](m.p. 2283°C) and La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> [LHO](m.p. 2418°C) are selected for target materials with high m.p. and the luminescent properties of Eu-doped LZO and LHO single crystals were evaluated.

Crystal growth was performed by a modified micro-pulling-down ( $\mu$ -PD) method using a W crucible [Fig.1(a)]. The W crucible was surrounded by the deoxygenated ZrO<sub>2</sub> insulators to keep worm and prevent oxidization of the W crucible. LZO and LHO sintered powders were prepared by sintering the mixed powders with the stoichiometric composition at 1600°C for 12 h in air. The LZO and LHO sintered powders in the W crucible were melted by high-frequency induction heating, and the crystal growth was performed by pulling down the melt using a W seed. As a result of crystal growths, the LZO and LHO single crystals could be obtained as shown in Fig.1(b)<sup>[1,2]</sup>. There is no reactivity with the W crucible and the deoxygenated insulators could prevent the oxidation of the W crucible. Polished specimens indicated high transparency after post-annealing in air while as-grown LZO and LHO crystals indicated black color. The details of crystal growth and luminescent properties of Eu-doped LZO and LHO crystals will be reported.



Fig.1 (a) Schematic diagram of the modified μ-PD method using W crucible.(b) LZO and LHO single crystals grown by the modified μ-PD method.

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## HIGH-RESOLUTION LUMINESCENT STUDIES OF LiYF4:Ho FOR SENSOR APPLICATIONS

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The narrow-line spectra of transitions within the  $4f^N$  shell of triply ionized RE elements cover the entire visible and infrared range. RE-doped materials are widely used as laser media, phosphors, scintillators, in solar cells, etc. Nowadays, the RE-based luminescence thermometry is successfully developing, demonstrating a wide working temperature range, high thermal sensitivity and spatial resolution [1]. Here, we explore the high-resolution photoluminescence (PL) spectra of LiYF<sub>4</sub>:Ho single crystals at low temperatures and in external magnetic fields and suggest to use them for remote magnetic-field sensing.

An experimental setup based on a Bruker 125 HR high-resolution Fourier spectrometer was developed. It includes a self-made vacuum luminescent module, a cryomagnetic system of our own design based on a Sumitomo RP096 closed-cycle helium cryostat (cooling down to 2.8 K, magnetic fields up to 1 T), and a self-made PL registration module. PL of LiYF<sub>4</sub>:Ho crystal was excited by the wavelength 638.3 nm of a diode laser. Using this setup, we have measured the PL spectra of a monoisotopic <sup>7</sup>LiYF<sub>4</sub>:Ho<sup>3+</sup> (0.1%) single crystal at 3.5 - 10 K, in the wavenumber range 2500-16000 cm<sup>-1</sup> with a resolution better than 0.001 cm<sup>-1</sup>, under magnetic field (0 to 500 mT) directed along the c axis of the crystal. Well-resolved hyperfine structure with PL lines as narrow as 0.002 - 0.004 cm<sup>-1</sup> and with magnetic g factors as large as 10 - 15 was observed, including in the telecommunication spectral range. We show that using the telecom-wavelength PL line at 6085.85 cm<sup>-1</sup> [the  ${}^{5}I_{5}\Gamma_{34}$  (11241.6 cm<sup>-1</sup>)  $\rightarrow$  <sup>5</sup>I<sub>7</sub>  $\Gamma_{34}$  (5155.75 cm<sup>-1</sup>) transition of Ho<sup>3+</sup>] with g = 14.9 it is possible to measure the strength of an external magnetic field with the precision  $\delta B \approx 17 \ \mu T$ . It is worth noting that the range of measured magnetic fields can be very broad. It is also possible to determine the direction of the magnetic field by installing two LiYF4:Ho crystals with the mutually perpendicular c axes ( $g_{\perp} = 0$  for all  $\Gamma_{34}$  states because of selection rules). To control small deviations of the magnetic field strength, the method developed for magnetometry with nitrogen-vacancy (NV) centers in diamond [2] can be applied. In ref. [2], a field-dependent position of a dip in the NV luminescence intensity was controlled with an accuracy of ~µT using AOM-modulated laser excitation and a lock-in amplifier. The authors of ref. [2] noted that their "technique can be extended to other magnetically sensitive features in the NV PL or absorption, as well as features associated with other spin defects in solid-state systems". In particular, a narrow hyperfine component in the PL spectrum of <sup>7</sup>LiYF<sub>4</sub>:Ho<sup>3+</sup> can be used instead of a dip in a broad luminescence spectrum of NV. Unlike the case of NV centers [2], no additional field (102.4 mT, to set at the ground-state level anti-crossing, and a secondary coil to apply small modulation of this field) is necessary in the case of LiYF<sub>4</sub>:Ho, which can be favorable for quantum technology devices. Similar to a ruby luminescent pressure sensor, a small piece of LiYF4:Ho crystal can be placed nearby a quantum-memory crystal in the repeater, operating at low temperatures, to control an external magnetic field used to adjust the energy levels.

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# IMPROVED LINEARITY OF DOSE RESPONSE IN THE THERMOLUMINESCENCE OF GAMMA IRRADIATED LIF:Mg,Ti (TLD-100) FOLLOWING OPTICAL EXCITATION

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Introduction: Thermoluminescent (TL) dosimeters based on LiF:Mg,Ti (TLD-100) are widely used to determine patient doses in radiation diagnostics and external beam radiotherapy. The dose range of interest for radiotherapy is 1-5 Gy. In intra-operative electron radiation therapy the applied radiation dose can be as high as 30 Gy. Unfortunately the TL response of composite glow peak 5 is supralinear above 1 Gy reaching values of f(D), the normalized relative efficiency, as high as ~ 1.3 at 10 Gy and 2.0 at 30 Gy. Accurate dosimetry therefore requires knowledge of the particle energy spectrum impinging on the sample. Theoretical simulations [1] predicted that appropriate photon excitation post-irradiation could extend the linearity of the dose response to 30 Gy.

**Results**: Figure 1(a,b) show that both 3.65 eV and 5.0 eV photon excitation can extend the dose response linearity of composite glow peak 5 to 30 Gy.



Figure 1. The effect of 3.65 eV(a) and 5.0 eV(b) photon excitation on f(D) as a function of photon fluence for different doses: A – 30 Gy;B – 20 Gy; C- 10 Gy.

**Conclusions**: Post-irradiation photon excitation at energies of 3.65 eV and 5 eV (F center) can lead to a linear dose response following beta/gamma irradiation at a level of dose up to 30 Gy. The action of both photon energies involve electron and hole charge transfer between the various centers involving TL production.. It is hoped that these results will\_lead to the implementation of photon excitation post-irradiation in clinical therapy routines. Current attempts are focused on the identification of a single photon fluence and energy that will create a linear response over the entire dose range up to 30 Gy.

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## **O - 19**

## Investigation on effect of trap on afterglow process in long wavelength PersL SrMgGe2O6: Mn2+, Sm3+

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The development history of persistent luminescent (PersL) materials is very long, and it has also been extensively studied and reported. At present, the research on short-wavelength visible PersL materials are relatively mature, however, the study and reports on long-wavelength (even near-infrared (NIR)) PersL materials are still deficient [1], therefore, exploring long-wavelength PersL materials are essential. So how to design and achieve long-wavelength PersL materials with good performance? Firstly, we choose the germanate as host in that it has suitable cation sites and smaller band gap [2]. Besides, Mn2+ ion is an excellent activator as its abundant energy level, which would prefer to generate long-wavelength emission [3]. Based on this, we realized SrMgGe2O6: Mn2+, Sm3+ (NIR) PersL materials, calculated the defect formation energy with VASP to judge which site the Mn2+ will occupy and to analyze what kind of trap it caused by that dominate the afterglow process [4,5], thereby the possible mechanism is proposed.



Figure. SrMgGe2O6: Mn<sup>2+</sup>, Sm<sup>3+</sup> (NIR) PersL materials

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#### Lanthanide MOFs linear and nonlinear optical properties

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Metal-organic frameworks (MOFs) are crystalline porous molecular materials, which consist of organic molecules (linkers) and metal centers, for example lanthanide (Ln) ions. In recent years, these materials have emerged as a new class of materials for photonics applications such as solid-state lighting, lasing and nonlinear optics.<sup>[1,2]</sup> In this work, we present a series of Ln-MOFs doped with terbium ( $Tb^{3+}$ ) and europium ( $Eu^{3+}$ ) ions with 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC) as linker. The crystallization process was monitored in situ using nonlinear scattering techniques and showed that the Ln-BTC MOFs crystallize in non-centrosymmetric space groups. The compounds crystallize in tetragonal space groups P4122 (Tb-BTC) and  $P4_{3}22$  (Eu-BTC), as well as the mixed doped Tb<sub>100-x</sub>Eu<sub>x</sub>BTC compounds with different molar ratios (x = 0.01, 0.05 and 0.1). The structures were characterized with single-crystal X-ray diffraction (XRD), powder XRD, FTIR and CHN analysis. The crystallization process was monitored in situ using nonlinear scattering techniques and showed that the Ln-BTC MOFs crystallize in non-centrosymmetric space groups. Additionally, the optical response of the Ln-BTC MOFs could be revealed by the combined power of linear and nonlinear spectroscopy (two-photon, SHG). The results obtained from the nonlinear optical study will be used as an input for the quantum spectroscopy investigation that is in progress, and it's based on the interaction of MOFs with entangled photons.



Figure 1. Graphical representation of a Ln-BTC MOF structure with linear and nonlinear excitation of luminescence and SHG.

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## Method to Improve Optical Refrigeration of Yb:LiYF4

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Optical refrigeration is the only method capable of reaching cryogenic temperatures in space and is therefore important for improving sensor performance in extreme environments. Unfortunately, laser cooling efficiencies are generally low and to date they have been found to be constant in any given material. However, we show that absorption saturation offers the prospect of operating devices such as imaging arrays with reduced noise at lower temperatures than previously attainable through laser cooling.

The cooling efficiency for optical refrigeration by Anti-Stokes Fluorescence was measured in a 10% Yb<sup>3+</sup>:LiYF<sub>4</sub> crystal by Differential Luminescence Thermometry (DLT) and Thermal Lens Spectroscopy (TLS) over a range of pump intensities [1]. The main result of this work is the observation of enhanced cooling efficiency at high intensities. Results for cooling of 10% Yb:LiYF<sub>4</sub> with continuous-wave Ti:Al<sub>2</sub>O<sub>3</sub> radiation are shown in Figure 1 where the black (high intensity) curves reach higher efficiency levels than the blue (low intensity) curves at wavelengths longer than 1000 nm. This enhancement is evident in Figures 1(a) and 1(b) and arises from saturation of the background impurity absorption which ordinarily limits cooling efficiency to a low, intensity-independent value. The behavior recorded in both TLS and DLT experiments is very unexpected because impurity absorption was previously thought to involve allowed transitions of transition metal ions which should be unsaturable with intensities below  $I \sim 10^4$  W/cm<sup>2</sup>. For wavelengths longer than 1000 nm, higher cw pump intensity nevertheless led to improved cooling efficiency because parasitic absorption and heating was diminished, yielding higher cooling efficiency for higher pump intensities.



Figure 1. Cooling efficiencies versus wavelength in Yb:YLF measured at high and low intensities by (a) TLS and (b) DLT techniques.

The enhancement of cooling efficiencies at long wavelengths agreed with an experimental determination of the saturation intensity of background impurities and theoretical estimates of the saturation parameters of Fe<sup>3+</sup> impurities. The results were at variance with the parameters for other valences of iron however. This suggests that in Yb<sup>3+</sup>:LiYF<sub>4</sub> forbidden transitions of trivalent iron may account for the observed cooling behavior versus pump intensity.

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## MgAl<sub>2</sub>O<sub>4</sub> AND ZnAl<sub>2</sub>O<sub>4</sub>: MICROSTRUCTURE, DEFECTS AND LUMINESCENCE

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Spinels present large compositional diversity and property tunability and thus are of interest to many fields. The cubic structure and broad optical transparency associated with a large band gap make these materials particularly attractive for optical applications [1]. The capacity of accommodating relatively large amounts of anti-site defects make them good candidates for applications involving radiation damage.

MgAl<sub>2</sub>O<sub>4</sub> and ZnAl<sub>2</sub>O<sub>4</sub> powders were prepared by the co-precipitation method and calcined at 900 °C for 1 hr in air. Natural ('spinel' and gahnite) and artificial crystals were also investigated. Structural characterization was executed by X-ray diffraction and Raman spectroscopy. Radioluminescence (RL) under X-ray excitation from room temperature to 400 °C was recorded towards the identification of all luminescence centers present in the samples. Thermoluminescence (TL) spectroscopy measurements up to 400 °C were executed towards the identification of the recombination centers involved in the TL process. RL measurements revealed that both spinels presented a broad band peaked at ~400 nm attributed to antisites and Cr<sup>3+</sup> and Mn<sup>2+</sup> impurities. TL spectroscopy measurements revealed mostly from Cr<sup>3+</sup> impurities. Analysis of the glow peak shape and behavior under different X-ray irradiation times revealed a complex behavior not described by either first or second order kinetics.

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RL spectra of MgAl<sub>2</sub>O<sub>4</sub> samples with different origins.

## **O** - 23

# Multifunctional NaYF<sub>4</sub>:Nd<sup>3+</sup>, Cr<sup>3+</sup> nanoparticles for luminescence thermometry and optical heating applications

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# Keywords: luminescent thermometry, light-to-heat conversion, transition metal ions, lanthanide ions

More recently, multifunctional nanoparticles have been the subject of intensive research in the field of nanotechnology.[1] The understating of the principles of operation of luminescent thermometers and nanoheaters and the significant progress in this field observed, caused that more and more efforts are being made currently to develop nanoparticles that allows combining these two functionalities. The development of such multifunctional materials requires the appropriate selection of the relevant host, optically active ion(s), and optimization of their concentration. The choice of host material is primarily determined by the requirements of specific application. In the case of biological application, the small particle size (below 100 nm) with narrow size distribution, high biocompatibility and the formation of stable colloidal systems in physiological solutions are the most important constraints. Additionally, from the luminescent thermometry perspective high sensitivity (S<sub>R</sub>) to temperature changes is important. The high sensitivity can be achieved by using transition metal ions (TM<sup>3+</sup>) and lanthanides (Ln<sup>3+</sup>) as a co-dopants.[2] In such systems, the Ln<sup>3+</sup> ion acts as a luminescence reference, not sensitive to temperature changes, whereas TM<sup>3+</sup> is temperature probe. The susceptibility of TM<sup>3+</sup> to temperature changes results from a high nonradiative relaxation probability which is observed for TM<sup>3+</sup> ions due to the strong electron-phonon interaction. An efficient nonradiative processes lead, in turn, to conversion of light into heat, which is released to the environment. Therefore, by taking advantage from these phenomena and by the optimization of the dopant concentration it is possible to develop a nanoparticle that serves as simultaneously as a nanoheater and luminescent thermometer.

Hence, this research focus on the optimization of the synthesis, structural and spectroscopic properties of NaYF<sub>4</sub> nanoparticles doped with transition metal and lanthanide ions for light-to-heat conversion and luminescent thermometry application.

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## NANOSCALE SENSING OF TEMPERATURE DURING CATALYTIC REACTIONS IN A BROAD TEMPERATURE RANGE

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Catalysis is performed on a broad pressure and temperature scale, ranging from ambient conditions to temperatures above 1000K, which depends on the catalyst and reaction of interest. Small variations in reactor temperature are known to affect the catalytic performance, but local heat effects during catalytic reactions can play an equally important role on the reaction rate or selectivity and are rarely studied in detail. To study local heat effects in catalytic reactions, nanoscale temperature measurements over a broad temperature range and with a high spatial resolution are necessary, which can be used to rationally improve the catalysts. In this work, we have developed thermally stable nanoscale temperature sensors and studied their optimal sensing properties in a broad temperature range (i.e., 300-1200 K, Figure 1a). These nanoscale thermometers comprised Y<sub>2</sub>O<sub>3</sub> doped with the lanthanide neodymium (Nd<sup>3+</sup>), which exhibits temperature-dependent emission in the near infrared (NIR). By analyzing the effects of temperature and doping concentration on luminescence quenching, we identified that the minimal measurement uncertainty is achieved with 1-1.5%Nd<sup>3+</sup> doping concentration (Figure 1a). Furthermore, the thermometry nanoparticles were applied to catalytic reactions with operating temperatures ranging from 300K to 1100K (Figure 1b). We revealed spatial temperature heterogeneities measured with µm resolution (in the order of a few degrees K) and with a temporal resolution of a second. CO<sub>2</sub> electroreduction was studied with thermometry particles in temperatures ranging from 300-320K, where a current density of  $-50 \text{ mA/cm}^2$  resulted in a temperature increase of  $\sim 10$ K. The exothermic CO<sub>2</sub> methanation reaction (using a Ni/TiO<sub>2</sub> catalyst,  $\Delta H_r = -165$  kJ/mol) was studied around 600-750K, while reactant gasses (e.g., CO<sub>2</sub>) were pulsed to study the heat generation during the formation of reaction products (e.g., CH<sub>4</sub>), observing jumps of ~10K. Finally, methane dehydroaromatization was studied around 900-1000K (using a Mo-ZSM-5 catalyst,  $\Delta H_r = +532$  kJ/mol), showing an endothermic jump of ~20K. The formation of products in the thermocatalytic reactions was detected with on-line mass spectrometry (MS) and correlated to the observed heat profile. The application of this sensor shines light on the temperature heterogeneity of catalyst particles on the nanoscale during catalysis and can be used to rationally design the optimal catalyst.



**Figure 1.** a) The relative temperature uncertainty at a temperature range of 300-1200 K and neodymium concentrations of 0.1-10%. b) Overview of the catalytic reactions in which the described  $Y_2O_3:Nd^{3+}$  was applied, with (1) CO<sub>2</sub> electroreduction on a silver catalyst, (2) CO<sub>2</sub> methanation with a nickel catalyst and (3) methane dehydroaromatization with Mo-ZSM-5.

# New ferroelectric photovoltaic devices: the origin of a large difference in power conversion efficiency between the hexagonal manganites and ferrites

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In order to convert solar energy into electricity, the conventional solar-cell technology employs the semiconductor p-n junctions in which the photogenerated electron-hole pairs are separated by the electric field formed at the p-n interface. An alternative way, explored in the last two decades, is based on the use of ferroelectric compounds, in which the photogenerated electron-hole pairs are separated by spontaneous electric polarization existing in this kind of material. The latter exhibit some advantages over the conventional photovoltaics [1]: their voltage can be a few orders of magnitude higher than the bandgap of the material, and the photo-current polarity can be switched by applying an electric field of reversed direction. However, the ferroelectric photovoltaics still exhibit much inferior power conversion efficiency (PCE) compared to the conventional ones. A tentative to improve this property turned this kind of material an object of intensive research lately [2].

In this work, we analyzed the origin of a very large PCE difference between two ferroelectric photovoltaic materials, LuMnO<sub>3</sub> (h-LMO) and LuFeO<sub>3</sub> (h-LFO), recently observed by the experiment [3,4]. These two compounds are typical representatives of larger families of hexagonal manganites and ferrites (space group P6<sub>3</sub>*cm*).

We concluded that the PCE difference arises from different fundamental properties of the materials, connected with the details of their electronic structure and optical response (calculated previously in the frame of DFT by our group [5,6]): (1) effective masses of the photocarriers, and (2) binding energy of the photo-created electron-hole pairs (excitons) [7].

The obtained results clearly demonstrate that the photogenerated charges in the h-LMO are lighter than in the h-LFO, causing superior charge mobility and a higher PCE value of the h-LMO. Binding energies of the excitons, estimated in the frame of the Wannier-Mott model, indicate that the dissociation of the electron-hole pair requires less energy in the h-LMO than in the h-LFO, also contributing to the higher PCE value of the h-LMO. Additionally, it was found that the electronic photocurrent exhibits high anisotropy in both compounds: electron effective mass is much higher when the carriers move along the hexagonal c-axis than along any direction within the hexagonal basal plane.

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### NEW POSSIBILITIES OF PHORSPHOR FROM A NANO PERSPECTIVE

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Advance of nanotechnology provides a new and powerful means for the in-depth understanding and development of phosphor materials. Many mechanism problems that are difficult to quantify in bulk materials can be solved with the aid of nanostructures, and nano-engineering also gives a new dimension to significantly optimizing luminescence performance. At the same time, the main restrictions encountered by the application of phosphor materials in important fields have also been alleviated or even eliminated, and application areas have been greatly expanded, for example, but not limited to, biology, medicine and photochemistry.

We have long been committed to exploring the dynamics of energy transfer and conversion in phosphor materials and designing functional nanophosphorus for photochemical and biomedical applications such as light induction therapy, imaging, immunoassays, and applications as light nanotransducers in photocatalysis/photosynthesis.

By designing nanostructures, we successfully and precisely customized the nonlinear luminescence dynamics of rare earth-based phosphors and identified the quenching mechanism of internal defects/impurities in upconversion luminescence for the first time. We also found channels that break through the inherent limits of upconversion luminescence efficiency, and the upconversion efficiency was therefore increased by ~100 times, indicating that there is still room for further improvement in nonlinear luminescence efficiency.

As the luminescence of nanophosphorescence increases, its application in photochemistry and biomedicine has also been strengthened, and examples will be introduced.

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## **O** - 27

# On the time dependence of white emission intensity and the temperature of transparent Cr-doped YAG ceramics

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Since its discovery in 2009 by Tanner and co-workers, laser-induced white emission (LIWE) has been the subject of numerous reports in the past decade [1]. LIWE was generated under a focused laser beam above a threshold in a vacuum ambient and is characterized by a high exponent of the power dependence characteristic for multiphoton absorption, long rise and decay times and a relatively low temperature of the light emitting sample [2]. These characteristics, including broadband light emission and pressure dependence may lead to the conclusions that LIWE is caused by thermal heating, which isn't the case. This is evidenced by the fact the most of the studied materials have low thermal conductivity, which contributes to the accumulation of thermal energy [3]. Therefore, the effect of temperature on LIWE is currently under discussion.

The purpose of this work is to study the effect of temperature on the LIWE characteristics. For this, a Cr-doped YAG transparent ceramics was synthetized by solid-state reaction sintering in vacuum at 1750 °C. LIWE was investigated under vacuum (10-5 Pa) excited by focused laser beam ( $\lambda_{exc}$  - 1064 nm, P - 3.4 W, D - 0,175 mm). More details were reported earlier [4,5].



Fig. 1: The photo of LIWE under CW excitation of the transparent Cr:YAG ceramics.

We have found that transparent Cr:YAG ceramics is able to generate bright LIWE at excitation power above a certain threshold. LIWE covers whole visible and near infrared region between 28000 cm<sup>-1</sup> (350 nm) and 10000 cm<sup>-1</sup> (1000 nm) [5]. It was shown that LIWE intensity increases with increasing excitation density. There are four photons involved in the LIWE process. LIWE intensity increased with an increase in the excitation time and reached a maximum with a subsequent decrease. An increase in LIWE intensity is probably caused by an increase in host temperature. The host temperature during LIWE was estimated from Cr<sup>3+</sup> emission. It was shown that the maximum at 300 °C. The host temperature during LIWE did not reach 600 °C. The IVCT model was used to explain the LIWE phenomena [4].

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## OPAL-LIKE PHOTONIC STRUCTURES MADE OF SINGLE CRYSTAL DIAMOND

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Opals are photonic crystals (PhC) with face-centered cubic lattice made of SiO<sub>2</sub> spherical particles usually several hundred nanometers in diameter. Spatially modulated dielectric constant of PhC allows control of light propagation, particularly, the Bragg peak in reflection spectrum occurs at a certain wavelength  $\lambda_{max}$ . For (111) plane the peak wavelength is

$$\lambda_{\max(111)} = 2d_{111} \cdot \sqrt{\varepsilon_{eff} - \sin^2 \theta} \tag{1}$$

where  $\theta$  is the incidence angle (0° at normal incidence),  $\varepsilon_{eff}$  is the effective dielectric constant of PhC,  $d_{111}$ =0.816 *D* is the opal lattice period consisted of spheres of diameter *D*. Filling of voids between the spheres with other materials preserves the composite structure to be PhC. Diamond provides both high dielectric contrast ( $\varepsilon$ =5.71) and optical transparency in the near-UV, visible or IR ranges, being an interesting material for PhCs with high mechanical strength and high thermal conductivity. Previously, inverse opal structures of nanocrystalline diamond were produced [1] using microwave plasma chemical vapour deposition (MPCVD) by template synthesis. Later, a bottom-up approach [2] to grow epitaxially single layer inverse opal structure of monocrystalline diamond was demonstrated. Here we report on fabrication of single crystal diamond multilayer opal-like PhC for the visible range.



Fig. 1. Schematic of template synthesis of opal-like single crystal diamond structures using MPCVD.

Opal layers of silica particles 240 nm in diameter were deposited on single crystal diamond substrate by vertical deposition technique (Fig. 1). Then, we epitaxially grew diamond under the following MPCVD conditions: 2.45 GHz magnetron power of 2.7-3.0 kW, pressure of 50-60 Torr, H<sub>2</sub>/CH<sub>4</sub> flow rate of 15/485 sccm, substrate temperature of 820-840°C. Optical reflection spectra of the SiO<sub>2</sub> template and ordered diamond-SiO<sub>2</sub> composites were measured within the angles of light incidence  $\theta$ =15-60° and compared with numerical simulations of the experimental reflection spectra by the scattering matrix method.

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# OPTICAL PROPERTIES OF DIATOM ALGAE: RESEARCH METHODS AND POTENTIAL APPLICATIONS

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Diatom algae are one of the most abundant and ecologically important microorganisms as they are responsible for almost 20% of the total amount of oxygen and 40% of the annual carbon production in the ocean [1]. One of the main features of diatoms is the astonishingly intricate design and architecture of their silica-based cell walls called frustule [2]. Diatoms represent an attractive object from the point of view of modern optics as well as material science, because of their hierarchically structured highly porous cell wall having unique optical and mechanical properties, optimized by millions of years of evolution to efficiently absorb light and produce biomass as a result of photosynthesis. Recent studies have revealed very interesting optical properties of diatoms such as light transmission, diffraction, focusing and photoluminescence, highlighting the photonic crystal behavior of silica shells [3]. Moreover, we studied mechanical properties of centric diatoms with and without organic components using atomic force microscopy (AFM) and nanoindentation technique. We also showed that the growth of diatoms during long-term batch cultivation can be readily monitored using photonic approaches, such as fluorescent imaging with the help of IVIS SpectrumCT Imaging system and optoacoustic visualization using raster scanning optoacoustic mesoscopy (RSOM) [4-7]. This set of monitoring techniques can be employed in aquaculture and bioreactor practice to facilitate the cultivation of diatoms and the extraction of bioactive substances for numerous applications. Owing to such silica-based structure, diatom frustules could be an inspiration for various photonic devices and potentially serve as biosensors, micro-lenses, micro-concentrators, membrane for optoacoustic sensors, optical filters, polarizers, gas detectors, etc. This work was supported by Russian Science Foundation (№ 22-14-00209).

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## Optical properties of InGaN epitaxial layers doped by Si and Ge

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Gallium nitride (GaN) is a wide band gap semiconductor with forbidden gap of 3.4 eV at room temperature. Due to its multiple advantageous optical properties, its derivatives have been applied in various application fields. InGaN/GaN quantum wells (QWs) are widely used in modern light-emitting diodes and lasers as the active region because of their surprisingly high luminous efficacy especially in the blue region of visible spectrum [1,2]. Furthermore, these structures may be also applicable in high-electron-mobility transistors (HEMTs). Recently, InGaN/GaN heterostructures have become of a great interest for scintillating applications as well, mainly due to their favourable high excitonic binding energy resulting in sub-nanosecond decay time, high density (6.15 g/cm<sup>-3</sup>), high radiation hardness, perfect temperature and chemical stability, feasibility of tuning emission wavelength by different In concentration and the availability of MOVPE (metal-organic vapour phase epitaxy) technology allowing growth of high crystallographic quality layers [3,4]. Therefore, the InGaN/GaN can be implemented in the *time-of-flight* techniques, e.g., in TOF-PET (positron emission tomography). On the other hand, the strong drawback of these GaN-based nanostructures is the limited thickness of the multiple quantum wells active region which significantly restricts detection efficiency, and the presence of slow defect-related band, origin of which in bulk GaN and InGaN/GaN MQW structures is still under consideration [5,6].

The n-type doping is well-established technique to suppress the polarization fields inherently present in the InGaN/GaN heterostructures. In scintillator application, the suppression of the polarization field is essential to obtain fast luminescence decays. However, n-type doping (usually accomplished by introduction of Si or Ge) might lead to formation of new (compensation) centres in the material affecting the luminescence properties as well.

Up to now, reports on Si-doped and especially Ge-doped InGaN properties are scarce. Therefore, we have prepared and characterized series of 100 nm thick Si or Ge doped InGaN layers by MOVPE technology. We will focus on characterization of the layers by means of time-resolved luminescence and scintillation spectroscopy. Special attention will be given to photoluminescence excitation and emission spectra, photoluminescence decay curves under various excitations together with their temperature dependences (8 - 800 K temperature range), time-resolved radioluminescence spectra with the time resolution below 100 ps and wavelength-resolved thermally stimulated luminescence.

Based on the combination of presented results, we will conclude the effect of Ge and Si-doping in InGaN-based layers on the properties of defect-related luminescence.

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### 0 - 31

# **OPTICAL PROPERTIES OF Sm<sup>3+</sup> IONS DOPED BISMUTH GERMANATE GLASSES FOR PHOTONIC APPLICATIONS**

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Sm<sup>3+</sup> ions doped bismuth germanate glasses with compositions  $(100-x)(0.2Bi_2O_3-0.8GeO_2)-xSm_2O_3$  (x=0.2, 1, 2 in mol%; labeled as BGOSx) have been synthesized by a conventional melt quenching method and characterized with x-ray diffraction (XRD), Fourier transform infrared (FT-IR), absorption, photoluminescence (PL) and decay time measurements. Moreover, other related physical and optical properties have been calculated. Fundamental vibrations of bismuth and germanate groups have been described by IR transmittance spectrum. Using the optical absorption spectra, the nephelauxetic ratio ( $\beta$ ), bonding parameter ( $\delta$ ) and optical band gap energy (Eg) values have been calculated. Judd-Ofelt (J-O) intensity parameters ( $\Omega_2$ ,  $\Omega_4$ ,  $\Omega_6$ ) have been determined from the absorption spectra. The emission spectra of BGSx glasses under 403 nm excitation present intense orange emission at 597 nm.

Using J-O parameters and emission spectra, various radiative properties like transition probabilities (A<sub>R</sub>), branching ratios ( $\beta_R$ ), stimulated emission cross section ( $\sigma_p^E$ ), radiative decay time ( $\tau_R$ ) and quantum efficiency ( $\eta$ ) for specific emission transitions of Sm<sup>3+</sup> ions have been determined. The nature of decay curves of  ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$  (597 nm) emission transition for Sm<sup>3+</sup> ions doped bismuth germanate glasses has been investigated using Inokuti–Hirayama model. Also, PL quantum yield values were calculated for the title glasses. The obtained results show that BGSx glasses are promising materials for photonic applications such as visible orange lasers.

## Strategies For Designing Ultra-Broadband Near-Infrared Long Persistent Luminescent Materials

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Near-infrared (NIR) long persistent luminescent (LPL) materials have attracted the interest of many researchers as they have potential applications in many aspects.[1] However, majority of studies on Cr<sup>3+</sup> ion-doped LPL materials have focused on Cr<sup>3+</sup> in octahedral, while studies on Cr<sup>3+</sup> luminescence in tetrahedral have been limited, which is detrimental to fully explore Cr<sup>3+</sup> ion-doped LPL materials with potential applications. Moreover, the luminescence of most Cr<sup>3+</sup> ion-doped LPL materials is limited to the short-wavelength NIR-I (700-900nm) region, which also makes the application of the samples limited.[2] In this presentation, we show a method to design ultra-broadband NIR LPL material Na<sub>2</sub>CaGe<sub>6</sub>O<sub>14</sub> (NCGO):Cr<sup>3+</sup> by combining the charge compensation principle and the multi-site occupation principle. Firstly, we meticulously discuss the emission peak attribution of NCGO:Cr<sup>3+</sup>. Secondly, we confirm the coordination environment of  $Cr^{3+}$  ions by electron paramagnetic resonance spectroscopy (EPR) and X-ray absorption near-edge spectroscopy (XANES). Finally, the application prospects of NCGO:Cr<sup>3+</sup> in many aspects were investigated in detail. In addition to providing a new ultra-broadband NIR LPL material with excellent prospects for multifunctional applications, this work can also provide implications for the study of multi-site Cr<sup>3+</sup> ion luminescence.



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# TAKING ADVANTAGE OF TRIVALENT LANTHANIDE IONS FOR REPROGRAMMABLE AND RECONFIGURABLE PHOTONIC MOLECULAR LOGIC GATES

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Since the first digital-programmable computer was developed the information technology has been growing up continually.<sup>1</sup> Computers and related systems have become more efficient and smaller because of the scaling shrinkage of the silicon-based components over a relatively short period of time. Nevertheless, there is a general interest to become computers even smaller, smarter and powerful and the only way to achieve such purpose is by designing a miniaturized scale of the computer circuit components.<sup>2</sup> Classical miniaturization of the computer with silicon-based components eventually is reaching its limits, in terms of physical limitations<sup>3</sup> and high economical costs.<sup>4</sup> In this sense, it is when molecular logic gates come into consideration, allowing the integration of self-assembly molecular technology whose dimensions are in the order of atom sizes.

Molecular logic devices constituted by luminescent signaling molecules are being reported since the 90's as an alternative approach towards molecular computing, showing that molecules can perform some of the computational functions achieved in semiconductor technology. The examples listed in the literature present molecules that are actuated almost exclusively by chemical species.

Recently we reported a Eu<sup>3+</sup>/Tb<sup>3+</sup> co-doped organic–inorganic hybrid is presented as an illustrative all-photonic logic platform constructed through the decay dynamics of both lanthanide and hybrid host emissions.<sup>5</sup> Besides combinatory AND, NAND, and INH logic gates, this system presents on-choice Eu<sup>3+</sup>, Tb<sup>3+</sup>, or host emission enabling the development of reprogrammable and reconfigurable photonic molecular logic gates. All-photonic temperature-reprogrammable changes from AND to INH logic gates and a reconfiguration among INH and AND1 or AND2 gates, based on the excitation wavelength are demonstrated, showing a clear step forward toward mirroring electronic logic counterparts.

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## Temperature-dependent Photoluminescence Saturation Effects in K<sub>2</sub>SiF<sub>4</sub>: Mn<sup>4+</sup>

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Blue light emitting diodes (LED) based on InGaN are increasingly used in team with phosphor powders to generate artificial light of varying colours. In warm white LED architectures the optically active  $Eu^{2+}$  ion is often used to emit red light. However, this ion has the drawback that a typical emission spectrum extends into the infrared, where human eyes cannot observe it anymore. An alternative is to use a red phosphor that has sharp emission lines around 600nm, such as optically active  $Mn^{4+}$  incorporated in K<sub>2</sub>SiF<sub>4</sub>.

 $K_2SiF_4:Mn^{4+}$  is well-known for its applications in display technology, but has found limited applications in consumer lighting. The problem is that if blue light with excitation intensities typical for blue LEDs is used, the efficiency of the red light emission drops. It has already been shown that the loss of efficiency is primarily caused by ground state depletion (GSD) due to strong absorption, slow ms decay and thermal quenching.<sup>1</sup> However, the temperature-dependent emission mechanism of Mn<sup>4+</sup> in this host material allows for the modulation of the luminescence decay time.

Here we show measurements on the highly similar  $K_2TiF_4:Mn^{4+}$  that capture the interplay between GSD and temperature by varying the temperature as a function of excitation density. Because of the temperature dependent emission mechanism in KTF:Mn<sup>4+</sup> material we are able to integrally study saturation and laser-induced heating effects.



**Figure 1.** Laser induced heating and *in-situ* analysis of the heating process. (a) Schematic depiction of the Stokes and anti-Stokes emission lines from the vibrational levels of the <sup>2</sup>E excited state to the <sup>4</sup>A<sub>2</sub> ground state of Mn<sup>4+</sup>. (b) Shows the emission spectra ( $\lambda_{exc} = 460$ nm) from 10-300K and clearly demonstrates the temperature-dependent Stokes and Anti-Stokes emission. The ratio between the anti-Stokes and Stokes emission is in Boltzmann equilibrium and allows us to monitor laser-induced heating effects. (c) Different temperature set-points from which the laser-induced heating is monitored over an intensity range of 0.05 - 9 W/mm<sup>2</sup>.

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## Thermal Luminescence quenching in Mn<sup>2+</sup>

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In the LED phosphor industry an important focus is on efficient warm white LEDs and improving the colour quality of displays (extending the colour gamut). A promising ion to fulfil both these qualities is Mn<sup>2+</sup>, as it can emit narrow band green or a narrow band red in tetrahedral or octahedral coordination, respectively. At elevated temperatures most luminescent ion lose their emissive properties. Since LEDs can locally reach temperatures up to 150°C this can form a problem. Understanding the mechanism that is responsible for the quenching is thus essential for future phosphors with Mn<sup>2+</sup>, but so far this has been hardly been investigated.

In this research, several host materials were doped with  $Mn^{2+}$  and the emission as well as the luminescence lifetime were measured for a wide temperature range (80K to 1250K). In addition, for four hosts (AlN,Zn<sub>2</sub>SiO<sub>4</sub>, MgGe<sub>2</sub>O<sub>4</sub>, ZnGe<sub>2</sub>O<sub>4</sub>) thermally stimulated luminesce measurements were performed under different excitation temperatures showing that for these hosts the luminescence quenching mechanism is thermal ionization of  $Mn^{2+}$ . We observe that the thermal quenching temperature for  $Mn^{2+}$  emission in different hosts can vary strongly, from room temperature to record high temperatures around 1200 K. The quenching temperature was correlated with the bandgap of the host material. This correlation is a further strong indication that the quenching mechanism is the same for  $Mn^{2+}$  in all ionic hosts.


## Thermoresponsive polymeric nanolenses magnify the thermal sensitivity of single upconverting nanoparticles

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Lanthanide-based upconverting nanoparticles (UCNPs) are trustworthy workhorses in luminescent nanothermometry [1-2]. The use of UCNPs-based nanothermometers has enabled monitoring of in vivo thermal therapies in real time [3]. However, UCNPs boast low thermal sensitivity and brightness [4], which, along with the difficulty in controlling individual UCNP remotely [5], make them less than ideal nanothermometers at the single-particle level. In this work we show how these problems can be elegantly solved using a thermoresponsive polymeric coating [6]. Upon decorating the surface of NaYF<sub>4</sub>:Er<sup>3+</sup>,Yb<sup>3+</sup> UCNPs with poly(Nisopropylacrylamide) (PNIPAM), a >10-fold enhancement in optical forces is observed, allowing stable trapping and manipulation of a single UCNP in the physiological temperature range (20-45 °C). This optical force improvement is accompanied by a significant enhancement of the thermal sensitivity —reaching a maximum value of 8% °C<sup>-1</sup> at 32 °C caused by the temperature-induced collapse of PNIPAM. Numerical simulations reveal that the enhancement in thermal sensitivity mainly stems from the interaction of trapping and reemitted radiations with the high-refractive-index polymeric coating that behaves as a nanolens of high numerical aperture. The results included in this work demonstrates how UCNP nanothermometers can be further improved by an adequate surface decoration and open a new avenue towards highly sensitive single-particle nanothermometry.



Figure 1. A novel single particle nanothermometer. Temperature responsive Poly(N-isopropylacrylamide) was coated on the surface of 30 nm-NaYF<sub>4</sub>:Er, Yb nanoparticles.

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# Unrevealing the optical properties of Dy<sup>2+</sup> and Ho<sup>2+</sup> doped in different halide host lattices

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Due to the low stability of  $Dy^{2+}$  and  $Ho^{2+}$  ions their luminescent properties are very rarely investigated. Especially direct doping in the divalent state was never presented before. In the past, samples doped with  $Dy^{3+}$  and  $Ho^{3+}$ -ions are presented which were reduced by X-rays,  $\gamma$ -rays, or metal vapor [1-3]. With such a procedure, it can be assumed that defects are produced and the coordination sphere of the divalent lanthanoids will be distorted.

In this work, direct doping of these divalent lanthanoids is presented for the first time. The materials  $SrX_2:Dy^{2+}$ ,  $Ho^{2+}$  and  $MFX:Dy^{2+}$ ,  $Ho^{2+}$  (M = Ca, Sr, Ba; X = Cl, Br) where achieved by melting synthesis of the hosts together with the dopants  $DyCl_2$  and the mixed valent compound  $Ho_5Cl_{11}$ , respectively, which were prepared before. In the emission spectra of both lanthanide ions one or two sharp lines could be observed (Figure 1 and 2). This emission bands can be assigned to the parity forbidden 4f-4f-transitions of the divalent ions. The observation of one or two emission bands depends on the energetic position of the 5d-level, which is determined by the structure of the host lattice, crystal field splitting, the nephelauxetic effect, bond lengths, site symmetries.



Figure 1: Emission spectra of  $Ho^{2+}$  doped in a) SrFCl and b) SrCl<sub>2</sub> at room temperature (red) and 10 K (blue)



Figure 2: Emission spectra of  $Dy^{2+}$  doped in SrFCl at 10 K

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## Flexible optoelectronic devices based on III-V nanowires encapsulated into polymer matrix

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Flexible optoelectronic applications and devices are in high demand in wearable electronics, touchscreens of foldable gadgets, light-emitting devices (LED) and bright screens, electronic papers, implanted sensors, etc. Nowadays, the most developed flexible devices are based on organic materials. However, III-V semiconductor materials have advantages over conventional organic compounds in terms of long-term stability, electroluminescence properties and quantum efficiency, especially in the blue and red spectral ranges. Nanowires owing to their high length-to-diameter aspect ratio and geometrical shape possess outstanding mechanical properties, their rod-like form also facilitates the light waveguiding and light directivity, which are very essential for efficient light-emitting device development. Modern III-V semiconductor technology allows bandgap engineering and waveguide properties tailoring.

In this work we present the synthesis of GaP nanowires with direct bandgap GaPAs insertions and their processing for efficient LEDs operating in red spectral range and IR-visualizers. The arrays of GaP/GaPAs nanowires grown by molecular beam epitaxy on Si substrate were encapsulated into optically transparent polymer matrix and released from the growth substrate providing flexibility and even stretchable properties. Applying the transparent conductive layers based on the net of single wall carbon nanotubes to the open ends of nanowires embedded into polymer matrix allows contacting of these nanostructures for electroluminescence. We have shown experimentally that such transparent flexible GaP/GaPAs nanowires-based membranes can emitted light in the red spectral range. The developed approach also was applied to InGaN/GaN microwires operating in blue spectral range. Thus, combining such membranes encapsulating different materials, which have electroluminescence in different visible spectral ranges, allows the development of RGB applications.

Moreover, such membranes based on GaP or Si nanowires can be used for efficient IR-to-visible light visualizers, the converted light of which can be detected by the naked eye. The principle of work is based on the phenomenon of second or third harmonic generation.

The proposed approach for nanowire processing to flexible membranes can be also applied for development of piezogenerators, solar cells or IR-photodetectors based on (In)GaN, GaAs and InAs nanowires, respectively. Thus, III-V, III-N and Si nanowires with fascinating optoelectronic properties pave the way for future flexible applications.

# STM nanolithography of hybrid structures for tunnel junction based localized optical sources

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Multicore CPU design is one of the best ways to improve the performance of a computing system. In this case, result performance of such systems are restricted by the efficiency of intercommunication between cores[1]. A way to overcome the restriction of common metallic interconnection is an optical interconnection. To realize this idea on chip, compact transistor-size light sources are required.

One of the approaches to realize such photon or surface plasmon-polariton (SPP) source is the use of light emitted tunnel junction (TJ) [2]. Local TJ contact is small (defined by the size of contacts), ultra-fast (quantum-mechanical process), does not need resonators such as in lasers, and is potentially easy to be implemented in modern integrated circuits. Unfortunately, a common tunnel junction has quantum efficiency about 10-5-10-6 photons per electron. The quantum efficiency can be improved by bringing nanoantenna in the tunnel junction region[3,4].

We developed a precision technique of nanoantennas formation by voltage pulse for amplification of tunnel junction light emission. This technique is applied in ultra-high vacuum of the scanning tunneling microscope on a layered sample of a thick metal film covered with a thin silicon layer. Typical sizes of these nanoantennas start from 30 nm. The estimated emission increase is about 13 times compared to a pure gold film.

This technique allows to form the arrays of nanosized light sources which can be used for high density multichannel electrically-driven optical interconnection.

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### Fundamental Loading-Curve Characteristics of the Persistent Phosphor SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>,B<sup>3+</sup>

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The compound SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup>,B<sup>3+</sup> is currently one of the best-performing persistent phosphors and numerous studies have been performed to understand the mechanisms involved in its afterglow process. One aspect which so far has received only limited attention is the "loading curve" characteristics. The so called "loading curve" is the time related luminescence (emission) of a fully decharged sample after switch on the excitation light. We will describe, that the measurement environment (temperature, pump intensity and excitation wavelength) as well as the sample properties (dopand concentrations) have a significant effect on the charging time (time to reach an equilibrium between trapping and de-trapping) and the shape of the curve (rising or decreasing luminescence) [1]. For a more complete description, one must consider that ET takes place between the Eu ions on different Sr sites with blue or green emission. As the blue emission is quenched at room temperature, there is a loss of photons which is reflected both in a lower quantum efficiency below 400 nm and in the lower integrated afterglow intensity for irradiation at 382 nm compared with irradiation at 444 nm with the same pump intensity [2].

The analysis of the decay curves suggests that the loading process is a local electron transfer,

as the Dexter ET rate constant (included in the Inokuti-Hirayama equation) and the electron transfer rate constant present similar radial dependence. The qualitative result is that a significant fraction of the excited  $Eu^{2+}$  ions can reach eventually the traps within the "Dexter" radius R0 and contribute to the initial faster decays observed [1].



Fig. 1: Loading curves of different samples at different excitation temperatures and excitation densities.

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## A novel ternary eutectic of CeCl<sub>3</sub>/LiCl/CaCl<sub>2</sub> as a thermal neutron scintillator

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**[Introduction]** Solid state scintillators for thermal neutron detection have been developed due to the diminishing resources of <sup>3</sup>He gas. Instead of <sup>3</sup>He gas, inorganic scintillators containing <sup>6</sup>Li have been developed and studied because of their high neutron capture cross section by <sup>6</sup>Li(n, $\alpha$ ) reaction. Recently, <sup>6</sup>Li containing eutectic scintillators such LiF/CaF<sub>2</sub>, LiF/LiGdF<sub>4</sub>, LaBr<sub>3</sub>/LiBr LiCl/Li<sub>2</sub>SrCl<sub>4</sub> and LiSrI<sub>3</sub>/LiI [1,2] has been reported. These eutectics consist of <sup>6</sup>Li based neutron-capturing phases and luminescent phases. CeCl<sub>3</sub> scintillator has attracted attention due to its low density of 3.9 g/cm<sub>3</sub>, high light yield of 46,000 photons/MeV, and fast decay time of around 25 ns. In this study, CeCl<sub>3</sub>/LiCl/CaCl<sub>2</sub> ternary eutectic was fabricated by the vertical Bridgeman (VB) method. CeCl<sub>3</sub> was selected as a scintillator phase to obtain enough scintillation light and fast decay time. Investigations of their crystal phase were performed. Luminescence and scintillation properties were also evaluated.

**[Exparimentals and results]:** The starting materials were prepared using CeCl<sub>3</sub>, CaCl<sub>2</sub> and <sup>6</sup>Li enriched (95%) LiCl powders with 99.99% purity. CeCl<sub>3</sub>/LiCl/CaCl<sub>2</sub> were grown at the eutectic composition of 17.4 mol% CeCl<sub>3</sub>, 62.7 mol% LiCl and19.9mol% CaCl<sub>2</sub>. Mixed powders were set in the quartz ample after the baking process at 100°C under a high vacuum (~10<sup>-4</sup> Pa) to eliminate water and oxygen. The ample was heated over its melting point and pulled down at speed of 0.2 mm/min. The CeCl<sub>3</sub>/LiCl/CaCl<sub>2</sub> eutectic was grown by the VB method (Fig.1). Circular samples with 1 mm thickness were cut and polished from the grown crystal and showed slight transparency. As results of BEI (Fig. 2) and powder XRD analysis, the existence of CeCl<sub>3</sub>, LiCl, and CaCl<sub>2</sub> phases was confirmed. In this eutectic, Li concentration was as high as 24.6 mol% and the density was as low as 2.98 g/cm<sup>3</sup>. Expected Ce<sup>3+</sup> 4f-5d emission was observed peaking at 350 nm. The light yield of the eutectic was around 15,000 photon/neutron under <sup>252</sup>Cf irradiation, and 250 % of a Li-glass standard with 6,000 photon/neutron. Details of eutectic growth, structure, scintillation properties and neutron responses will be reported in the presentation.



Fig.1 The fabricated CeCl<sub>3</sub>/LiCl/CaCl<sub>2</sub> eutectic (left) and polished wafer

Fig.2 The BEI of CeCl<sub>3</sub>/LiCl/CaCl<sub>2</sub>

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#### ACCELERATED CATHODOLUMINESCENCE RESPONSE OF YAP:Ce,Mg SINGLE-CRYSTALLINE FILMS

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"Defect engineering" method was used for cerium-activated yttrium aluminum perovskites co-doped with various  $Mg^{2+}$  concentration (YAP:Ce,Mg). The aim of this work was to improve cathodoluminescence (CL) performance, especially the acceleration of CL decay, as was done in garnets previously [1].

Samples were prepared by liquid phase epitaxy using lead-free  $BaO-B_2O_3-BaF_2$  flux [2]. CL was studied on specially adapted CL apparatus [3]. CL spectra (Figure 1a), CL decays after pulsed excitation (Figure 1b), thermoluminescence and other CL characteristics at various temperatures were studied.



Figure 1: Cathodoluminescence (CL) characteristics of YAP:Ce,Mg single-crystalline films with various Mg co-doping at room temperature. a) CL spectra; b) CL decays after 50 ns excitation time.

At 120 ppm Mg concentration, improvement of spectral CL emission intensity was noticed, higher Mg co-doping caused CL decay acceleration (1/e decay time decreased from 15 ns to < 4 ns for 0 ppm and 4000 ppm Mg films, respectively) and emission quenching.

The results showed that the  $Mg^{2+}$  co-doping in YAP:Ce was not as effective as in garnets. However, YAP:Ce,Mg films can still serve as scintillators in applications where the fastest possible CL response is crucial and a partial decrease in light yield is acceptable.

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#### **P** - 4

### ALD DEPOSITED ZnO:AL FILMS ON RIGID AND FLEXIBLE SUBSTRATES FOR ORGANIC/INORGANIC HYBRID STRUCTURES

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Here, we demonstrate functionality of aluminum-doped zinc oxide (AZO) thin films deposited on glass and on mica substrates by using an atomic layer deposition (ALD) technique. AZO thin films possess very high optical transmittance at visible and near-infrared spectral range and excellent electrical properties competitive to the commercial ITO layers. AZO layers deposited on flexible mica substrates show stable sheet resistance over 1000 bending cycles [1]. Several applications of AZO as transparent conductive layers combined with organic materials as liquid crystals (LC) and polymer dispersed liquid crystals (PDLC) are shown - AZO/glass-supported LC display and AZO/mica-based flexible PDLC devices [3].



Fig.1. (a) Structure (b) set-up and (c) voltage-transmittance characteristics with image change from "off" to "on" states

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## ANTHOCYANINS FROM ARONIA POWDER AS PH-RESPONSIVE SENSORS

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Anthocyanins represent a large group of naturally occurring, water-soluble polyphenolic pigments responsible for vivid purple, blue and red colors in plants. When exposed to alkaline or acidic conditions, the chemical structure of anthocyanins shifts as a function of pH which results in visually observable color changes.

In this study, a solvent extraction method with polar solvents is used to extract anthocyanins from aronia berries powder. Colorimetric changes and optical properties of anthocyanins as pH responsive molecules are investigated. Photoluminescence spectroscopy shows a clear difference between photoemission spectra of aronia anthocyanins in acidic and in base environments.

These properties of anthocyanins open up possibilities for the production of intelligent pH sensing films. Chitosan, as a natural and biodegradable polysaccharide, has the ability to entrap the pigments due to interactions between its polymer chains and the phenolic compounds of the anthocyanins. Plant-based dyes incorporated in biopolymers serve as perfect candidates for development of real-time quality indicators for the nontoxic food packaging systems.

## APPLICATION OF AMPHIPHILIC CARBON DOTS FOR POTENTIAL IMPROVEMENT OF LIGHT HARVESTING IN OPTOELECTRONIC DEVICES

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The development of strategies to compensate for losses in light harvesting is important in further improvements in the efficiency of solar cell devices [1]. This can be achieved by development of multilayer active materials, which are composed of nanolayers with efficient absorption in different spectral regions. To date, one of the promising materials for solar energy harvesting is metal-halide perovskites, whose major drawback is the destruction under UV irradiation. To decrease the influence of UV irradiation, it is proposed to use an additional layer, which will efficiently absorb in that spectral region and convert it to lower-energy emission. For that, luminescent carbon nanoparticles as efficient light absorbers in the range of 200 - 400 nm are attractive [2]. Carbon dots are functional nanostructured composites whose structural parameters and physicochemical properties can be precisely controlled with photophysical characteristics that are not inferior to those of semiconductor nanostructures [3]. The obtained nanostructures have a great potential due to the low toxicity of both precursors and the final product. They are usually synthesized in polar media, and thus are hydrophilic [4]. However, solution-processible optoelectronics demands hydrophobic inks, including conductive polymers; thus, further applications of carbon dots in such devices are highly limited. In this work, the amphiphilic carbon dots are developed and proposed to convert the UV spectral range of sun radiation into visible light via energy down-conversion.

The amphiphilic carbon dots were synthesized by solvothermal method using amines and organic acids as precursors dissolved in acetylacetone. In this case, the solvent not only facilitates the reaction of the precursors as media, but also participates in the formation of carbon dots. The morphology and optical properties of synthesized carbon dots were studied in detail. These nanoparticles can be efficiently redissolved in a set of polar and nonpolar solvents such as tetrachloromethane, chloroform, isopropanol, and water. The energy of optical transitions while changing the solvent is almost the same; moreover, the photoluminescence quantum yield is largest for nonpolar solvents. This observation opens an opportunity to use these carbon dots to fabricate photoactive functional films based on them for the improvement of the working parameters of optoelectronic devices based on perovskites.

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## BIOCOMPATIBLE UPCONVERTING Yb<sup>3+</sup>-Er<sup>3+</sup> CO-DOPED INORGANIC Na<sub>3</sub>ZrF<sub>7</sub> NANOPARTICLES AND HYBRID PMO@Na<sub>3</sub>ZrF<sub>7</sub> AND PMO@NaYF<sub>4</sub> NANOPARTICLES FOR TEMPERATURE SENSING IN THE PHYSIOLOGICAL RANGE

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The theranostic field in nanomedicine and nanobiotechnology aims to combine diagnosis and therapy in a singular multifunctional particle offering innovative and non-invasive multimodal platforms. Various diseases such as cancer manifest hyperlocal but subtle temperature gradients which could be monitored by hypersensitive temperature measurements. Inorganic luminescent upconversion materials have been widely exploited for these purposes, however, their non-biodegradability, non-modifiability, bioaccumulation, as well as the uncertainty of long-term exposure toxicity significantly affect their applications. On the other hand, hybrid materials could be readily functionalized and have the advantage of combining organic and inorganic moieties resulting in enhanced biocompatibility as compared to the inorganic counterparts [1,2].

Hereby, we present the synthesis and characterization of purely inorganic  $Yb^{3+}$ -Er<sup>3+</sup> co-doped Na<sub>3</sub>ZrF<sub>7</sub> and NaYF<sub>4</sub> nanoparticles, and their hybrid PMO@Na<sub>3</sub>ZrF<sub>7</sub> and PMO@NaYF<sub>4</sub> counterparts respectively. Na<sub>3</sub>ZrF<sub>7</sub> is a promising lanthanide ion-host material for biomedical applications due to its biodegradability to smaller residues in an aqueous environment, which could be potentially excreted without retention in vital organs, as already reported for its alkali-metal equivalent K<sub>3</sub>ZrF<sub>7</sub> [3]. Periodic Mesoporous Organosilicas (PMOs) as a highly promising materials class are obtained through the condensation reaction of organo-bridged alkoxysilane precursor molecules in the presence of a structure-directing agent [4]. In our study, we exploit PMO particles to accommodate the inorganic upconversion materials within their pores forming hybrid materials. Moreover, we compare the aqueous stability and the thermometric performance of the as-synthesized materials. The biocompatibility and future potential for *in vivo* applications of these materials are further evaluated using a toxicity assay on *in vitro* cultured healthy human cells.

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## CHARGE TRANSFER COMPLEX FORMATION BETWEEN SILVER NANOPARTICLES AND AROMATIC AMINO ACIDS: EXPERIMENTAL AND DFT STUDY

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The optical properties of surface-modified silver nanoparticles (Ag NPs) with aromatic amino acids tryptophan (Trp) and histidine (His) were examined using the cluster model for density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Also, the redistribution of electronic charges upon chemisorption of ligand molecules onto silver's surfaces is determined. The obtained theoretical data, on one side, undoubtedly indicate the interfacial charge transfer (ICT) complex formation between silver and this type of ligands, and, on the other side, partial oxidation of surface silver atoms accompanied by an increase of electron density in ligand molecules. The ICT complex formation, based on noble metal nanoparticles, has never been reported previously to the best of our knowledge. The experimental spectroscopic measurements support the theoretical data. The new absorption band in the visible spectral range appears upon surface modification of Ag NPs, and, when exposed to air, oxidation of surface-modified Ag NPs is significantly faster than oxidation of unmodified ones.

### Composition dependence of recombination behavior of electrons and holes at high temperature in Ag-doped phosphate glasses

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Ag-doped phosphate glasses have been used in fluorescence dosimeters owing to their radiophotoluminescence (RPL) property. RPL is an emission phenomenon caused by the photoexcitation of RPL centers formed by ionizing radiation. In Ag-doped phosphate glasses,  $Ag^{2+}$  and  $Ag_2^+$  are formed by ionizing radiation and emit orange RPL. In addition, these  $Ag^{2+}$  and  $Ag_2^+$  can be removed by heating at 673 K for 1 h. Hence, fluorescence dosimeters composed of Ag-doped phosphate glasses are reusable. The formation mechanism of  $Ag^{2+}$  and  $Ag_2^+$  has been studied extensively <sup>[1, 2]</sup>; however, the disappearance mechanism of  $Ag^{2+}$  and  $Ag_2^+$  has received little attention. Therefore, we have previously investigated and reported on the disappearance mechanism of  $Ag^{2+}$  and  $Ag_2^+$  in Ag-doped Na and Al phosphate glass (Na–Al/Ag) with Ag concentration of 0.09 mol% <sup>[3]</sup>, which is the same composition as that used in glass dosimeters sold as glass badge. In this study, we aimed to elucidate the dependence of the disappearance mechanism of  $Ag^{2+}$  and  $Ag^{2+}$  and  $Ag_2^+$  on the composition of Ag-doped phosphate glasses using electron spin resonance (ESR) spectra and thermoluminescence (TL) glow curve.

Na–Al/Ag with Ag concentrations of 0.009, 0.18, and 0.45 mol% were synthesized by the melt-quenching method. ESR spectra for the samples irradiated with 1 kGy X-rays were measured at room temperature after heating at 400–673 K for 1 h.

Figure 1 shows the temperature dependence of the ESR spectra. In all the samples, the ESR

signals were observed at 310, 325, and 370 mT. The singlet ESR signal at 310 mT and the doublet ESR signal at 325 and 370 mT are attributed to  $Ag^{2+}$  and  $Ag_2^{+[2]}$ . Figure 2 shows the temperature dependence of the ESR signal intensities of  $Ag^{2+}$  and  $Ag_2^{+}$ . In Na–Al/Ag with a Ag concentration of 0.009 mol%, the ESR signals increased at 400–430 K and decreased at 500–590 K. On the other hand, in Na–Al/Ag with Ag concentrations of 0.18 and 0.45 mol%, the ESR signals decreased at 400–550 K. These results indicate that the thermal stabilities of  $Ag^{2+}$  and  $Ag_2^{+}$  decreased with increasing Ag concentration.

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Fig.2 Temperature dependence of the ESR signal intensity of  $Ag^{2+}$  and  $Ag_{2^{+}}$ 

# Control of defects and applications of persistent luminescence materials at various sizes

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In persistent luminescence materials, energy can be stored by controlled traps/defects under brief irradiation (namely few minutes under various wavelengths ranging from x-rays to natural daylight) [1]. This energy is then released at room temperature for several hours via light emission once the excitation is stopped. Trap centers can be due to lattice defects, impurities or various codopants which are introduced to enhance trapping efficiency. Defect stability and materials control at different shape and size is challenging and require lots of scientific tools including simulation [2]. The project PERSIST which gathers several Laboratories in Orleans, Nantes and Paris and a Swiss company is focused on the better understanding of the properties and promotes new applications of the persistent materials.

Very recently extending the range of the powdered phosphors, in addition to nanoparticles [3], thin films [4] were also proposed as well as crystals which are well adapted to various measurements and various applications. We will review at the conference the state of the art and application of the persistent materials at various size.



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#### **P** - 10

#### Crystal growth and scintillation properties of Mo co-doped Ce:Gd<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub> single crystal scintillators

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**[Introduction]** Rare earth activated wide band gap oxide crystals have been found very useful as detectors of ionizing radiation in nuclear and high-energy physics, astrophysics, nuclear medicine, and industry. A number of crystals activated by  $Ce^{3+}$  ions have been studied as potential fast and efficient scintillators. The cerium doped multicomponent Gadolinium Aluminum Gallium Garnet (Ce:Gd<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>, Ce:GAGG) is one of the recently developed scintillator materials [1]. Our group reported that Ce:GAGG offers excellent scintillation properties of high light yield and fast decay time [2,3]. Recently, Mg and Ca co-doped GAGG was reported and noticeable decay time acceleration was obtained [4,5]. And co-doping effects of Li<sup>+</sup> ions on Ce:GAGG was also reported [6]. Also, Mo co-doping with  $Pr^{3+}$  and  $Ce^{3+}$  [7] in the several host materials were investigated such as YAIO<sub>3</sub> (YAP), LuAIO<sub>3</sub> (LuAP), Lu<sub>x</sub>Y<sub>1-x</sub>AIO<sub>3</sub> (LuYAP), and Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (LuAG). Those studies showed that the co-doping of Mo is capable of improving the scintillation properties. However, there were no reported results about the Mo co-doping with Ce for GAGG host. In this study, we investigated Mo co-doping effects on scintillation properties of ce:GAGG scintillator with various Ce and Mo concentrations.

**[Exparimentals and results]** A stoichiometric mixture of 4N MoO<sub>3</sub>, CeO<sub>2</sub>, Gd<sub>2</sub>O<sub>3</sub>,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders were used as starting material. Mo co-doped Ce:GAGG crystals with various Ce and Mo concentrations were grown by the micro pulling down ( $\mu$ -PD) method with an RF heating system

and an Ir crucible under the Ar+2%O<sub>2</sub> atmosphere. Typical puling rates were 0.06–0.08 mm/min and the dimension of rod-shaped single crystals was about 3 mm in diameter. <100> oriented GAGG crystals were used as a seed. Plates of 1mm thickness were cut and polished for the optical measurements, while the rest of the rods were used for the chemical composition analyses. Absorption and luminescence spectra were measured together with several other scintillation characteristics, namely the scintillation decay and light yield to reveal the effect of Mo co-doping and optimal Ce concentration. The photographs of the grown crystals are shown in Figure 1. Light output was increased with the small amount of Mo concentration in Ce0.5%:GAGG crystals. Details of changes in scintillation properties with Mo co-doping will be reported in my presentation.

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Fig. 1. Photos of the as-grown non co-doped and Mo co-doped Ce:GAGG crystals.

#### **P** - 12

## Development of Ce-doped GAGG nanoparticle scintillators using sol-gel method

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Recently, applications of nanoparticle scintillators in living bodies have emerged as a novel technology to control the behavior of living bodies via X-ray irradiation [1]. In such applications, bright nanoparticle scintillators with high density are necessary to effectively function inside the living body in a non-invasive manner. From these viewpoint, Ce-doped GAGG nanoparticles are appropriate owing to the high density and high scintillation efficiency. In this study, we developed Ce-doped GAGG nanoparticle scintillators via sol–gel method.

We synthesized the nanoparticles in a procedure similar to that in a previous paper [2]. Nitrates of Gd, Al, Ga, and Ce were dissolved in distilled water in stoichiometric amount. Citrate acid was added to this solution at twice molar amount of the total metal ions. The solution was stirred for 1 d at room temperature and subsequently at 80°C at 2 h. The solution was then dried at 120°C to obtain gel. The gel was calcined at 1100–1500°C for 6 h to obtain the nanoparticles.

Figure 1 (a) presents the TEM image of the nanoparticles of  $Gd_3Al_3Ga_2O_{12}$  doped with Ce 1% with respect to Gd obtained after calcination at 1100°C. We observed nanoparticles < 100 nm with irregular shape. Figure 1 (b) shows the photoluminescence quantum yield as functions of Ce concentration with respect to Gd and calcination tempearture. The highest quantum yield of 90% was achieved for the Ce concentration of 0.1% and the calcination temperature of 1300°C. The quantum yield was higher than that of a commercially available GAGG:Ce scintillator of 87%.



Figure 1. (a) TEM image of nanoparticles of  $Gd_3Al_3Ga_2O_{12}$  doped with Ce 0.1% with respect to Gd obtained after calcination at 1100°C. (b) Photoluminescence quantum yield as functions of Ce concentration with respect to Gd and calcination tempearture.

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# Development of new transparent ceramics for laser applications in the 1.7 – 2.7 $\mu$ m window

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Optoelectronic devices operating in the mid-infrared region are useful for many applications such as telecommunications, defence and healthcare. To improve the efficiency of such devices, it is important that compact, high-energy laser sources in the 1.7 - 2.7  $\mu$ m window, are developed.[1] In order to produce mid-infrared laser emission, a gain material, whose emission extends beyond the NIR, can be used. In this work, the Ho<sup>3+</sup> ion was chosen as the optically active element due to its <sup>5</sup>I<sub>7</sub> - <sup>5</sup>I<sub>8</sub> transition between 1.95 and 2.15  $\mu$ m. [2],[3]

The aim of this project is to explore the  $(Gd_{1-x}Ho_x)O_3 - Ga_2O_3 - Nb_2O_5$  phase diagram in order to synthesise new transparent ceramics that can be used as laser gain media. In principle, these transparent ceramics would be easier and cheaper to synthesise than the usual single crystals. In addition, it is possible to use higher concentrations of dopant than in the case of single crystals.[4] The syntheses were carried out by out-of-equilibrium phase crystallisation from the glass or liquid melt using aerodynamic levitation coupled with laser heating (CO<sub>2</sub>). This technique has several advantages over the conventional synthesis method of obtaining ceramics by powder sintering. Firstly, the sample can be heated to a very high temperature (up to  $3000^{\circ}$ C), the cooling rate is of the order of several hundred degrees per second, and finally the sample is levitated, which prevents any heterogeneous crystallisation by contact during cooling. The structural and optical properties of the new phases are then studied.



**Figure 1** – Aerodynamic levitation chamber



**Figure 2** – Scheme of an aerodynamic levitation device coupled with laser heating (CO<sub>2</sub>)



**Figure 3** – Bead from Gd<sub>2</sub>O<sub>3</sub> - Ga<sub>2</sub>O<sub>3</sub> - Nb<sub>2</sub>O<sub>5</sub> system synthesised by aerodynamic levitation device

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## Development of plastic scintillators doped with silole-based aggregationinduced-emission phosphors for light yield improvement

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Plastic scintillators with fast scintillation decay are anticipated to be used for prompt detection of X-rays in synchrotron radiation experiments and next-generation medical imaging. However, plastic scintillators exhibit low light yield ( $\leq 10,000$  photons/MeV) because of the competition between concentration quenching and the efficient energy transfer from a polymer matrix to organic phosphors, which increases with organic phosphor concentration. Aggregation-induced emission (AIE)-active phosphors exhibit high luminescence intensity in solid and aggregated states, and have been applied in the development of plastic scintillators <sup>[1, 2]</sup>.

Herein, we fabricated plastic scintillators containing 1,1,2,3,4,5-hexaphenyl-1*H*-silole (HPS), which has favorable AIE behavior, as the organic phosphor. Poly(9-vinylcarbazole) (PVK) was used as the host polymer. PVK and HPS were dissolved in tetrahydrofuran, and samples were obtained from the solution by drying at 25°C. In these samples, the concentration of HPS relative to 9-vinylcarbazole units ranged from 0.10–10 mol%. The photoluminescence quantum yield (PLQY) of the samples was measured. The light yield of the samples was estimated on the basis of the pulse height spectra of scintillation detectors incorporating the samples, using 59.5 keV  $\gamma$ -rays from <sup>241</sup>Am.

Fig. 1 (a) shows the photographs of the synthesized samples upon visible light and ultraviolet (UV) irradiation. The emission under UV radiation was enhanced as the HPS concentration increased. Fig. 1 (b) shows the PLQY and light yield of the samples. The PLQY and light yield decreased with increasing HPS concentration, which is attributed to concentration quenching. The 0.50-mol%-HPS-doped sample exhibited the highest light yield of 9300 photons/MeV.



Fig. 1 (a) Photographs of the synthesized samples upon visible light (upper images) and UV irradiation (lower), and (b) PLQY and light yield. The samples have HPS concentration of 0.10–10 mol%.

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### Development of thermoluminescent Li<sub>2</sub>CaSiO<sub>4</sub>:Tm ceramics for neutron detection

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Neutrons are widely used in various applications such as diffractometry or scattering measurements in basic science, electric power generation, and radiation therapy (boronneutron radiation therapy: BNCT). To detect neutrons via ionizations and electronic excitations, the neutrons are generally converted into energetic charged particles via nuclear reactions with <sup>6</sup>Li or <sup>10</sup>B. To fulfill the needs for simple neutron measurement method in various applications, We have developed several kinds of thermoluminescent glasses [1–3] and ceramics [4, 5]. Based on the results obtained for the materials, we found that the use of <sup>6</sup>Li is advantageous over that of <sup>10</sup>B because of the higher energy of the nuclear reaction and the light particles generated in the nuclear reaction, which have lower linear energy transfer. Hence, we have developed Li-containing thermoluminescent materials for neutron detection. In this lecture, we report the neutron detection capability of Tm-doped Li<sub>2</sub>CaSiO<sub>4</sub> ceramics. We synthesized the Li<sub>2</sub>CaSiO<sub>4</sub> ceramics doped with Tm at 2% with respect to Ca with

enriched <sup>6</sup>Li and <sup>n</sup>Li (Li at natural abndance: 7.5% <sup>6</sup>Li and 92.5% <sup>7</sup>Li). These samples are referred as 6Li and nLi, respectively. Figure 1 (a) presents the thermoluminescence glow curves of 6Li and nLi after X-ray irradiation to 1 Gy. The thermoluminescence properties were similar. Figure 1 (b) shows the thermoluminescence glow curves of 6Li and nLi after neutron irradiation at  $1.0 \times 10^8$  neutrons/cm<sup>2</sup>. The thermoluminescence intensity of 6Li was significantly higher than that of nLi, which indicates that the neutrons were successfully detected using the couple of the ceramics.



Figure 1. (a) thermoluminescence glow curves of 6Li and nLi after X-ray irradiation to 1 Gy. (b) Thermoluminescence glow curves of 6Li and nLi after neutron irradiation at  $1.0 \times 10^8$  neutrons/cm<sup>2</sup>. References

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### Dual-emission luminescence thermometry using LaGaO<sub>3</sub>:TM<sup>3+</sup>, Ln<sup>3+</sup> phosphors

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The first biological window (650–950 nm) is the area within the NIR spectrum able to penetrate skin more effectively than shorter wavelengths.<sup>1</sup> The  $TM^{3+}$ ,  $Ln^{3+}$  activator combination has attracted attention due excitation/emission within this wavelength range.<sup>2</sup>

In this investigation, a series of La<sub>1-x</sub>Ga<sub>0.99</sub>O<sub>3</sub>: Cr<sub>0.01</sub>, Nd<sub>x</sub> phosphors (where x = 0.005, 0.01, 0.02) were synthesised by conventional solid-state methods and structurally characterised by Rietveld refinement of a structural model and powder diffraction data.<sup>3</sup>

Room temperature photoluminescence was undertaken with excitation spectra of both the  $Cr^{3+}$ and the Nd<sup>3+</sup> showing energy transfer to the other emission centre alongside showing the characteristic  $Cr^{3+}$  broadbands, and sharp Nd<sup>3+</sup> line excitations. Emission spectra showed both the  $Cr^{3+} {}^{2}E$  sharp peak at 729 nm, and the Nd<sup>3+</sup> 4I<sub>3/2</sub>  $\rightarrow$  4I<sub>9/2</sub> emission of Nd<sup>3+</sup> *ca*. 890 nm.

Variable temperature thermometric analysis was undertaken, with the La<sub>1-x</sub>Ga<sub>0.99</sub>O<sub>3</sub>: Cr<sub>0.01</sub>, Nd<sub>x</sub> (x = 0.02) sample exhibiting the emissions from the Cr<sup>3+</sup> and Nd<sup>3+</sup> centres at comparable intensities. Monitoring by luminescence intensity ratio (LIR) showed Cr<sup>3+</sup> emission being quenched slower than Nd<sup>3+</sup> emission. The phosphor produced a relative sensitivity of ~2.0% K<sup>-1</sup> at 300 K, high absolute sensitivity, and a temperature resolution of 0.04 K at 300 K.



Figure 1: Variable temperature emissions (excitation = 473 nm) of La<sub>1-x</sub>Ga<sub>0.99</sub>O<sub>3</sub>: Cr<sub>0.01</sub>, Nd<sub>x</sub> (x = 0.02) (left), Sensitives of the La<sub>1-x</sub>Ga<sub>0.99</sub>O<sub>3</sub>: Cr<sub>0.01</sub>, Nd<sub>x</sub> (x = 0.02) phosphor (right).

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## EFFECT OF THE LEVEL DEGENERACY ON KERR NONLINEARITY IN THREE-LEVEL LADDER-TYPE SYSTEM

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Investigation of optical Kerr effect attracts attention in the past decades due to its application in generating optical solitons [1], all-optical switches [2] and logic gates [3] for using in optical communications. It is observed that Kerr nonlinearity can be significantly enhanced in the presence of electromagnetically induced transparency (EIT) effect [4].

In this paper we study the Kerr nonlinearity in the three-level ladder-type system, where the first excited level is three-fold degenerated, interacting with the weak probe and strong control laser [5]. Starting from Liouville equation [6], the system of optical Bloch equations is obtained and solved in the stationary regime using perturbation theory with the probe Rabi frequency as a small parameter. In that way, the expression for the third-order susceptibility of the probe filed, reflecting the Kerr nonlinearity, is obtained. Adjusting the system parameters in a way to achieve EIT effect, the real part of the susceptibility, along with its derivative, are plotted as the function of the probe field detuning for different values of control Rabi frequency and spontaneous decay rates.

To examine the influence of the level degeneracy, the comparison with standard three-level ladder-type system is made. With the suitable choice of the system parameters, the value of the nonlinear susceptibility as well as the slope of dispersion curve inside the transparency window can be made different for the system with level degeneracy related to the system without degeneracy. This fact then can be used to manipulate the group index value under given conditions.



Figure 1. Kerr nonlinearity in the system with (left) and without (right) level degeneracy.

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## Electron-hole trapping centers in alkaline earth metal sulfates with Mn impurity

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In sulfates of alkaline earth metals, the formation of electron-hole trapping centers is associated with the generation of long-wavelength recombination emission at 3.0-3.1 eV, 2.6-2.7 eV and 2.3-2.4 eV. We have experimentally shown that these recombination or tunneling emissions are effectively created upon excitation by photons with energies from 6 eV to 12 eV, where free electron-hole pairs are generated. By measuring the excitation spectrum of recombination emissions of 3.1 eV and 2.6 eV for the  $CaSO_4$ ,  $BaSO_4$ crystal and for a number of other alkali metal sulfates, it was shown that these emissions are excited at photon energies of 3.9-4.0 eV and 4.4-4.5 eV. Pre-irradiated with UV or X-rays in sulfates, where the created electron-hole trapping centers, when excited by photons with an energy of 3.9-4.0 eV and 4.4-4.5 eV, receive back recombination emission at 3.0-3.1 eV and 2.6-2.7 eV. Based on these experimental data, it is assumed that electron-hole pairs in the transparency region of the matrix correspond to local levels at energy distances of about 3.9-4.0 eV and 4.4-4.5 eV.

The effect of Mn impurities on the creation of impurity electron-hole trapping centers was studied for a  $CaSO_4 - Mn$  crystal. In an irradiated  $CaSO_4 - Mn$  crystal at 80 K, shortwavelength bands at 5.0-5.5 eV and 3.8-4.2 eV, as well as long-wavelength recombination radiations of 3.0-3.1 eV, 2.25-2.4 eV and 1.82 eV are effectively created. Measurement of the excitation spectrum of the emission bands associated with impurities  $Mn^{2+}$  at 2.25-2.4 eV and 1.82 eV for the  $CaSO_4 - Mn$  crystal showed that the emission bands 2.25-2, 4 eV correspond to the emission center of the  $Mn^{2+}$  ion in the  $CaSO_4$  crystal. The emission band 3.0-3.1 eV is associated with recombination emission at the  $SO_4^{3-} - SO_4^{-}$ -trapping centers. The excitation of the  $Mn^{2+}$  impurity at photon energies of 2.9 eV and 2.4 eV is associated with impurity trapping centers  $Mn^+ - SO_4^-$  in the anisotropic  $CaSO_4$  crystal. An increase in the efficiency of creating short-wavelength intrinsic emission bands at 5.0-5.5 eV and 3.8-4.2 eV is associated with the formation of a  $SO_4^-$  hole above the top of the valence band during electron trapping by the  $Mn^{2+}$ . During the recombination of electrons with non-equivalently located holes in the host, short-wavelength emission bands are formed at 5.0-5.5 eV and 3.8-4.2 eV. The nature of intrinsic and impurity electron-hole trapping centers and the formation of shortwavelength intrinsic emission bands will be discussed in this paper.

## ENHANCEMENT OF Nd<sup>3+</sup> EMISSION THROUGH Cr<sup>3+</sup>→Nd<sup>3+</sup> ENERGY TRANSFER IN La<sub>3</sub>Ga<sub>5</sub>GeO<sub>14</sub>: Nd<sup>3+</sup>, Cr<sup>3+</sup>

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Over the past few years, the use of optical imaging techniques in biomedical research has received increasing attention. Particularly the near infrared spectral range of emission is especially interesting, due to the reduced absorption and scattering of light in this range by biological molecules and tissues [1].

The use of neodymium ions as a dopant allows obtaining phosphors of versatile biorelated applications including bioimaging and luminescence thermometry, etc. that can be excited with a wavelength of 808nm, which falls in the range of the first optical biological window [1]. However, a low absorption cross section of Nd<sup>3+</sup> ions related to the nature of the 4f-4f electronic transitions results in low emission brightness of Nd<sup>3+</sup> phosphors. One of the methods to improve the emission brightness is to sensitize the Nd<sup>3+</sup> emission through  $Cr^{3+} \rightarrow Nd^{3+}$  energy transfer, since  $Cr^{3+}$  is characterized by absorption bands of much higher absorption cross-section comparing to Nd<sup>3+</sup> counterpart [2].

Therefore in this work proposed approach is evaluated in La<sub>3</sub>Ga<sub>5</sub>GeO<sub>14</sub>:Cr<sup>3+</sup>,Nd<sup>3+</sup>. In this host material, Cr<sup>3+</sup> ions are localized in the weak crystal field, which provides red shift of their absorption bands. Thus, the spectral overlap between absorption bands of Nd<sup>3+</sup> and Cr<sup>3+</sup> ions facilitates efficient Cr<sup>3+</sup> $\rightarrow$ Nd<sup>3+</sup> energy transfer [3]. The effect of Cr<sup>3+</sup> ion concentration (Cr<sup>3+</sup>: 0-20%) on spectroscopic properties of La<sub>3</sub>Ga<sub>5</sub>GeO<sub>14</sub>: 2% Nd<sup>3+</sup>, Cr<sup>3+</sup> at different excitation wavelengths were investigated and discussed.



Figure 1. Emission spectra of La<sub>3</sub>Ga<sub>5</sub>GeO<sub>14</sub>: 2%Nd<sup>3+</sup>; x% Cr<sup>3+</sup> measured upon three different wavelength:  $\lambda_{exc}$ =668nm and .

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### Enhancement of red upconversion in NaBiF<sub>4</sub>:Yb,Er(Ho) by Ce<sup>3+</sup> co-doping

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Hexagonal NaREF<sub>4</sub> materials are considered as among the most efficient APTE or upconversion (UC) known matrices due to some of its inherent properties such as chemical stability and low phonon energy. Due to its similar size and oxidation state, one can also envision the preparation of hexagonal NaBiF<sub>4</sub> for UC applications, with Bi<sup>3+</sup> cations substituting rare earth cations, commonly  $Y^{3+}$  or Gd<sup>3+</sup> for these materials. Lei *et al* reported NaBiF<sub>4</sub>:Yb,Ln (Ho, Er or Tm) compounds with sub-micrometric size and upconversion properties elaborated through an ultrafast co-precipitation process.<sup>[1]</sup>

Adapting the synthesis proposed by Lei et al<sup>[1]</sup>, a series of NaBiF<sub>4</sub>:Yb,Er(Ho),xCe (x = 0, 4) compounds were synthesized within this project. The introduction of Ce<sup>3+</sup> is responsible for the enhancement of the red emission in regards to the green one for both Ho<sup>3+</sup> and Er<sup>3+</sup> due to alternative pathways for non-radiative relaxations involving the population of the <sup>2</sup>F<sub>7/2</sub> state. <sup>[2,3]</sup> The normalized emission spectra for NaBiF<sub>4</sub>:Yb,Er(Ho),xCe are shown in Figure 1. Finding (near-)single red-emitting materials under 980 nm excitation could be interesting due to the biological window offers within these wavelengths for applications in bioimaging.



Fig. 1 – Upconversion emission spectra of (a) NaBiF<sub>4</sub>:Yb,Ho,x% Ce; (b) NaBiF<sub>4</sub>:Yb,Er,x% Ce. Strong variation of the red/green ratio obtained by trivalent cerium codoping.

While there is an increase in the red-to-green ratio, all emissions from  $Er^{3+}$  and  $Ho^{3+}$  had a lifetime reduction when  $Ce^{3+}$  was added to NaBiF<sub>4</sub>:Yb/Er(Ho). As for the enhancement of the red emission, this can be explained by the increase of alternate, non-radiative pathways for relaxation with the introduction of  $Ce^{3+}$ . Risetimes are also reduced, as intermediate states are also affected by the presence of  $Ce^{3+}$ .

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### EPR STUDY OF CHARGE TRANSFER COMPLEX BETWEEN TIO<sub>2</sub> AND NON-AROMATIC LIGAND SQUARIC ACID

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The attachment of squaric acid, a non-aromatic molecule, to the surface of  $TiO_2$  powder induced the optical absorption of the obtained hybrid material in the visible spectral range due to the interfacial charge transfer complex formation. The optical characterization of the hybrid is supported by the density functional theory calculations of the model cluster. The paramagnetic species generated upon excitation with ultraviolet or visible light, in both  $TiO_2$ powders, pristine and surface-modified, were identified conducting low-temperature solidstate and indirect electron paramagnetic resonance (EPR) spectroscopy experiments (spin trapping and spin scavenging). The solid-state EPR experiments indicated the promotion of electrons from the organic moiety to the titania conduction band under visible-light excitation of hybrid. Also, the spin scavenging experiments showed that the electrons generated in the hybrid upon the visible-light activation facilitate the reduction of the radical cations present in the dispersion, while these effects are not observed for pristine TiO<sub>2</sub>.

## EVALUATION OF SITE SYMMETRIES OF Er<sup>3+</sup> DOPED CaF<sub>2</sub> AND BaF<sub>2</sub> CRYSTALS BY HIGH RESOLUTION PHOTOLUMINESCENCE SPECTROSCOPY

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A thorough analysis of the site symmetry of dopant ions in host materials using optical spectra of these materials provides for better understanding of their optical properties and opens further perspectives for non-destructive identification of doped materials.

In this work, the  $CaF_2$  and  $BaF_2$  crystals doped with 0.1 mol%  $ErF_3$  were investigated using high resolution photoluminescence (HRPL) spectroscopy at low temperatures. The structural data for both crystals were obtained from the refined XRD diffraction patterns.

At low temperatures (10 K), Stark splitting of the  $Er^{3+}$  energy levels was identified using HRPL. These measurements allows for differentiation between  $C_{3v}$  and  $C_{4v}$  site symmetries using erbium green emission peaks specific to the  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  transition. For  $CaF_2:Er^{3+}$  crystal, we completed and confirmed the literature reported experimental data and the crystal field calculated data of Stark splitted energy levels [1]. For the less studied  $BaF_2:Er^{3+}$  crystal, we provided the experimental PL data on the Stark energy levels.

At the room temperature, the green emission curves specific to erbium  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  transitions were about nine times more intense in CaF<sub>2</sub>:Er<sup>3+</sup> compared to BaF<sub>2</sub>:Er<sup>3+</sup> when pumped into the  ${}^{4}G_{11/2}$  manifold. This could correlate with the structural data but also with a observed presence of mostly the C<sub>4v</sub> and less C<sub>3v</sub> isolated centers formation in CaF<sub>2</sub>:Er<sup>3+</sup> and mostly C<sub>3v</sub> isolated centers formation in BaF<sub>2</sub>:Er<sup>3+</sup>. Such site symmetries of isolated centers were also confirmed earlier by the dielectric measurements on similar crystals [2, 3].

Analyzing the site symmetry based on the PL data offers possibility to delimitate better isolated centers which are responsible for higher emission intensity and gives opportunity for more detailed understanding mechanism responsible for emission. This open a new opportunities to design more efficient materials with desired luminescence properties.

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### FABRICATION OF ZnO/SnO<sub>2</sub> NANOCOMPOSITES FOR EFFICIENT WATER REUSE

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An improvement of water quality and purification can greatly contribute to the human health and ecosystems. The incorporation of nanomaterials with photocatalytic properties into the polymer matrix is a new way to obtain novel water purification systems. This approach takes the advantage of the immobilization of nanoparticles with no need of recovery of the nanoparticles after the water treatment, which is time consuming procedure. On the other hand, binary semiconducting oxides, like zinc oxide (ZnO) and tin oxide (SnO<sub>2</sub>) nanoparticles exhibit a large potential for photocatalytic applications in environmental treatments, such as degradation of wastewater and sterilization of drinking water[1]. Coupled oxide semiconductors, such as ZnO/SnO<sub>2</sub> nanoparticles have been proven as even more effective photocatalysts[2]. Here we report a novel method of encapsulation of ZnO/SnO<sub>2</sub> nanoparticles in PMMA matrix and formation of nanocomposite films with high photocatalytic activity and reusability. The efficiency of PMMA ZnO/SnO<sub>2</sub> films with different weight fractions of nanoparticles was examined in the photocatalytic degradation of methylene blue suspended in water. Beside the photocatalytic and reusability experiments, we performed detailed morphological and optical analyses of nanocomposites. Optimization of this method would extend the potential of semiconducting oxide nanoparticles for future practical large-scale applications in environment-related fields.

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#### FOUR WAVE MIXING (FWM) IN ALKALI ATOM VAPORS

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Four Wave Mixing (FWM) in alkali atom vapors exists only under very specific conditions, it is necessary that density of alkali vapor, intensities and frequencies of pump and probe laser beams, have their values within rather narrow ranges. FWM is nonlinear phenomena that can be regarded as scattering of laser beams on nonlinear index grating, generated by the same laser beams. Such scattering results in conversion of two pump photons to additional probe photon, and to conjugate photon at frequency (much) different form the pump and probe frequencies.

We have investigated probe and conjugate pulse propagation through potassium vapor under conditions of FWM. The initial probe pulse enters K vapor as 80 ns Gaussian. We are defining, experimentally and theoretically, values of FWM parameters, vapor density, pump and probe detuning, that allow pulse propagation without distortion. Theoretical model is helping to understand dynamics of pulse propagation and the cause for their distortion, when FWM parameters take "wrong" values. Model allows us to "peak" inside the K vapor and observe moments of pulse splitting. There are very few (theoretical) papers that have discussed possible causes for pulse splitting in coherent [1] and nonlinear medium [2]. We will discuss their and our views of what is happening in the FWM medium when initial Gaussian probe pulse starts to brake.

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### Growth of Er-doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> Single Crystal by Micro-Pulling-Down **Method and Optical Properties**

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#### **1. Introduction**

La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> with a relatively high density and a high melting point of 2418°C has been developed as a noble material with promising properties such as high radioactive stability, high reffractive index, high-temperature stability and low thermal conductivity. In the previous reports of the Pr, Ti and Eu-doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>, the luminescent properties were reported as red phosphor and Xray scintillator<sup>[1]</sup>. Recently, we developed a modified micro-pulling-down ( $\mu$ -PD) method using a W crucible for crystal growth of the material with a high melting point (> 2100 °C), and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> single crystals could be grown by the growth method<sup>[2,3]</sup>. In this study, we focus on the effects of Er<sup>3+</sup>-doping for the La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> single crystal on the luminescent properties. The Er-doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> single crystal was grown by the growth method and the luminescent properties were investigated.

#### 2. Experimental method

Er-doped La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> single crystal was grown by the  $\mu$ -PD method using a W crucible. The mixed powder was prepared as a nominal composition of  $(La_{0.99}Er_{0.01})_2Hf_2O_7$  using starting materials,  $La_2O_3$  (> 4N), HfO<sub>2</sub> (> 3N5) and  $Er_2O_3$  (> 4N) powders, and it was sintered at 1600°C for 24 h in air. The sintered powder was set in the W crucible and the crucible was surrounded by deoxygenated zirconia insulators. The crucible was heated by high-frequency induction heating and crystal growth was performed at 0.03-0.05 mm/min pulling rate in Ar. Photoluminescence (PL) spectra of the polished specimen were measured by the spectrofluorometer (EDINBURGH INSTRUMENTS FLS920).

#### 3. Results & discussion

 $(La_{0.99}Er_{0.01})_2Hf_2O_7$  crystal grown by the  $\mu$ -PD method using the W crucible is shown in Fig.1. The grown crystal showed transparency with black color, which is suggested to be due to the oxygen defect. Figure 2 is the excitation and emission spectra of the  $(La_{0.99}Er_{0.01})_2Hf_2O_7$  polished specimen. In the emission spectrum, emission peaks were observed around 550 and 560 nm, which were attributed to the  ${}^{4}S_{3/2} {}^{-4}I_{15/2}$  and  ${}^{2}H_{9/2} {}^{-4}I_{13/2}$  transitions of  $Er^{3+}$ , respectively. In this presentation, we report details of the crystal growth and luminescent properties.

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Fig.1  $(La_{0.99}Er_{0.01})_2Hf_2O_7$  crystal grown by the µ-PD method



Fig.2 PL spectra of (La<sub>0.99</sub>Er<sub>0.01</sub>)<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> polished specimen.

## Hybrid metal nanostructures as photodynamic therapy agents: the case of riboflavin-functionalized gold nanoparticles

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The mechanism of photodynamic therapy (PDT) is based on the pronounced generation of reactive oxygen species (ROS) by irradiation of active centers localized in malignant tissue that induces cell death in the target area. The active agents for PDT have several functional parts, with the most important being the photosensitizing (PS) compound responsible for ROS generation. The introduction of nanotechnology into PDT research widened the candidate criteria in the exploration of suitable PS agents. Metallic nanostructures, for example, can enhance the desirable properties of standard PS molecules. However, metals strongly influence the optical properties of the surrounding molecules, which is the reason one has to carefully choose the constituents as the final metal-based hybrid nanostructure could have significantly different properties from the starting elements. In this study, we report on the influence of gold nanoparticles (Au NPs) functionalized with photosensitizing molecule riboflavin (vitamin B2, Rb) on the efficiency of generation of reactive oxygen species, probed in various aqueous and biological environments. We show that the gold nanoparticles enhance the ROS activity of riboflavin, even when a smaller number of the biomolecules is present in the colloid. By comparing EPR signals of bare nanoparticles, functionalized nanoparticles and the molecular solution in water, the strongest signal was observed for the Au-Rb nanosystem, while bare nanoparticles yielded no signal whatsoever. Furthermore, by having adsorbed riboflavin onto the NPs, the signal stability of riboflavin's generation of ROS was of a higher degree than the molecular solution, with a time span of several minutes. We will also present our results on an imaging study of the bacterial survival rate of the colony of Escherichia coli incubated with the Au-Rb nanosystem. These results will shed light on the physical mechanisms of the photosenzitizer's activity and help advance the knowledge in metal-based nanoplatforms developed as novel agents for photodynamic therapies.

# Indications for Local processes in SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> :Fitting of the Luminescence Decay

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The compound  $SrAl_2O_4:Eu^{2+},Dy^{3+}$  is one of the best known and most widely used persistent phosphors. It has also been the object of numerous studies over the past decades, nevertheless the full details of the trapping and detrapping mechanisms yet remain to be clarified.

To bring light to some of these yet hidden details, low temperature as well as room temperature studies of the emission lifetimes in a series of samples with different dopant and co-dopant concentrations were performed [1][2]. The results of the measures were fitted using either biexponential or different Inokuti-Hirayama [3] functions.

The fits give an indication to the characteristics of the involved processes. The electron transfer from the blue to the green emitting  $Eu^{2+}$  could be quantitatively associated to a Förster energy transfer process whereas the observed emission decays can be described using the Inokuti-Hirayama equation for a Dexter energy transfer indicating a local trapping mechanism.

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### JUDD-OFELT PARAMETERS OF SINGLE CRYSTALS OF THE BaF<sub>2</sub> -SrF<sub>2</sub> - ErF<sub>3</sub> SOLID SOLUTIONS.

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 $MF_2$  single crystals (M = Ca, Sr, Ba) doped with rare earth elements are well known as active media for lasers [1–3]. To date, laser media have been developed with a generation efficiency of more than 80% based on three-component disordered solid solutions with the fluorite structure [4]. Particular attention should be paid to materials capable of generating in the infrared range of the spectrum, including those doped with thulium, erbium, and holmium ions.

Single crystals of the  $BaF_2 - SrF_2 - ErF_3$  solid solutions have been obtained by the method of vertically directed crystallization (the Bridgman method). The Judd-Ofelt parameters were calculated from the experimental absorption spectra of the crystals to estimate the degree of symmetry/asymmetry of the  $Er^{3+}$  crystal field. The data obtained are shown in Figure 1. The spectral intensity parameters are influenced by many crystal effects, including the chemical bonds between the atoms in the host, the charge distribution on the atoms in the cell and the lattice distortion.



Fig. 1. Judd-Ofelt parameters of the  $BaF_2-SrF_2-ErF_3$  single crystals with  $Er^{3+}$  concentration of 5-10 wt.%

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## LASER-INDUCED PHOTOCATALYTIC HYDROGEN PRODUCTION OF La<sub>0.25</sub>Nd<sub>0.75</sub>AlO<sub>3</sub> IN METHANOL

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Fossil fuels are considered a non-renewable source of energy, which raises concerns about how to deal with their finite reserves. Not only that, but energy production through these sources have major environmental impact, such as high emission of pollutants. Taking this into consideration, new ways of producing energy should be explored, and hydrogen is regarded as one of the alternatives to produce clean energy. One very promising way is the use of light as a catalyst; usually utilizing a semiconductor with an appropriate bandgap energy, it is possible to excite one electron from the valence band to the conduction band and initiate electron transfer reactions at the semiconductor surface, thus being able to produce H<sub>2</sub> [1]. However, this method utilizes light in the ultraviolet region in order to perform the reaction, which limits their possible applications. Recently, graphene was used to produce hydrogen with excitation with a laser in the infrared region [2]. Using a focused 975 nm laser, it was possible to observe a white light emission and, concurrently, production of H<sub>2</sub>. A downside was found: after long exposition time of the sample, a yellow colored solution was obtained, possibly due to the formation of carbon dots, which may hinder further hydrogen production. Herein, we present the photocatalyst properties of La<sub>0.25</sub>Nd<sub>0.75</sub>AlO<sub>3</sub>. This material, using a focused laser excitation in the near-infrared (808 nm) is able to produce white light, so its capability of producing H<sub>2</sub> in methanol was analyzed. Herein, we will present the hydrogen production using La<sub>0.25</sub>Nd<sub>0.75</sub>AlO<sub>3</sub> as a photocatalyst with excitation by a focused 808 nm laser. It can be seen that H<sub>2</sub> was produced in highest quantity than in graphene when comparing the same excitation power. Moreover, the process utilizing this material was more advantageous due to the low production of CH<sub>4</sub> gas and also due to not producing byproducts in the starting solution.



Fig. 1. White light emission and simultaneous H<sub>2</sub> generation from La<sub>0.25</sub>Nd<sub>0.75</sub>AlO<sub>3</sub> in methanol.

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## Lost in the heat of the moment: bringing losses in persistent phosphors to light with a set of thermoluminescence measurements

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Persistent phosphors are special types of luminescent materials that have the distinctive ability to continue emitting light long after excitation has ceased. Beyond their current applications as safety signage and glow-in-the-dark toys, their potential use as glowing road marks [1], and in areas of dosimetry [2] and in-vivo imaging are also being investigated.

In order for the material to act as such an optical battery, it must have special defects, so-called traps, where the energy can be stored for a certain amount of time. However, a large amount of these trapped charges never result in the emission of a photon, hinting at losses in the material that are not well understood. For the most part, the evaluation of persistent phosphors focuses on the emission spectrum, the afterglow decay curve, and the total duration of persistent luminescence. These measurements, however, do not allow insight into these losses, let alone explain them.

To gain a more detailed understanding of the losses we propose to use a well-chosen, standardized set of thermoluminescence measurements that can be compared to a simple model, to give insight in the underlying mechanisms. This way it becomes possible to start unravelling the nature of the losses and we can attempt to decouple them into losses of trapped charges and losses at the activator ion.

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## MgAl<sub>2</sub>O<sub>4</sub>:Cr<sup>3+</sup> PROBE FOR LUMINESCENCE THERMOMETRY IN THE PHYSIOLOGICAL TEMPERATURES RANGE

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Temperature sensing from the photoluminescence of MgAl<sub>2</sub>O<sub>4</sub>:Cr<sup>3+</sup> powder is systematically examined and presented. The material was prepared by the self-propagating high-temperature synthesis method and its structure was confirmed by X-ray diffraction analysis. In this host, Cr<sup>3+</sup> ions are in a strong crystal field, so the overlapping emissions from <sup>2</sup>E and <sup>4</sup>T<sub>2</sub> energy levels are observed. Emission and excitation spectra were recorded in the 300 - 540 K temperature range. The broad photoluminescence attributed to <sup>4</sup>T<sub>2</sub>→<sup>4</sup>A<sub>2</sub> transition increases in intensity with an increase in temperature on account of <sup>2</sup>E→<sup>4</sup>A<sub>2</sub> emission intensity until 460 K when both emissions start quenching. The emissions were separated by deconvolution at each temperature and used for the luminescence intensity ratio temperature readout method. The obtained relative sensitivity displayed high values in the physiological range, from 3.5 %K<sup>-1</sup> at 300 K to 2.9 %K<sup>-1</sup> at 330 K, above 2 %K<sup>-1</sup> below 400 K, and above 1 %K<sup>-1</sup> between 400 K and 540 K.



Figure 1. Temperature-dependent emission spectra of  $MgAl_2O_4$ : $Cr^{3+}$  sample recorded under 550 nm excitation.

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## ENHANCEMENT OF Eu<sup>3+</sup> EMISSION INTENSITY IN LaPO<sub>4</sub>/Ag NANOPARTICLES

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A promising route to improve the performance of luminescent materials is to combine them with noble metal nanoparticles. Herein, a set of silver/europium-doped lanthanum orthophosphate (Ag/La<sub>0.95</sub>Eu<sub>0.05</sub>PO<sub>4</sub>) nanostructures with different concentrations of silver nanoparticles were prepared and investigated. Presented overlapping between the strongest europium (Eu<sup>3+</sup>) excitation line and broad silver nanoparticles surface plasmon resonance makes the combination feasible. X-ray diffraction confirmed the monoclinic monazite structure and transmission electron microscopy revealed particles with rod-like shape and ~ 4 aspect ratio. Photoluminescence spectra show characteristic Eu<sup>3+</sup> ion red emission; the emission intensity increases due to the nanoparticles' close packing and aggregation. The emission intensity of La<sub>0.95</sub>Eu<sub>0.05</sub>PO<sub>4</sub> increases more than 3 times when Eu<sup>3+</sup> excitation is supported by the localized surface plasmon resonance in the Ag/La<sub>0.95</sub>Eu<sub>0.05</sub>PO<sub>4</sub> nanostructures.



**Figure 1** Enhancement of  $Eu^{3+}$  emission intensity in LaPO<sub>4</sub>/Ag nanoparticles together with transmission electron microscopy image and graph presenting overlapping between the strongest europium excitation line and broad silver nanoparticles surface plasmon resonance.
## HYDROTHERMAL SYNTHESIS AND PROPERTIES OF Yb<sup>3+</sup>/Tm<sup>3+</sup> DOPED Sr<sub>2</sub>LaF<sub>7</sub> UPCONVERSION NANOPARTICLES

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Fluoride nanoparticles are difficult to synthesize due to their hygroscopic nature when using conventional methods. Herein, we employed the hydrothermal synthesis to prepare ultrasmall Yb<sup>3+</sup>/Tm<sup>3+</sup> doped Sr<sub>2</sub>LaF<sub>7</sub> upconversion phosphors. The additional advantage of the hydrothermal over conventional preparation methods is obtaining the particles with controlled size and morphology. In this work, a set of Sr<sub>2</sub>La<sub>1-x-y</sub>F<sub>7</sub> phosphors with different concentrations of  $Yb^{3+}$  (x = 10, 15, 20, and 25 mol%) and  $Tm^{3+}$  (y = 0.75, 1, 2, and 3 mol%) ions with respect to La<sup>3+</sup> ions are prepared at 180 °C. The crystal structure and morphology of the obtained samples were thoroughly investigated using X-ray powder diffraction and transmission electron microscopy techniques. Under near infrared excitation ( $\lambda_{ex} = 980$  nm), the room temperature photoluminescence spectra of  $Yb^{3+}/Tm^{3+}$  co-doped Sr<sub>2</sub>LaF<sub>7</sub> phosphor were measured. The upconversion emission are clearly observable in 460-476 nm, 650-700 nm, and 770-800 nm spectral ranges from  ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ ,  ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$ , and  ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$  electronic transitions of Tm<sup>3+</sup> ions, respectively. The optimal synthesis conditions for upconversion photoluminescence of Yb<sup>3+</sup>/Tm<sup>3+</sup> co-doped Sr<sub>2</sub>LaF<sub>7</sub> are discussed and determined to be 20 mol%  $Yb^{3+}$  and 1 mol%  $Tm^{3+}$  with EDTA as the chelating agent and a pH value of around 9. This study found that the optimized Yb<sup>3+</sup>/Tm<sup>3+</sup> co-doped Sr<sub>2</sub>LaF<sub>7</sub> fluoride phosphors are good and promising alternatives to the most studied  $Yb^{3+}/Tm^{3+}$  doped NaYF<sub>4</sub> nanoparticles.



## Multiple temperature readings from Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O:Mn<sup>5+</sup> steady-state nearinfrared emission in a physiological temperature range

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The Mn<sup>5+</sup>-activated Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O phosphor is described in this paper as a versatile nearinfrared luminescence thermometry probe in a physiological temperature range. It is focused on several steady-state approaches to luminescence thermometry operating entirely in the first (excitation  $\lambda_{ex}$ =635 nm) and the second (emission) biological transparency windows. This material was synthesized by a solid-state reaction using CaCO<sub>3</sub>, BaCO<sub>3</sub>, (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> and MnO as precursor materials. Starting chemicals were thoroughly mixed in an agate mortar for 1 hour with an appropriate amount of etanol. A mixture of the raw materials was heated at 600°C for 6 hours, ground in an agate mortar, and further calcinated at 1280°C for 10h. The exploited features of Ca<sub>6</sub>Ba(PO<sub>4</sub>)<sub>4</sub>O:Mn<sup>5+</sup> emission spectra were (*Figure 1*): *i*) luminescence intensity ratio (LIR) between spin-allowed  ${}^{3}T_{2} \rightarrow {}^{3}A_{2}$  and spin forbidden  ${}^{1}E \rightarrow {}^{3}A_{2}$  ( $S_{r}^{MAX} = 2.04\% K^{-1}$  (a) 20 °C, dT < 0.36 K); ii) LIR between Stokes peak corresponding to the bending deformation vibronic mode  $\delta$ (O-Mn-O) and spin forbidden  ${}^{1}E \rightarrow {}^{3}A_2$  ( $S_r^{MAX} = 0.57 \% K^{-1}$  @ 100 °C, dT < 2 Kabove 50 °C); iii) LIR between Stokes and Anti-Stokes peaks corresponding to the bending deformation vibronic mode  $\delta$ (O-Mn-O) ( $S_r^{MAX}=0.52$  % $K^{-1}$  @ 100 °C,  $dT \approx 3$  K); iv) red-shift of the position of the  ${}^{1}E \rightarrow {}^{3}A_{2}$  peak (S<sub>a</sub>=0.21 cm<sup>-1</sup>K<sup>-1</sup>, dT<0.33 K) and v) the broadening of the full with at half maximum (FWHM) of the same peak with the temperature increase  $(S_r^{MAX}=0.34 \ \%K^{-1} \ @) 100 \ ^{o}C, \ dT < 0.38 \ K)$ . The steady-state approach facilitated quick measurements of emission spectra and, consequently, a large number of acquired spectra (50) for each temperature point, which were used to experimentally determine the temperature resolution for each thermometry method.



Figure 1) Illustration of different readouts from the  $Ca_6Ba(PO_4)_4O:Mn^{5+}$  emission spectra as described in abstract i-v; low-right image shows temperature dependence of averaged emission spectra and position of the  ${}^1E \rightarrow {}^3A_2$  and vibronic peaks.

## MICROWAVE DRIVEN HYDROTHERMAL GROWTH OF Eu<sup>3+</sup>/Ce<sup>3+</sup> DOPED Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> NANOPOWDERS - OPTICAL AND STRUCTURAL CHARACTERIZATION

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Perovskites, garnets and monoclinic forms doped with rare-earth ions (RE) are of great interest due to their broad application potential. Considering their photovoltaic properties, RE-doped ceramic nanopowders can be very efficient in absorbing light and enable the construction of smaller and cheaper devices to capture the same amount of solar energy compared to conventional absorbers [1,2].

In view of the growing use of nanomaterials, more research on quick, cheap and simple methods of their production is being conducted. At present, many methods of obtaining nanomaterials require high vacuum, very high temperature and high purity of reagents to ensure crystals of sufficiently good quality [3]. Among the fast and relatively cheap growth techniques, the microwave driven hydrothermal method is a very promising way to yttrium aluminum oxide nanopowders production. It is shown that the selection of appropriate growth parameters allows to control of the content of pure phases of yttrium aluminum garnet, yttrium aluminum perovskite or yttrium aluminum monoclinic in the obtained nanopowders and to minimize the presence of other parasitic phases. Synthesis, optical and structural properties of europium/cerium doped  $Y_3Al_5O_{12}$  grown by microwave driven hydrothermal technique will lead to cheaper and faster creation of compounds as described.

The work presents structural and optical properties of  $Y_3Al_5O_{12}$  doped with europium and cerium, synthesized as a nanoparticles using microwave driven hydrothermal technique. X-ray diffraction, scanning electron microscopy and photoluminescence studies were performed. All the structures have been doped with  $Eu^{3+}/Ce^{3+}$  ions, which are known as local symmetry sensors [4,5].

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## MN<sup>4+</sup>/MN<sup>2+</sup> CONVERSION IN ALKALI-ZINC-GERMANATE GLASS-CERAMICS

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The global problem of providing food for the world's population necessitates the development of environmentally friendly, highly efficient technologies for growing plants. By controlling the parameters and characteristics of light, you can influence the intensity of plant growth processes and their storage of nutrients. Since most pigments has absorption in the NIR range that is not covered by standard industrial LEDs, development of new luminescent materials is required. Luminescent glass-ceramics activated with Mn can be promising for these purposes.

Mn-doped lithium-zinc-germanate glass had the composition of  $(30-x)Li_2O-xZnO-70GeO_2$ , where x=10; 15; 20 mol.%. Glass-ceramics synthesis was carried out via homogeneous crystallization followed by interfacial-controlled growth. Glass-ceramics synthesized at 540– 570°C demonstrated narrow luminescence of a doublet structure near 670 and 680 nm (Fig. 1), corresponding to the  ${}^{2}T_{1g}$ ,  ${}^{2}E_{g}(G) \rightarrow {}^{4}A_{2g}(F)$  transitions in Mn<sup>4+</sup> ions. Glass-ceramics synthesized at 590–640°C possessed broad luminescence near 540 nm corresponding to Mn<sup>2+</sup> ions. With a subsequent increase in the synthesis temperature, the fraction of the crystalline phase in the material volume increased, along with it, the intensity of green luminescence also increased. According to the XRD data, crystals of Li<sub>2</sub>ZnGeO<sub>4</sub> and Li<sub>2</sub>Ge<sub>7</sub>O<sub>15</sub> were nucleated in the glass-ceramics. Mn<sup>4+</sup> ions were incorporated into the crystals' structure instead of Ge<sup>4+</sup> ions. However, lithium ions were responsible for the formation of the crystalline phase. Mn<sup>2+</sup> ions were embedded in the crystal structure instead of Zn<sup>2+</sup> ions. So, the final intensity ratio of different Mn luminescence bands depended on the Li/Zn ratio in the glass composition.



Fig. 1. Photograph of Mn-doped 15Li-15ZnGe glass under UV lamp after polythermal treatment and luminescence spectra corresponding to different temperatures under 330nm excitation. This research was supported by Russian Science Foundation (Agreement #19-72-10036).

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## NANOPARTICLES SIZE DISTRIBUTION ASSESSMENT BY DIRECT OPTICAL PARTICLE TRACKING

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Nanotechnology, is an innovative field within material science, aiming to manufacture nanostructured materials. The novel properties are caused by the nanometer range size, therefore a size characterization in the early synthesis stages is crucial. However, for such small dimensions, in the range of a few to tens of nanometers, specific techniques are required. Dynamic Light Scattering (DLS) [1] and Atomic Force Microscopy (AFM) are currently used for assessing the size in the above mentioned range. A novel optical method which we name Direct Particle Tracking (DPT) is an alternative that can be used to output the particle size distribution of particles suspended in a carrier fluid. The mean square displacement of each particle is assessed by analyzing a succession of images recorded using an optical microscope with a modified light source. The diffusion coefficient of each particle is computed and herefrom the diameter of each particle is assessed, followed by the size distribution. The work presents a realistic computer simulation of nanoparticles diffusion to verify the code written for Direct Particle Tracking. The simulated paths of 4 nanoparticles and the DPT assessed diameter distribution of the simulated diffusion of 60 nm diameter Ag nanoparticles are illustrated by the figure below, revealing that the results are consistent with the diameter used for simulation. The code was used to analyze a recording and to produce the size distribution of synthesized Ag nanoparticles [2], as well. DLS and AFM were used as control methods and the results are presented in the extended work.



Figure 1 - The simulated paths of 4 nanoparticles and the histogram of the diameters assessed using DPT for the simulated diffusion of 60 nm diameter Ag nanoparticles

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## Novel thermal decomposition syntheses route of Ln<sup>3+</sup>-doped LaF<sub>3</sub>

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LaF<sub>3</sub> is a well-known low phonon energy matrix. However, respective nanoparticles synthesised in a thermal decomposition Schlenk line synthesis route are rare. The optimisation of such a synthesis regarding morphology, crystallinity and particle size can be very challenging. However, this route allows for precise control of the afore mentioned parameters if optimised correctly, while also not requiring an additional heat treatment step. In the case of LaF<sub>3</sub> the hydrothermal step involved is known to cause particle aggregation, which is a serious issue for further applications.

In this presentation we describe two Schlenk line syntheses of well-dispersed nanosized LaF<sub>3</sub> using NaOH or NaF as bases in a thermal decomposition route. We employed the idea of influencing the pH value of the reaction to accelerate the release of CF<sub>3</sub>COO<sup>-</sup> ions and respective nanocrystal growth, as presented by Chien *et.al.*<sup>1</sup> We varied the reaction conditions in terms of high boiling point solvents, temperature, time and base added to achieve homogeneous well-dispersed nanoparticles in the size range of 15-25 nm in thickness and 40-50nm in length (2.5 mmol NaOH) or 5-30 nm in size (NaF), as shown in Fig.1a,b. For both routes pure LaF<sub>3</sub> materials was obtained, as shown in the PXRD patterns (Fig. 1c).

Nanosized particles can be used in nanothermometry to measure temperature remotely, in a precise and reliable way, while also being non-invasive. This is interesting for e.g. biological applications, where they have to be nontoxic. We have proven that such LaF<sub>3</sub> nanoparticles show very low toxicity to human cells. They were subsequently doped with 2%Er,18%Yb and a triple-doped 2%Er,18%Yb,X%Tm-system and were investigated for nanothermometry in the biological temperature range.



**Figure 1:** TEM images of 2%Er,18%Yb:LaF<sub>3</sub> prepared with 2.5 mmol NaOH(a) and 2 mmol NaF(b) as base. The addition of 2.5 mmol NaOH yields particles in honeycomb structures with a size around 15-25 nm or rod-like shaped particles with a length of around 40-50 nm and a thickness of around 10-25 nm. The morphologies are likely the same particles, one time standing up and one time laying on the TEM grid. The addition of 2 mmol NaF results in homogeneously shaped cubic particles that ranges from 5-30 nm in size. Their PXRD patterns are shown in (c) in reference to LaF<sub>3</sub> ICSD ID 23972<sup>2</sup>.

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## Optical and scintillation properties of a tetraphenylethylene crystal exhibiting aggregation-induced emission

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Organic crystal scintillators are widely used for the detection of particle radiations, such as neutrons,  $\alpha$ -rays and  $\beta$ -rays, owing to their low sensitivity to high energy photons that serve as the background. Organic scintillators typically show excellent time resolution, and thus, they can be applied for radiation monitoring in high dose fields; however, the light yields are inferior to those of typical inorganic scintillators. Therefore, we focused on molecules that exhibit aggregation-induced emission (AIE) to improve the light yields. AIE phosphors differ from ordinary organic phosphors because their emission intensities are weak in good solvents, but they increase significantly in the aggregated (solid) state<sup>[1]</sup>. This property has the potential to improve the light yields of organic crystal scintillators. In this study, we chose tetraphenylethylene (TPE) as the AIE phosphor and developed a TPE crystal scintillator.

To prepare the sample, commercially available TPE powder was dissolved in toluene at a concentration of 30 g/L. The vial containing the solvent was placed in a constant-temperature dryer at 25°C. The TPE crystal was grown by slowly evaporating toluene. To confirm whether this exhibited AIE, the photoluminescence quantum yields of the TPE solution and crystal were compared. The scintillation spectrum was obtained by irradiating the sample with X-rays. Subsequently, the pulse height spectrum was measured using a <sup>241</sup>Am  $\alpha$ -ray source.

The quantum yields of 30 g/L TPE solution and TPE crystal were 1.1 and 45%, respectively. This suggests that the TPE molecules exhibited AIE in the solid state. Figure 1 shows the scintillation spectrum of the TPE crystal. A scintillation peak was observed at 460 nm, corresponding to previously reported TPE emission data<sup>[2]</sup>. Figure 2 shows the pulse height spectra under <sup>241</sup>Am  $\alpha$ -ray irradiating. To estimate the light yield of the sample, the spectrum of GS20 was also measured (calculated to be 6600 photons/5.5 MeV( $\alpha$ )<sup>[3]</sup>). In the TPE crystal spectrum, a clear peak of 5.4 MeV  $^{241}$ Am  $\alpha$ -ray was observed near channel 260. The light yield was estimated to be 930 photons/5.5 MeV( $\alpha$ ). These results demonstrate that we succeeded in developing a novel organic crystal scintillator exhibiting AIE.

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Fig. 2.  $^{241}$ Am  $\alpha$ -ray pulse height spectra of TPE crystal and GS20.

## PERSISTENT LUMINESCENCE NANOPARTICLES FOR BIMODAL BIOIMAGING IN THE NIR-I / II TRANSPARENCY WINDOW

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The persistent luminescence nanoparticles (PLNPs) emitting in the NIR-I (700–1100 nm) and NIR-II (1300–1700 nm) are able to avoid background noise. Several groups reported the use of PLNPs in preclinical studies<sup>[1]</sup>. However, actually no example of NIR-II is reported *in vivo*. The gallates (ZnGa<sub>2</sub>O<sub>4</sub>) and garnets (Y<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>) doped with lanthanides (such as Ce<sup>3+</sup>, Nd<sup>3+</sup> and Er<sup>3+</sup>) or transition metals (such as Ni<sup>2+</sup> and Cr<sup>3+</sup>)<sup>[2-4]</sup> have been further optimized by the reduction of surface defects and ensuing longer afterglow in NIR range *via* glass-crystallization techniques and core-shell structure<sup>[5-7]</sup>.

Recently, we prepared lanthanides and transition metals co-doped tin-gallates  $(Zn_{1+x}Ga_{2-2x}Sn_xO_4: Er^{3+}, Cr^{3+}, Ni^{2+})$  PLNPs and modified their surface for an effective passivation and a better stability in aqueous solvent. The PLNPs could be well excited by UV and emit persistent luminescence at ~700 nm and ~1300 nm (Fig. 1B). The afterglow could be collected for more than 1 hour in the NIR-I and for 15 minutes in the NIR-II, respectively.

Towards the potential imaging application, the signal (from> 0.2 mg/ml of PLNPs in the water) could be obtained with the help of an InGaAs camera (Fig. 1C). In the near future, the PLNPs will be tested for *in vivo* imaging (Fig. 1D) by analyzing their extended emission in the tissue transparency, efficient functionalization, stability in aqueous and blood solution and persistent emission with different excitation sources.



**Figure 1.** A) Absorption and B) emission spectra of  $Zn_{1+x}Ga_{2-2x}Sn_xO_4$ : Er<sup>3+</sup> Cr<sup>3+</sup> Ni<sup>2+</sup> PLNPs. C) Images of the PLNPs photoluminescence in the NIR-II range. D) *In vivo* imaging principle.

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## PERSISTENT LUMINESCENCE OF UNDOPED ZINC GALLOGERMANATES

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Unprecedented persistent luminescence of  $Cr^{3+}$ -doped zinc gallogermanates with the nominal formula  $Zn_3Ga_2Ge_2O_{10}$ , reported by Pan in 2012 [1] has gained considerable attention due to their potential application in bioimaging [2] and photodynamic therapy of cancer [3]. However, up to now little attention has been paid to the structure of this material and the reasons behind such extraordinary persistent luminescence compared to the other substituted gallates.

Since the fact that the knowledge on both origin and mechanism of persistent luminescence is pivotal to improve the properties of existing persistent phosphors and develop new phosphors, the main goal of our studies was to fill the gaps in the understanding of persistent luminescence generation in undoped zinc gallogermanates. Therefore, a detailed studies of photoluminescence spectra, persistent luminescence spectra and decays as well as thermoluminescence glow curves, combined with various material characterisation techniques were performed on undoped zinc gallogermanate samples with different stoichiometries.

Three overlapping photoluminescence and persistent luminescence emission bands, with very strong temperature dependence, have been identified at 3.0, 2.6 and 2.4 eV. Their origin has been assigned to transitions from  $F^+(^2T_1 - ^2A_1)$  and  $F^0(^3T_1, ^1T_1 - ^1A_1)$  centres, respectively. [4] The series of thermoluminescence glow curves recorded after thermal cleaning procedure and further analysed by initial rise method [5] revealed that the room temperature persistent luminescence at 2.4 eV results from a distribution of traps, ranging from 0.1 eV to at least 0.6 eV, which is attributed to the different geometry and distances of traps feeding  $F^0$  centres. The nature of the traps constituting the identified trap depth distribution and its connection to the stoichiometry of the material is currently under investigation.

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## PHOTOCHROMIC SODALITE MIXES FOR ADVANCED RADIATION SENSING APPLICATIONS

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Photochromic sodalites are found in nature and have been synthesized in laboratories since the mid-twentieth century. The typical composition of these materials is  $(Na_8(AlSiO_4)_6(Cl,S)_2)$ , and through substitution of particularly sodium and chlorine,<sup>1,2</sup> the photochromic properties can be tuned. In order to further exploit this tuned photochromism, different sodalites can be mixed together to allow their properties to function simultaneously.

In this work, photochromic sodalites with different excitation thresholds and colours were synthesized and mixed to produce a sensor material whose observed colour change is indicative of the type of radiation it has been exposed to. Figure 1a shows some examples of different mixes, while Figure 1b shows an image produced by one of the mixes when exposed to three different wavelengths of UV radiation through a stencil. Figure 1c shows how the reflectance minimum (or absorbance maximum) of the material in Figure 1b changes with respect to the excitation wavelength.



Figure 1: (a) three photochromic sodalite mixes pre-exposure and after 1 min exposure to the given wavelength. (b) an image produced by exposing a sodalite mix to UVA, UVB, and UVC radiation. (c) change in reflectance minimum of the mix in (b) with respect to excitation wavelength. The background represents the observed colour after exposure.

These kinds of mixes could see future applications as smart sensors, where the colour of the photochromism after exposure to a source of UV can help determine the nature, particularly the energy, of that radiation. They may also see use in optical multiplexing systems, where different signals can be processed as different observed photochromism colours. These mixes also display photo- and persistent luminescence, which further adds to their potential applications as sensors and detectors.

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### **P - 42**

# PHOTOLUMINESCENT PROPERTIES OF THE Eu<sup>3+</sup> ION IN YNbO<sub>4</sub>-LuNbO<sub>4</sub> SOLID SOLUTION

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Lanthanide (Ln) activated phosphors are a major topic in both basic and applied science. The trivalent europium ion (Eu<sup>3+</sup>) is well recognized for its intense luminescence in the orange/red spectral region, making it useful for a wide range of applications. Because Eu<sup>3+</sup> has an even number of electrons in its 4*f* shell ([Xe]4*f*<sup>6</sup>), the ion has non-degenerated ground (<sup>7</sup>F<sub>0</sub>) and excited (<sup>5</sup>D<sub>0</sub>) energy states, as well as non-overlapping <sup>2S+1</sup>L<sub>J</sub> multiplets, resulting in emission spectra that are predictable in relation to the host material site symmetry.

The solid-state reaction synthesis method was used to make a set of five Eu-doped  $Y_xLu_{1-x}NbO_4$  samples (x=0–1) with a fixed Eu concentration (5%). All the structures crystallize as beta-Fergusonite, in which the Eu ion replaces the Y or Lu ion in a large, low-symmetry octahedron. The excitation and emission spectra of the Eu<sup>3+</sup> ion in all composition hosts show characteristic *f-f* transitions from which Stark energy levels were calculated.

Specific features and energy positions of the distinctive  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  magnetic dipole transition were determined when measured with higher resolution and spectra deconvolution was utilized. The maximum  $\Delta E$  splitting of the  ${}^{7}F_{1}$  manifold's Stark splitting and the asymmetry ratio R all show Y/Lu content-dependent trends.

Calculations based on Judd-Ofelt theory were utilized to determine specific quantities. The lowest non-radiative deexcitation rate was observed with x = 1, resulting in the conclusion that LuNbO4 is a better host-matrix for Eu<sup>3+</sup> emission than other compositions.

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### **P - 44**

## DOUBLE-ACTIVATED LUMINESCENCE INTENSITY RATIO THERMOMETRY IN Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Eu<sup>3+</sup>, Mn<sup>4+</sup> NANOCRYSTALS

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The potential for double-activated luminescence intensity ratio thermometry using  $Eu^{3+}$ ,  $Mn^{4+}$  co-doped YAG is examined. A modified Pechini method was used for the synthesis of four samples (the 0.5 mol%  $Mn^{4+}$  concentration was fixed, while the doping concentrations of  $Eu^{3+}$  were 1, 3 and 5 mol%). Their cubic structure with an Ia3d (230) space group (ICDD card no. 01–073–3184) was validated by X-ray diffraction. An average crystallite size of less than 20 nm was assessed from XRD patterns. SEM revealed that materials are composed of ellipsoidal-shaped particles smaller than 50 nm. Temperature-dependent photoluminescent emission spectra of co-doped materials (ex = 465 nm, temperature range 98–473 K) showed emission bands in the red spectral region which originate from electronic transitions in both  $Eu^{3+}$  and  $Mn^{4+}$ . The luminescence intensity ratio used in this work is defined as the ratio between the integrated intensities of the  $Eu^{3+} 5D_0 \rightarrow^7 F_1$  transition and the  $Mn^{4+} 2E \rightarrow^4 A_2$  transition [1], which was obtained after the deconvolution method recently introduced in Ref. [2]. This approach provided a maximal relative sensitivity of  $S_Rmax = 5.06 \ \% K^{-1}$  at 321 K, similar to that obtained in Ref. [3]. With the double activated ratiometric approach using co-doping with  $Mn^{4+}$ , the obtained sensitivity is almost two times higher than one that uses emissions from  $Eu^{3+} 5D_0$  and  $^5D_1$  levels.

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# THERMAL HISTORY MEASUREMENTS USING THE RATIO OF ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ AND ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ Eu<sup>3+</sup> EMISSIONS

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Thermal history sensors, also known as off-line thermometers, can provide evidence of the temperatures they experience during thermal events of interest. These sensors are crucial for obtaining information on temperatures in high-temperature environments such as chemical reactors, engines, or gas turbines.

We have proved that thermal history measurements, founded on the emission intensity ratio of  $Eu^{3+}$ -doped matrix, have photoluminescence properties suitable for thermal history forensics. An increase in phosphor's crystallite size with annealing temperature caused a significant and permanent increase in the emission intensity and symmetry ratio ( $Eu^{3+5}D_0 \rightarrow {}^7F_1$  and  ${}^5D_0 \rightarrow {}^7F_2$  emissions ratio). This  $Eu^{3+}$ emissions ratio shows the potential application of the forensic indicator of the maximal exposed temperature of made phosphor (Fig. 1).

The crystallite size and, consequently, the symmetry ratio do not depend on the duration of temperature exposure. Therefore, it is possible to calibrate symmetry ratio values to temperature and use vanadate phosphor as a thermal history sensor; thermal history measurements show readings at any temperature.

In the proof-of-concept, the proposed approach and forensic application at high temperatures, up to 900 °C, was validated on a steel plate layered with YVO<sub>4</sub>:Eu<sup>3+</sup> phosphor.



Fig. 1. Photographs of the steel plate covered with as-prepared YVO<sub>4</sub>:Eu<sup>3+</sup>, emission spectra ( $\lambda_{exc}$  = 365 nm) of theYVO<sub>4</sub>:Eu<sup>3+</sup> (as prepared and annealed 2h at different temperatures) normalized to the intensity <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>1</sub> emission and the relationship between symmetry ratio and crystallite size of phosphor.

## POPULATION CONTROL OF THE FIVE-LEVEL V-SYSTEM BY THE LASER INTERACTION

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The study of the effects occurring in the laser-matter interaction is of fundamental and applicative interest for light-based quantum technologies [1]. One of the aspects is examining the inversion population, which is the basis for lasing [2].

In this paper the interaction of one five-level atom with 2 lasers, control and probe, in V configuration is studied in order to find the conditions under which population pumps from the ground to the excited levels. A physical system that is studied is the <sup>87</sup>Rb atom in weak magnetic field, whose role is to remove the level degeneracy. Some of the magnetic fine structure sublevels responsible for the D-line are chosen [3]. Starting from the Liouville equation [4] and setting different laser polarizations and sublevels, the optical Bloch equations are derived. The dynamics of the population is obtained by solving these equations. In order to explain the results, solutions of the stationary optical Bloch equations are used.

Finally, it was concluded that it is possible to get the population inversion by varying the relevant parameters. As it can be seen from the figures, in one case population completely pumps to the higher sublevel of the ground term, while in the other case the populations of the first four levels are almost equal.



Figure 1: Population dynamics for different configurations

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## RED AND NIR PERSISTENT LUMINESCENCE OF MAGNESIUM GERMANATE BASED MATERIALS

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Persistent luminescence also called long-lasting phosphorescence or simply afterglow is a luminescence characterized by the emission of radiation from a few seconds to several days after the excitation source has been switched off. Over the last 25 years, research on persistent luminescence materials, both in fundamental and applied physics, has developed rapidly, however, the explanation for the physical processes that cause afterglow is still somewhat ambiguous and there are many unanswered questions and unexplored potential applications.

Today, persistent luminescence materials are used mainly for purposes such as luminescent paints, safety signs and decorations. At the same time research is underway into the use of such materials in medicine, information storage, anti-counterfeiting technology, etc.

Most of the well-developed materials have emission in the visible part of the spectrum, especially green, and despite the high potential for application, there is relatively less research on materials with emission bands in the red and near-infrared regions. In addition, it should be noted that most of the currently used persistent luminescence materials use rare earth element ions as activators, which makes these materials significantly more expensive. Transition metal ions, such as  $Mn^{2+}$  and  $Cr^{3+}$ , can be considered an excellent alternative, which, when introduced into a properly chosen matrix, can provide red afterglow in the case of  $Mn^{2+}$  and near-infrared afterglow in the case of  $Cr^{3+}$ .

Within the framework of this research, MgGeO<sub>3</sub>:  $Mn^{2+}$ ; MgGeO<sub>3</sub>:  $Cr^{3+}$  and Mg<sub>2</sub>Si<sub>0.1</sub>Ge<sub>0.9</sub>O<sub>4</sub>:  $Mn^{2+}/Mn^{4+}$  materials have been synthesized using solid state reaction synthesis. All materials have undergone thorough investigation using such methods as X-ray diffraction, optical spectroscopy, electron paramagnetic resonance and, especially, thermally stimulated luminescence. It was concluded that all three materials are excellent persistent phosphors characterized by a detectable afterglow well over 10 h. The focus of the research is on the trap properties and their impact on the persistent luminescence mechanism. It was concluded that in the case of MgGeO<sub>3</sub>:  $Mn^{2+}$  there are several discrete trap levels while in the case of MgGeO<sub>3</sub>:  $Cr^{3+}$  a quasi-continuous trap distribution is present. In Mg<sub>2</sub>Si<sub>0.1</sub>Ge<sub>0.9</sub>O<sub>4</sub> both types of traps were detected.

Summarizing the results, conclusions are drawn about the processes of long persistent luminescence of MgGeO<sub>3</sub>:  $Mn^{2+}$ ; MgGeO<sub>3</sub>:  $Cr^{3+}$  and Mg<sub>2</sub>Si<sub>0.1</sub>Ge<sub>0.9</sub>O<sub>4</sub>:  $Mn^{2+}/Mn^{4+}$  materials and their potential applications.

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## **RED PERSISTENT LUMINESCENT NANOFIBERS:** A flexible and water-stable composite prepared by electrospinning

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Persistent luminescence materials can absorb radiation and emit light continuously after the excitation source has been removed. These have been attracting attention due to their widespread applications, ranging from decoration, safety displays and LEDs to advanced fields such as biomedicine, theranostics, energy and environmental engineering. Alkaline earth sulfides are cost-effective and provide easy color tunability, where doping with transition metals or rare earth ions gives rise to emission in the most varied wavelengths, thus allowing numerous applications [1,2].

Eu,Sm-doped strontium sulfide is a red-emitting long persistent phosphor which, as most sulfide systems, is sensitive to moisture and undergoes hydrolysis which irreversibly suppresses its emission. To overcome this problem, encapsulation with a hydrophobic polymer is proposed. PVDF-co-HFP is a fluorinated polymer which presents larger free volume and superior hydrophobicity compared to PVDF [3]. Among encapsulation approaches, electrospinning is probably the most versatile way to produce fiber-like nanomaterials with tailored compositions and architectures [4,5].

In this work, electrospinning technique was carried out to produce SrS:Eu<sup>2+</sup>,Sm<sup>3+</sup>@PVDF-co-HFP composite nanofibers, which exhibited improved mechanical strength, flexibility and great resistance to water at room and boiling temperatures. Thermal stability and morphological changes were also investigated. SrS:Eu<sup>2+</sup>,Sm<sup>3+</sup> optical properties, such as emission intensity and persistence decay time, were considerable preserved after encapsulation and water treatment. This methodology, therefore, proves to be effective for preparing water-proof phosphors and afterglow textiles.



**Figure 1.** Persistent luminescent SrS:Eu<sup>2+</sup>,Sm<sup>3+</sup>@PVDF-co-HFP nanofibers obtention methodology. Electrospinning setup scheme is adapted from [4].

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## ROOM TEMPERATURE DOPING OF PEROVSKITE NANOCRYSTALS AND NANOPLATELETS WITH NIR-EMITTING LANTHANIDE IONS

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Due to a high absorption cross-section, convenient synthesis, defect tolerance, and favorable coordination number, metal-halide perovskite nanocrystals (NCs) serve as a perfect matrix for the insertion of guest ions with their intrinsic photoluminescence (PL) bands. In particular, doping of metal-halide perovskites with lanthanide ions allows tuning the PL far to the near-infrared (NIR) spectral region [1,2]. To date, the synthetics routes for achieving lanthanide-doped perovskite nanostructures are almost limited to obtaining cubic NCs by a hot injection method [3] at high temperatures.

In the current work, we have developed the room-temperature method for obtaining ytterbium-doped perovskite NCs ( $Yb^{3+:}CsPbCl_3$ ) both in nanocube and nanoplatelet shapes. The method is based on anion-assisted cation doping of  $CsPbBr_3$  perovskite nanostructures as a starting material with ytterbium salts. This approach allows taking advantage of the availability of a large number of techniques for obtaining initial nanostructures with a high degree of shape and size control, including synthesis methods carried out at room temperature.

After the anion-assisted post-synthetic doping both NCs and nanoplatelets demonstrate a new emission band centered at 980 nm which is attributed to the emission from inserted Yb<sup>3+</sup> ions. The optical properties of these nanostructures are investigated and compared for those demonstrated by Yb<sup>3+</sup>:CsPbCl<sub>3</sub> NCs obtained by the hot-injection method.

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# Silver bismuth iodide rudorffites as potential lead-free hybrid photovoltaic materials

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Methylammonium lead halide perovskites, as light absorbing materials, exhibit high values of photoconversion efficiency (PCE) in solar cell devices that can exceed 25%. However, concerns about lead toxicity induced extensive research on less toxic replacements. Silver-bismuth iodide (Ag-Bi-I) rudorffites are non-toxic and the most stable materials among all similar hybrid systems. It is also shown that the best PCE of 4.3 % can be achieved using AgBiI rudorffite as a light absorber [1]. In our previous study, we successfully fabricated Ag<sub>3</sub>BiI<sub>6</sub> rudorffite nanoparticles in the form of aerosols and studied their electronic structure by using synchrotron-based photoelectron spectroscopy [2]. Here, we present an investigation of the electronic structure of Ag-Bi-I materials obtained *via* solid-state synthesis, i.e. by heating mixtures of AgI and BiI<sub>3</sub> powders in a vacuum-sealed quartz tube at 600°C. The electronic structure of the obtained particles was investigated by using both conventional X-ray photoelectron spectroscopy (XPS) and X-ray aerosol photoelectric response of the Ag-Bi-I powders and the photodielectric response of the polymer composite films containing Ag-Bi-I powders films that were obtained using several well-defined excitation wavelengths.

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## SINTHESIS AND CHARACTERIZATION OF Tb<sup>3+</sup> INCORPORED AT Ag@PVP AND Tri-Ag-Citrate NANOPARTICLES

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Silver nanoparticles (AgNPs) are being widely investigated for applications in different areas, mainly due to their physicochemical properties [1,2]. When prepared in systems with the addition of rare earth ions, AgNPs can assist in the process of energy transfer to luminescent ions, significantly improving the spectroscopic characteristics of the emitting agent and providing new applications. The literature presents several detailed processes for the synthesis of AgNPs, which may be of a physical, chemical or biological nature. In this study, the AgNPs were prepared using the conventional chemical method, using two routes: one with sodium citrate and the other with polyvinylpyrrolidone (PVP), the latter being ascorbic acid used as a reducing agent. In both routes, silver nitrate was used as a precursor and the luminescent ion Tb<sup>3+</sup> was incorporated into AgNPs at different concentrations. The material obtained was characterized through the techniques of X-ray Diffraction (XRD), Fluorescence spectroscopy and lifetime. From the X-ray diffractograms, the AgNPs synthesized showed the crystalline phases of (a) Trisilver citrate (Tri-AgCit), (b) Ag@PVP and (c) Ag@AgNO<sub>3</sub>. In AgNPs prepared with Tb<sup>3+</sup>, the diffractograms showed crystalline phases. The excitation and emission spectra for the different concentrations of  $Tb^{3+}$  are shown in Figure 1, being (a) the Tri-AgCit with variation of 0.3, 0.6, 0.9 and 1.2% of  $Tb^{3+}$ , which showed greater excitation and emission for the concentration of 0.9%. In the set shown in (b), we have Ag@PVP with a variation from

1.0 to 5.0% of  $Tb^{3+}$ , and the sample with 3% was better in terms of both emission intensity and lifetime. Finally, the set (c) of Ag@AgNO<sub>3</sub> with variation from 3.0 to 7.0% of  $Tb^{3+}$ , and the sample with 5.0% of  $Tb^{3+}$ showed the best luminescent characteristics. The Tb<sup>3+</sup> emission lifetime changed with the concentration, with the highest value obtained being 0.65, 0.75, 0.75 ms for sets (a), (b) and (c), respectively, which are in good condition according to the values reported in the literature. The results demonstrate that the syntheses were successful, indicating that luminescent characteristics of AgNPs with  $Tb^{3+}$  can be interesting for applications as luminescent optical devices.



Figure 1: Excitation and emission photoluminescence of NPs synthesized at different concentrations of  $Tb^{3+}$ : (a) Tri-AgCit, (b) Ag@PVP, (c) Ag@AgNO<sub>3</sub>.

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## SPECTROPHOTOMETRIC TECHNIQUES FOR STUDYING THE PROPERTIES OF OPTICAL MATERIALS

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Sample testing by capabilities of optical spectrophotometry is a fast, non-destructive method of the direct measurements. Nowadays there is a high request for measuring possibilities of refractive indices N and birefringence  $\Delta n$  of solid single crystal materials, specific angle of polarization plane rotation of the optical anisotropic materials and parameters of layered structures: N, thickness t and absorption  $\alpha$ . These parameters can be obtained by the spectrophotometric techniques (SPT) based on the fundamental laws of the optics [1-7]. These techniques are introduced into practice in out testing laboratory "Single Crystals and Stock on their base" and implemented on the UV-Vis-NIR spectrophotometer Cary-5000 with universal measurement accessory UMA in the wave-range (250 – 2800) and in case of polarized light we use Glan-Taylor polarizing prisms in the wave-range (350 – 2300) nm.

*Refractive indices* [1, 2]. *N* are obtained from Fresnel equations from the multiangle reflection *R* measurements. SPT requires sample with one polished face. In the case of sufficient thickness, if the second face is ground or not parallel to the working face of the sample, the technique of measuring reflection at an angle of incidence close to normal  $R_0$  is used. In this case, we obtain *N* dispersion. Otherwise we use technique based on the Brewster's law measurement of *p*-polarized light and obtain discrete *N* values.

Specific angle of polarization plane and rotation [3-5]. This technique is based on measuring of the intensity of light T transmitted through the polarizer-crystal-polarizer system and requires the samples in form of polished plates cut with certain orientation:  $\rho$  can be measured only along optical axis, in case of  $\Delta n$  measurements optical axis lies in the plane of the sample. Discrete values of  $\rho$  and  $\Delta n$  are calculated from the extremum points of the obtained sinusoidal intensity dependences.

Parameters of the layered structures [6, 7]. N, t and  $\alpha$  of the thin film (layer) deposited on a substrate are obtained by the multiangle spectrophotometric technique based on the measurements of T and R.

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#### Stability of necklace beams in media with cubic-quintic nonlinearity

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In this paper, we have studied numerically two-dimensional soliton-like structures in the form of necklaces in media with cubic-quintic nonlinearity. Self-trapped necklace-ring beams are of special interest because of their unique properties. A necklace beam is a ring-shaped beam with a periodic intensity and phase change along the azimuthal direction, where the effective radius of the ring is much larger than its thickness.

We applied variational approach [1] to the necklace-like solitons in media with cubic-quintic nonlinearity. The procedure is to determine optimal input parameters for the given beam structures utilizing variational principles. Then we launch a optimized necklace beam into the medium, and observe the subsequent behavior. Their stability and evolution were tested by a direct numerical simulation of propagation [2, 3]. Numerical procedure applied to the propagation equation is the split-step beam propagation method based on the fast Fourier transform (fourth-order symplectic algorithm).



Fig.1. The maximum propagation distance over which a necklace beam preserves the same transverse intensity distribution, as a function of the S, for the amplitudes A = 0.7825 (red symbols), A = 0.9 (green symbols), A = 0.95 (yellow symbols), A = 0.97 (blue symbols) and A = 1.0 (pink symbols).

We execute a series of numerical simulations of necklaces with different input parameters. Necklace beam rotates during propagation and can exhibit stable propagation for very large distances. At the end, modulational instabilities lead to the breakup of necklace beam arrangements into several filaments. The dependence of the length of the stable propagation of the necklace beam as a function of the necklace's parameter S (S is a half of the number of the pearls N), for five values of the amplitude A is presented in Fig. 1. We obtain that for carefully chosen input parameters, the maximum propagation distance for necklace beams in media with cubic-quintic nonlinearity can be  $z \approx 800$ , for A = 0.7825 and S = 6.

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## STRUCTURAL FEATURES OF THE BIXBYITE-TYPE YTTRIUM SCANDATE: X-RAY POWDER DIFFRACTION AND MICRO-RAMAN SPECTROSCOPY

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Rare-earth ( $RE^{3+}$ ) doped Sc<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, and Lu<sub>2</sub>O<sub>3</sub> sesquioxides exhibit high thermal conductivity (two times more than YAG) and large window of transparency of 0.25 µm to 9.6 µm. These materials are predestined for high-power ultrafast solid-state lasers, in particular in infrared (IR) spectral region, and may be an alternative for the well-known YAG crystals.  $RE^{3+}$ -doped sesquioxide materials show strong prospects for variety of applications as solid-state light-emitting devices, high-efficiency luminescent materials, rare-earth magnets, magneto-optical recording materials, and so on.

Yttrium scandate, YScO<sub>3</sub>, has polymorphic nature. The high-temperature modification belongs to the bixbyite-type structure [1] like yttria (Y<sub>2</sub>O<sub>3</sub>) and scandia (Sc<sub>2</sub>O<sub>3</sub>). Nd lasers have been realized successfully in the YScO<sub>3</sub> and isostructural (Lu<sub>1-x</sub>Sc<sub>x</sub>)<sub>2</sub>O<sub>3</sub> seqioxide. Moreover, due to disordered structure the bixbyite-type YScO<sub>3</sub> crystals their luminescence lines are broadened, and the active media have promising applications in ultrafast lasers and their further chirped pulse amplification.

Yttrium scandate is a high-temperature melting compound (2400 °C) and tend to be strained or transit to other phase at slow cooling down to room temperature. Therefore, the method of synthesis plays a critical role in this case. Here we report structural characterization of YScO<sub>3</sub> crystal fiber obtained through the laser-heated pedestal growth (LHPG) technique [1]. The features of the laser-heated pedestal growth (LHPG) technique are high temperature of heating under laser irradiation and following quick cooling. The method allows to obtain crystals in the form of a fiber. The small cross section of fibers might lead to growth of lowstrain samples with relative ease, and the large surface-to-volume ratio of lasers made from short lengths of fiber might conduce to efficient cooling.

The structural feature of the YScO<sub>3</sub> crystal fiber have been studied by the X-ray powder diffraction and micro-Raman spectroscopy methods.

The XRD pattern exhibits well-defined narrow peaks pointing to a homogeneous sample of high crystallinity. According to X-ray powder diffraction data the yttrium scandate belongs to a bixbyite-type cubic structure (SG  $Ia\overline{3}$ , a = 10.224(1) Å).

The micro-Raman spectra of the precursors ( $Y_2O_3$ ,  $Sc_2O_3$ ) and the YScO<sub>3</sub> crystal fiber have been recorded in the range of 120 to 660 cm<sup>-1</sup> at room temperature. Phonon lines of the yttrium scandate are broader than ones of both yttrium and scandium oxides due to the presence of both Y and Sc cations statistical distributed between two positions in the YScO<sub>3</sub> bixbyite-type structure. Also, Raman lines in the experimental spectra of the YScO<sub>3</sub> fiber crystal are few and overlapping each other.

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## STRUCTURE, OPTICAL AND SCINTILLATION PROPERTIES OF HYBRID BROMOCUPRATES (I) BASED ON METHYLAMMONIUM AND FORMAMIDINIUM CATIONS

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Scintillators have broad applications in modern devices used for X-ray imaging in tomography, radiography, flaw detection, security control systems, as well as for detecting ionizing radiation. Among the commercially available materials, single crystals of doped iodides and bromides of alkali, alkaline earth metals, and lanthanides (CsI:Tl, SrI2:Eu, LaI3:Ce) have the highest light yields (the number of photons per 1 MeV of energy radiation absorbed by scintillator), but they are usually extremely hygroscopic, expensive to produce (Bridgeman growth) or contain toxic elements.

As an alternative, inorganic scintillators based on halocuprates (I) of composition  $A_mCu_nX_{n+m}$  (X = I<sup>-</sup>, Br<sup>-</sup>; A = K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>) have recently been proposed. These materials demonstrate record high light yields, good stability to external factors (moisture and oxygen), photoluminescence quantum yields close to 100%, and a large Stokes shift excluding self-absorption [1].

In this work, "hybrid" bromocuprates containing organic cations of methylammonium  $(CH_3NH_3^+ - MA^+)$  and formamidinium  $(HC(=NH_2)NH_2^+ - FA^+)$  were studied for the first time. In particular, phases of the composition MA<sub>2</sub>CuBr<sub>3</sub> [2], FA<sub>3</sub>CuBr<sub>4</sub>, MACu<sub>2</sub>Br<sub>3</sub>, FACu<sub>2</sub>Br<sub>3</sub>, MACuBr<sub>2</sub>, FACuBr<sub>2</sub> were obtained in the forms of single crystals, powders and thin films.

The crystal structures parameters of the obtained compounds were determined by XRD. All crystal structures are either one-dimensional (endless chains of edge-sharing [CuBr<sub>4</sub>] tetrahedra) or zero-dimensional (isolated [CuBr<sub>4</sub>] tetrahedra); the dimensionality of the phases reduces with increase of the A : Cu ratio. The absorption edge of the studied phases was estimated to be in the range of 300-410 nm. It was demonstrated that the ACuBr<sub>2</sub> and ACu<sub>2</sub>Br<sub>3</sub> compounds exhibit photoluminescence only at low temperatures (70-120 K,  $\lambda_{max} = 600-610$  nm for ACu<sub>2</sub>Br<sub>3</sub>,  $\lambda_{max} = 480-540$  nm for ACuBr<sub>2</sub>), while the MA<sub>2</sub>CuBr<sub>3</sub> phase demonstrates bright green photoluminescence at room temperature ( $\lambda_{max} = 515$  nm) with PL QY up to 90%. The clear trend of the bandgap broadening and PL<sub>max</sub> blue shift with the A:Cu ratio increase (and corresponding reduce of dimensionality) can be observed for both MA<sup>+</sup>- and FA<sup>+</sup>-containing phases.

Under the radiation of X-ray tubes with silver and copper anodes  $MA_2CuBr_3$  exhibits bright radioluminescence ( $\lambda_{max} = 520$  nm) even at room temperature. The light yield of the  $MA_2CuBr_3$ was estimated as 13700 photons/MeV, which is a relatively high value for a hybrid and polycrystalline material. At present,  $MA_2CuBr_3$  is the second discovered hybrid halocuprate exhibiting radioluminescence at room temperature. The obtained results demonstrate the perspective of using hybrid bromocuprates, in particular the  $MA_2CuBr_3$ , as materials for scintillation detectors.

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## SYNTHESIS AND CHARACTERIZATION OF (Y,Me)NbO<sub>4</sub>:Er,Yb PHOSPHORS: INFLUENCE OF LOCAL LATTICE DISORDERS

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Yttrium niobate (YNbO<sub>4</sub>) is considered to be a self-activated phosphor with a strong emission band in the blue region originating from the  $NbO_4^{3-}$  group, but also an effective host for various luminescent-based doping-altered applications with different rare-earth ions [1-4]. Here,  $(Y_{0.8-z}, Me_z)NbO_4$ : Er, Yb (z = 0, 0.1, 0.2) phosphors with 0.05 erbium and 0.15 ytterbium as up-conversion (UC) activator and sensitizer, respectively, and different metal ions (Me) replacements of  $Y^{3+}$  ions that launch the host local lattice disorders, were synthesized by the traditional solid-state reaction method. The starting metal oxide precursors in the appropriate molar ratio were mixed in a ball mill at 100 rpm for 8 hours, then preannealed at 800 °C for 4 hours, and finally annealed at 1200 °C for 4 hours. The morphology of the synthesized phosphors and their particle size and shape were examined by scanning electron microscopy. X-ray diffraction measurements were used to confirm the crystal structure of samples. The emission spectra of  $Y_{0.8}Er_{0.05}Yb_{0.15}NbO_4$  at room temperature under the excitation of 980 nm show green and red visible UC and near-infrared emission bands of very low intensity, which originate from energy transfer UC processes between Yb<sup>3+</sup> and Er<sup>3+</sup> ions and which are attributed to  $({}^{2}H_{11/2}, {}^{4}S_{3/2}) \rightarrow {}^{4}I_{15/2}, {}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ , and  ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$  transitions of Er<sup>3+</sup> ions, respectively. The lifetime of the  ${}^{4}S_{3/2}$  excited energy level of Er<sup>3+</sup> in Y<sub>0.8</sub>Er<sub>0.05</sub>Yb<sub>0.15</sub>NbO<sub>4</sub> that depends on the host and plays an essential role in infrared to visible UC is 0.198 ms. UC mechanisms, the intensity of the UC emission, and changes in lifetime caused by different Me-ions entering the host lattice were discussed.

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## SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF Cr<sup>3+</sup> IONS DOPED Li<sub>2</sub>Mg<sub>3</sub>TiO<sub>6</sub> NANOCRYSTALS

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Recently, there has been an ongoing search for new efficient near infrared phosphors, which are particularly attractive in bioimaging, due to the fact that biological tissues show low absorption coefficient in the aforementioned spectral range.[1] Of particular recent interest are studies focusing on luminescence tuning by crystal field engineering, for which  $Cr^{3+}$  ions are extremely attractive due to the fact, that their emission is determined by the strength of the crystal field (CFS).[2][3] By controlling the CFS, it is possible to adjust the position of the maximum emission, full width at half maximum (FWHM), but also the emission intensity.

Therefore, in this work Li<sub>2</sub>Mg<sub>3</sub>TiO<sub>6</sub>:Cr<sup>3+</sup>, obtained for the first time by the Pechini method, and detailed studies of the spectroscopic properties of Cr<sup>3+</sup> ions were analyzed in a function of dopant concentration. The performed investigations revealed that in the obtained compound there are two octahedral crystallographic sites which can be occupied by Cr<sup>3+</sup> ions - Ti<sup>4+</sup> site (strong crystal field) and Mg<sup>2+</sup> site (weak crystal field). It was found that by controlling the dopant concentration, it was possible to tune the spectral position of the emission bands from about 700 to 900 nm and its FWHM from 35 to 200 nm (at 120 K). Many studies have been carried out to characterise LMTO nanocrystals - from XRD, which was used to calculate the size of the crystallographic unit cell, allowing to determine the substitution site of Cr<sup>3+</sup> ions, through the emission spectra, to the excitation spectra, from which the following has been calculated the strength of the crystal field.



Figure 1. XRD patterns (a) and emission spectra measured at 123 K upon  $\lambda_{exc}$  = 445 nm (b) of  $Li_2Mg_3TiO_6:x\%Cr^{3+}$  (x = 0.1-10).

#### Acknowledgement

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## Synthesis with plant extract of Tb<sup>3+</sup> -doped CaMoO<sub>4</sub> nanocrystals for luminescent thermometric sensor

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In recent years, several materials doped with rare earth ( $Re^{3+}$ ) have been investigated as possible candidates for luminescence probe for temperature sensor based on fluorescence intensity ratio (FIR) of luminescent thermometric sensors due to the applicability of measuring temperatures in objects or biological tissue on a smaller scale. The temperature effect on these materials change the luminescence properties and therefore it is possible to estimate the temperature of the medium they are inserted. Recent investigations show that Tb<sup>3+</sup>-doped CaMoO<sub>4</sub> is an interesting material for FIR sensors. Currently, beyond to understanding the processes involved in luminescence process, there is a concern to simplify the synthesis processes of these materials and to reduce or exclude the use of chemical reagents and thus mitigate the disposal of potential contaminants in the environment. In this sense, nanoparticle co-precipitation syntheses using plant extract as a solvent have shown positive results, such as the formation of small particles with desirable luminescent properties. Compounds from plant extracts presents reactive molecular groups in the reaction medium, as do polyols, which are products used in co-precipitation syntheses. The objective of this work was to synthesize Tb<sup>3+</sup>doped CaMoO<sub>4</sub> using aqueous plant extract as a solvent. The syntheses were performed at 95 °C using different dilutions of distilled water, diethylene glycol and the plant extract to obtain a final solution of 100 mL. The precursor agents of synthesis were Calcium Chloride, Sodium Molybdate and a solution of Tb<sup>3+</sup> ions. After the synthesis the samples was thermally annealed for 24 hours to eliminate the organic residues.

The X-ray Diffraction results of the samples shown in Figure 1*a* indicates a pure crystalline phase of CaMoO<sub>4</sub>. The luminescence spectra Figure 1*b* shows the intense emission bands at 488 nm, 544 nm, 586 nm, 620 nm and 650 nm referring to electronic transitions of Tb<sup>3+</sup> from the excited energy level <sup>5</sup>D<sub>4</sub> to the lower energy levels <sup>7</sup>F<sub>6</sub>, <sup>7</sup>F<sub>5</sub>, <sup>7</sup>F<sub>4</sub>, <sup>7</sup>F<sub>3</sub> and <sup>7</sup>F<sub>2</sub>, respectively. The image Figure 1*c* shows the scanning electron microscopy of the sample synthesized in a reaction medium with diethylene glycol and plant extract showing the micro grains of Tb<sup>3+</sup>:CaMoO<sub>4</sub>. The transitions <sup>5</sup>D<sub>4</sub>  $\rightarrow$ <sup>7</sup>F<sub>6</sub> and <sup>5</sup>D<sub>4</sub>  $\rightarrow$ <sup>7</sup>F<sub>5</sub> are particularly interesting for FIR sensors due the possibility of thermal phonon coupling of the electronic population of the ground state <sup>7</sup>F<sub>6</sub> to <sup>7</sup>F<sub>5</sub>. The population increase of the <sup>7</sup>F<sub>5</sub> contributes for the excited state absorption excitation (ESA) at 413nm (<sup>7</sup>F<sub>5</sub> $\rightarrow$ <sup>5</sup>D<sub>4</sub>), and the simultaneous decrease of the population of <sup>7</sup>F<sub>6</sub> decreasing the ground state absorption (GSA) (<sup>7</sup>F<sub>6</sub> $\rightarrow$ <sup>5</sup>D<sub>4</sub>) at 377nm. Therefore, this material can be interesting for FIR nano-sensors application, with a relatively simple, cheaper methodology and with less disposal of potential contaminants in the environment.



1. Results of analyzes performed on samples of CaMoO<sub>4</sub> with  $Tb^{3+}$ : *a*) X-ray diffraction; *b*) luminescence spectra; *c*) scanning microscopy.

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### THE EFFECT OF INSTABILITY OF KCI:Na SINGLE CRYSTALS

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Stable arrangement of light small-radius Na<sup>+</sup> impurity ions that substitute cations in a KCl matrix were studied by luminescence and optical absorption methods. The location of Na<sup>+</sup> at regular cation sites was proved via the appearance of luminescence band peaked at 2.8 eV and related to near-sodium-localized (bound) excitons as well as absorption bands at 6.35 and 3.5 eV connected with halogen interstitial ion/atom nearby a Na<sup>+</sup> ( $I_A(Na)$  and  $H_A(Na)$  centers, respectively). In KCl:Na crystals regrown from a ultrapure matrix, the effect of sodium precipitation was detected and interpreted as the result of homogeneous decomposition stimulated by local lattice deformation in the vicinity of sodium ions.

## THE INFLUENCE OF REABSORPTION EFFECT ON THE FIR THERMOMETRIC PARAMETERS IN Nd<sup>3+</sup>- DOPED LITHIUM TELLURITE GLASSES

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Temperature sensors are fundamental in several technological areas [1,2]. However, the practical applications of these devises are limited at macroscopic scale and non harsh environments. Some of these drawbacks arise for temperature measurements at scales smaller than hundreds of micrometers. Fluorescent thermometers have been shown a promisor way to supply these needs, like Nd<sup>3+</sup> doped materials. Nevertheless, under high Nd<sup>3+</sup> concentration, energy transfer processes affect the Nd<sup>3+</sup> emission such as the optical reabsorption and crossrelaxation. Few reports have described these process on the fluorescent intensity ratio (FIR) parameters therefore, their effect on the sensitivity is unclear. In order to study the effects of reabsorption and Nd<sup>3+</sup> concentrations on FIR parameters, lithium tellurite glasses – TL with nominal composition (100-x) ( $80TeO_2 + 20Li_2O$ ) + x/2 Nd<sub>2</sub>O to x= 0.2 to 4.0 mol% were synthetized. The precursors were melted at 850°C and casted in an inox mold. The luminescence were performed pumping the sample under a laser at 583 nm from a Rhodamine 6G laser (2.8  $\pm$  0.2) mW and by a laser at 532 nm (4.0  $\pm$  0.1) mW. The samples where fixed by a conductive silver paint at a copper plate with a heating resistance and the temperature was controlled by a temperature controller, from 293 to 371K in steps of 6K. The dependence of the emission with the temperature was recorded with a spectrometer. To record the reabsorption and crossrelaxation effects in the relative sensitivity, the samples were excited at 532nm with laser non focused and at 583nm with laser focused and non focused. The relative sensitivity (Sr) is shown in Figure 1.

A strong dependence of the FIR parameters with the concentration was observed due to the changing of emission bands profiles caused by the reabsorption process. The decrease on the relative sensitivity of the ratio  ${}^{4}F_{5/2} \rightarrow {}^{4}I_{9/2} / {}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$  to higher doped sample was only 5% in the *S<sub>r</sub>* values at 299K for the higher concentration of 4.0 mol% of Nd<sup>3+</sup>. The maximum relative sensitivity found here at 299K was 3.00 %K<sup>-1</sup>, that is one of highest reported to Nd<sup>3+</sup> ions until now.



Figure 1: Relative sensitivity (Sr) for the three systems to the ratio  $[{}^{4}F_{5/2} \rightarrow {}^{4}I_{9/2}/ {}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}]$ : a) 532nm (no focused), b) 583nm (no focused) and, c) 583nm (focused).

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## THE PHOTOLUMINESCENT AND ELECTRICAL PROPERTIES OF AI-DOPED ZnO THIN FILMS

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Aluminum doped zinc oxide (AZO) is among the most promising Transparent Conductive oxides (TCOs) materials because of its excellent optical and electrical properties [1] and used as an anode material in photoelectronic devices [2]. In this work, aluminum doped zinc oxide thin films on sapphire substrates were prepared using Atomic Layer Deposition (ALD) method. The effects of post-deposition UV-ozone treatment on the properties of Al-doped ZnO thin films were studied by AFM, optical spectroscopy, Hall effect, and photoluminescence. An improvement of the optical and electrical properties as well as photoluminescence was observed relevant to the targeted application as transparent electrode for optoelectronic devices.



Fig.1. Transmittance spectra of sapphire and AZO before and after UV-ozone treatment.



Fig. 2. AZO photoluminescence spectra before and after UV-ozone treatment.

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## **Transparent Films Featuring Persistent Luminescence**

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Transparency is a property long desired for persistent luminescence materials. In this work, we demonstrate, for the first time, the production of transparent and flexible persistent composites based on  $Sr_2MgSi_2O_7:Eu^{2+},Dy^{3+}$  (SMSO),  $ZnGa_2O_4:Mn^{2+}$  (ZGO), and  $Y_2O_2S:Eu^{3+},Ti,Mg^{2+}$  into ether cellulose matrix film. The composites were successfully prepared through the dispersion of the particles in hydroxypropyl methylcellulose (HPMC) by drop-casting process. The films HPMC/SMSO, HPMC/ZGO, and HPMC/YOS exhibit persistent luminescence emission at 475 nm (blue), 500 nm (green), and 625 nm (red) wavelength, respectively. The films feature high transmittance in the visible range. To understand the fine distribution of the nanoparticles in the matrix, we have investigated their structure and dispersion by using Synchrotron Radiation X-ray fluorescence mapping and Scanning Transmission X-ray Microscopy. These innovative composites could bring new perspectives to the class of persistent luminescence materials, enhancing technologies in progress and throwing light to new applications.



Figure 1: (A) Pictures of HPMC/SMSO, HPM/YOS, and HPMC/ZGO films. Pictures under room light of composites showing flexibility and transparency of (B) HPMC/SMSO, (C) HPM/YOS, and (D) HPMC/ZGO films. Pictures of the afterglow of (E) HPMC/SMSO, (F) HPM/YOS, and (G) HPMC/ZGO films

## VISIBLE AND MID-INFRARED EMISSION PROPERTIES OF PR<sup>3+</sup> AND TM<sup>3+</sup> DOPED BGO SINGLE CRYSTAL FIBERS

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Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> (BGO) single crystals are well-known high density crystals characterized by broad absorption and emission bands as well as a short emission lifetime suitable for scintillation. They are very stable crystals which present excellent physical properties which can be used advantageously for laser applications. In this work, BGO crystal fibers singly doped and co-doped with  $Pr^{3+}$  and  $Tm^{3+}$  trivalent rare-earth ions were successfully grown by using the  $\mu$ -PD technique. Singly doped crystals were used to complete previous preliminary studies [1,2] by a complete Judd-Ofelt analysis of the absorption spectra, in order to derive radiative lifetimes and branching ratios, then by using these data to present emission spectra in the visible as well as in the near- and mid-infrared spectral regions in cross section unit.

Crystals co-doped with  $\text{Tm}^{3+}$  and  $\text{Pr}^{3+}$  ions were then used to investigate, for the first time in BGO as well as in any other materials, the quenching effect caused by  $\text{Pr}^{3+}$  ions on the emission intensity and decay time of the  ${}^{3}\text{F}_{4}$  terminal level of the  ${}^{3}\text{H}_{4} \rightarrow {}^{3}\text{F}_{4}$  emission of the  $\text{Tm}^{3+}$  ions at about 1.5 µm, and to examine the possibility of a true four-level laser operation of this emission transition. For example, in co-doped crystal 1%Tm,1%Pr:BGO, the intensity of the mid-infrared emission is reduced by nearly two orders of magnitude compared to that found in the 1%Tm:BGO singly doped one. These results clearly show the depopulation of the  ${}^{3}\text{F}_{4}$ emitting level of the Tm<sup>3+</sup> ions induced by the Pr<sup>3+</sup> codopants, such a depopulation effect being likely due to some kind of Tm<sup>3+</sup> to Pr<sup>3+</sup> energy transfer which can be written  ${}^{3}\text{F}_{4}(\text{Tm}^{3+})+{}^{3}\text{H}_{4}(\text{Pr}^{3+})$  $\rightarrow {}^{3}\text{H}_{6}(\text{Tm}^{3+})+{}^{3}\text{F}_{2}(\text{Pr}^{3+})$ . Such Tm<sup>3+</sup> to Pr<sup>3+</sup> energy transfer was further confirmed by lifetime measurements and its efficiency was proved to be larger than in the case of other well-known crystalline materials doped with Tm<sup>3+</sup> and co-doped with Tb<sup>3+</sup> or Eu<sup>3+</sup> ions [3].

Therefore, the present investigation does not only show the interest of diode-pumped (~445 nm) Pr:BGO crystals for green, orange and red laser emissions, and of diode-pumped (~792nm) Tm:BGO crystals for 1850-2050 nm mid-infrared laser emission, it also shows the possibility of a true four-level laser operation of the codoped Tm,Pr:BGO crystals around 1450-1550 nm after one-step or two-step diode-pumping around 792 nm or 1050 nm, respectively.

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# Zinc gallogermanate nanoparticles produced by pulsed laser ablation in liquid media aiming biomedical applications

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In the last decade, persistent luminescence nanoparticles (PLNPs) emitting in the red/nearinfrared region have been produced using wet-chemical methods and extensively explored for diagnostic and bioimaging purposes. These NPs demonstrate great potential to be excited *ex vivo* and *in vivo* monitoring of cells since they continue to emit for minutes, up to hours, after ceasing the excitation. Consequently, this property prevents tissue interference and autofluorescence and enhances the signal-to-noise ratio and imaging sensitivity [1].

In this work, a promising, fast, and up-scalable method for NPs preparation is explored. First, pellets of Cr doped zinc gallogermanate  $(Zn_{1+x}Ga_{2-2x}Ge_xO_4:Cr^{3+}, ZGGO:Cr)$  presenting  $Cr^{3+}$  long-lasting red luminescence (up to 8 h) were prepared by solid-state reaction [2]. Then, using these pellets as targets, the NPs were produced via pulsed laser ablation in liquid (PLAL). The morphology and optical characterization of these NPs were assessed by scanning electron microscopy (SEM) and room temperature photoluminescence (PL), respectively.

Three different morphologies were identified for the NPs' samples: microparticles with diameters between 100 and 300 nm (red arrow on **Figure 1a**), agglomerated NPs with diameters between 2 to 5 nm (green arrow on **Figure 1a**), and needle-like structures (yellow arrow on **Figure 1a**). The PL data (**Figure 2**) shows an intense red/NIR luminescence related to  $Cr^{3+}$  ions for both pellets and NPs, with a displacement of approximately 1 nm for all the emissions, suggesting that the emitting ions are not in the same position/environment in the pellet and NPs.



Figure 1: a) SEM image of ZGGO:Cr NPs. b) PL spectra obtained under 310 nm light for both the pellet target and the NPs sample.

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## First spectroscopic investigation of M(AlCl<sub>4</sub>)<sub>2</sub>:Sm<sup>2+</sup> (M = Ca, Sr, Ba) – Influence of the local site symmetry on the luminescence of Sm<sup>2+</sup>

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For the longest time, research on luminescent materials for e.g. LED applications or nanophosphors was mainly focused on Eu<sup>2+</sup>, since it's stability provides a wide range of applications [1]. In that regard, other lanthanides such as  $\text{Sm}^{2+}$  have received significantly less attention mostly due to their lower stability, which can be solved by coating of the materials, and rather difficult synthesis processes. However, as the research on divalent lanthanides continues, also the less stable representatives receive more attention [2]. Sm<sup>2+</sup> ions are also of fundamental interest due to the interaction of the closely located excited 4f<sup>5</sup>5d<sup>1</sup> and 4f<sup>6</sup> states. In this work, the spectroscopic properties of  $M(AlCl_4)_2$  (M = Ca, Sr, Ba) doped with Sm<sup>2+</sup> are presented for the first time. All samples show strong parity-forbidden  $4f^6 \rightarrow 4f^6$  emission in the range between 650 nm and 825 nm (15385-12121 cm<sup>-1</sup>) at 10 K (exemplary shown for Ba(AlCl<sub>4</sub>)<sub>2</sub>:Sm<sup>2+</sup> in Fig. 1). Additionally, at elevated temperatures Sr/Ba(AlCl<sub>4</sub>)<sub>2</sub>:Sm<sup>2+</sup> feature a  $4f^55d^1 \rightarrow 4f^6$  emission band at 695 nm (14385 cm<sup>-1</sup>) and 650 nm (15381 cm<sup>-1</sup>), respectively. Furthermore, the influence of the local symmetry on the excitation spectra is analyzed. Temperature-dependent photoluminescence and decay time measurements reveal strong quenching processes of the  $4f^6 \rightarrow 4f^6$  transitions due to close proximity to the excited  $4f^55d^1$ levels. Therefore, this system is promising to investigate the structure-luminescence behavior of divalent lanthanides.



Fig. 1: Emission and excitation spectrum of Ba(AlCl<sub>4</sub>)<sub>2</sub>:Sm<sup>2+</sup> recorded at 10 K.

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#### CRYSTAL FIELD EFFECTS ON MN IONS IN DOUBLE PEROVSKITE Sr2MnTiO6

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Perovskite based layered oxides have been widely investigated in recent times owing to their interesting electronic and magnetic properties including colossal magnetoresistance, metal-insulator transition, giant magnetoelectricity and multiferroic behavior [1]. Properties of these compounds strongly depend on the composition, number of layers oxygen deficiency, etc. Perovskites may be useful for different kind of device applications. Double perovskites were used as photocatalytic materials. The example of such double perovskite is layered  $Sr_2MnTiO_6$  [2].

The photocatalytic properties of such materials are depended on the crystal field and its effects onto the 3d metal centers. In order to find the describe these effects, the crystal field parameters have to be calculated. The exchange charge method will allow to obtain the crystal field parameters and parameters like g-factors which then can be compared with the results of the electron spin resonance measurements.

In addition, EPR spectra were measured at temperatures 4.5 - 600K using a Bruker spectrometer. Figure 1 shows obtained ESR spectra in temperature range 25-46K where two ESR lines with effective g- values  $g_1 \sim 2$  and  $g_2 \sim 12$  were observed which connected with phase separation in Sr<sub>2</sub>MnTiO<sub>6</sub>. We do not associate the observation of the second line with  $g_2 \sim 12$  with the presence of an impurity in the sample, but we assume the formation of correlated regions of one valence manganese during the transition to the paramagnetic state of regions where manganese of another valence predominates.



Figure 1. ESR spectra for Sr<sub>2</sub>MnTiO<sub>6</sub> for temperatures 25-46 K

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## The CW EPR and pulsed EPR studies of the <sup>51</sup>V<sup>4+</sup> ions in Sc2<sup>28</sup>SiO<sub>5</sub>

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Orthosilicate monocrystals  $Sc_2SiO_5$  and  $Y_2SiO_5$  and with different dopants rare earth and iron groups are widely used in numerous applications. For example, yttrium and scandium orthosilicates with 4f- and 3d- dopant ions (Nd<sup>3+</sup>, Yb<sup>3+</sup>, Cr<sup>3+</sup>) are used in various lasers and related applications. In recent years more attention was drawn towards these materials since it is possible to use them for quantum computing applications, one of which is quantum memory devices [1,2]. In order to use orthosilicates with 4f- and 3d- dopant ions, it is necessary to measure key properties such as spin – lattice relaxation times and phase memory lifetimes. In addition to that, it is useful to measure orientation dependencies ESR spectra in the monocrystals in order to obtain g-factors and hyperfine constants.

In this work we present the results of the CW EPR and pulsed EPR experiments for  ${}^{51}V^{4+}$ :Sc<sub>2</sub><sup>28</sup>SiO<sub>5</sub> (0.005 %at.). The CW EPR method was used to obtain the angular dependencies of the ESR spectra in different crystallographic planes in X- and Q- bands. The CW EPR spectra also allowed to identify the valence state of the vanadium ions in the crystal as 4+. From the approximation of the experimental results the g-factor values and hyperfine constants were found.



<u>relaxation times T<sub>1</sub> for <sup>51</sup>V<sup>4+</sup>: Sc<sub>2</sub><sup>28</sup>SiO<sub>5</sub> (0.005 %at.). lifetimes T<sub>m</sub> for <sup>51</sup>V<sup>4+</sup>: Sc<sub>2</sub><sup>28</sup>SiO<sub>5</sub> (0.005 %at.). The temperature dependencies of the relaxation times were measured using the pulsed EPR which are shown on Fig. 1, with fitting line and its components shown by dashed lines. It was found that  $T_1^{-1}$  is approximated by the sum of the direct process and Aminov – Orbach process with decent accuracy  $T_1^{-1} = A \cdot T + B \cdot exp\left(-\frac{A}{k \cdot T}\right)$ , where A= 20.6 s<sup>-1</sup> K<sup>-1</sup></u>

 $B=1.09\cdot10^6 \text{ s}^{-1}; \Delta=98 \text{ K}.$ 

The phase memory lifetimes were measured by Hann two-pulse method at various temperatures and the results are shown on Fig. 2. The exchange charge method used for calculating the crystal field parameters for  $V^{4+}$  ions in Sc<sub>2</sub>SiO<sub>5</sub>.

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## STRUCTURAL PROPERTIES OF FEMTOSECOND LASER IRRADIATION INDUCED BISMUTH OXIDE BASED NANO – OBJECTS IN Bi<sub>12</sub>SiO<sub>20</sub> (BSO) SINGLE CRYSTAL

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Single crystal of  $Bi_{12}SiO_{20}$  was grown from the melt by Czochralski technique. The crystal growth was in the [111] direction. The surfaces of the polished sample were irradiated by a femtosecond pulsed laser beam of varying power. The influence of laser power on structural properties of modified  $Bi_{12}SiO_{20}$  crystal, as well as on its phase composition, was studied.

The surface morphology of our samples was investigated by AFM. The surface of the sample before exposure is rather smooth with no cracks observed. After irradiation, the presence of small spherical islands on the surface was registered. The dimensions of the islands and their densities mostly depend both on the applied power and exposure time. There were also significant changes in far-infrared spectra of irradiated sample in comparation to non-irradiated sample.

Based on these results, the material obtained after femtosecond pulsed laser irradiation can be described as a new type of nanocomposite consisting of bismuth oxide based nano-objects, formed as nanocrystals (dimensions below 20nm in diameter), which are arranged in a matrix of  $Bi_{12}SiO_{20}$ .
#### HIGH PRESSURE SYNTHESIS OF PRASEODYMIUM SILICATES

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Oxoanionic salts of the lanthanoids are an ongoing field of research of our group. While many of such compounds are well investigated for the trivalent lanthanoids, structural and physical analysis of tetravalent lanthanoid compounds is mostly restricted to  $Ce^{4+,[1]} Pr^{4+}$  and  $Tb^{4+}$  can be stabilized in oxides, fluorides and, as was shown recently, even in metal organic complexes.<sup>[2-4]</sup>  $Pr^{4+}$  is of particular interest since its 4f<sup>1</sup>-configuration promises unique optical and magnetic properties. However, as of today no structural characterization was possible for oxoanionic salts of  $Pr^{4+}$  due to its high proclivity to be reduced to its trivalent form.

We herein present the synthesis of  $Pr_4Si_3O_{12}$  and  $PrSi_3O_8$  by reacting praseodymium dioxide and quartz in a diamond anvil cell at 30 GPa. The latter compound contains praseodymium in the formal oxidation state +IV and is metastable at ambient pressure. The structures of both compounds were determined through *in situ* single crystal diffraction at *PETRA III* (beamline P02.2) at DESY.

Both silicates form three-dimensional networks of condensed  $[SiO_6]$ -octahedra, in which all praseodymium ions are found in a 12-fold coordination sphere of oxygen atoms.



**Fig. 1** Crystal structures of  $Pr_4Si_3O_{12}$  (left) and  $PrSi_3O_8$  (right). Pr = light green; Si = brown; oxygen = dark blue.

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# Multifunctional NaYF<sub>4</sub>:Nd<sup>3+</sup>, Cr<sup>3+</sup> nanoparticles for luminescence thermometry and optical heating applications

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# Keywords: luminescent thermometry, light-to-heat conversion, transition metal ions, lanthanide ions

More recently, multifunctional nanoparticles have been the subject of intensive research in the field of nanotechnology.[1] The understating of the principles of operation of luminescent thermometers and nanoheaters and the significant progress in this field observed, caused that more and more efforts are being made currently to develop nanoparticles that allows combining these two functionalities. The development of such multifunctional materials requires the appropriate selection of the relevant host, optically active ion(s), and optimization of their concentration. The choice of host material is primarily determined by the requirements of specific application. In the case of biological application, the small particle size (below 100 nm) with narrow size distribution, high biocompatibility and the formation of stable colloidal systems in physiological solutions are the most important constraints. Additionally, from the luminescent thermometry perspective high sensitivity (S<sub>R</sub>) to temperature changes is important. The high sensitivity can be achieved by using transition metal ions (TM<sup>3+</sup>) and lanthanides (Ln<sup>3+</sup>) as a co-dopants.[2] In such systems, the Ln<sup>3+</sup> ion acts as a luminescence reference, not sensitive to temperature changes, whereas TM<sup>3+</sup> is temperature probe. The susceptibility of TM<sup>3+</sup> to temperature changes results from a high nonradiative relaxation probability which is observed for TM<sup>3+</sup> ions due to the strong electron-phonon interaction. An efficient nonradiative processes lead, in turn, to conversion of light into heat, which is released to the environment. Therefore, by taking advantage from these phenomena and by the optimization of the dopant concentration it is possible to develop a nanoparticle that serves as simultaneously as a nanoheater and luminescent thermometer.

Hence, this research focus on the optimization of the synthesis, structural and spectroscopic properties of NaYF<sub>4</sub> nanoparticles doped with transition metal and lanthanide ions for light-to-heat conversion and luminescent thermometry application.

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# HIGHLY STABILE MAGNETO-FLUORESCENT COLLOID BASED ON BARIUM HEXAFERRITE NANOPLATELETS WITH POLYPHENOL COATING

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Ferrofluids are colloidal suspensions of magnetic nanoparticles that displays both the fluidity of a liquid and the magnetic behavior of a solid. The application of this kind of material is very wide; ferrofluid can be used for magnetic resonance imaging (MRI), dynamic loudspeakers, magneto-optic sensors, heat transfer/dissipation, etc. [1]. Colloids based on barium hexaferrite nanoplatelets (BaFe<sub>12</sub>O<sub>19</sub>), obtained with the hydrothermal method, are a suitable platform for further functionalization and preparation of stabile ferrofluids [2].

If we coat barium hexaferrite nanoplatelets with polyphenol coatings, we could obtain ecofriendly, anti-microbial magnetic material with promising fluorescent properties. As a source of polyphenol, we used low-cost tannic acid, a natural polyphenol (extracted from plants), and tested how different concentrations of tannic acid influenced the coatings formations onto barium hexaferrite nanoplatelets (Figure 1) [3]. As-prepared barium hexaferrite nanoplatelets coated with tannic acid, possess high colloidal stability, porous coating, and sharp green fluorescence signal.



Figure 1. Example of barium hexaferrite nanoplatelets coated with tannic acid

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# Low-temperature sintering of persistent luminescent glassy composites.

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Persistent luminescent (PersL) materials are known for their long emission of light with no needing for a continuous excitation. Therefore, the PersL materials can be seen as a luminescent battery, which can store the energy of incident light and then, emit it for hours.[1] However, these materials are commonly obtained in powder form, which can limit their application. One way to overcome this problem is to incorporate these compounds into stable hosts, such as glasses. Nevertheless, the high temperature required in the glass preparation by the melt-quenching technic can quench the luminescence of the composites, due to material degradation, and oxidation, among others.[2] In this context, the preparation of pellets composites can reduce the temperature required to obtain a well-formed material, due to the pressure used in the process. Therefore, in this work, we present the preparation of PersL pellets glassy composites prepared at low temperatures. The 80NaPO<sub>4</sub> – 20Ga<sub>2</sub>O<sub>3</sub> glass host was mixture with different PersL compounds in order to obtain different emission color compounds, such as  $Sr_2MgSi_2O_7$ :  $Eu^{2+},Dy^{3+}$  (blue)  $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$  (Light-blue),  $SrAl_2O_4:Eu^{2+},Dy^{3+}$  (green) and  $CaS:Eu^{2+}$  (red). The composite powders were pressed to obtain cylindrical pellets. For the increased mechanical resistance, the raw pellets were annealed at 500 °C for 3h. The photoluminescence properties were investigated through excitation, emission, PersL emission spectra, and PersL decay curves. The results indicate that the PersL was not affected by the sintering process, resulting in more efficient glassy composites with potential applications in safety lighting and luminescent markers.

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# X-RAY AS A METHOD FOR MANIPULATION OF COLOR CENTERS CHARGE STATE IN DIAMONDS

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Crystals with color centers are widely used in various fields of industry and science. They can be applied to optical quantum memory, quantum sensorics and quantum cryptography. Color centers are a defect in the crystal lattice that absorbs and/or radiates in the wavelength range outside the intrinsic absorption of the crystal.

In this work, we studied the charge states changing of color centers in diamond, such as nitrogen (NV), silicon (SiV), germanium-vacancy (GeV) centers, after their irradiation with X-rays.

The study of color centers in the X-rays was carried out on a Bruker IFS 125HR highresolution Fourier spectrometer with a cryogenic attachment based on an X-ray tube BSV-30 with a copper anode, with a nominal power of 500 W and a characteristic radiation Cu K $\alpha$ 8027 eV. The results of the research were absorption spectra obtained at a temperature of 5 K. The absorption method is a well-resolved structure of lines in the spectra, which makes it possible to quantify the concentration of color centers.

The obtained spectra illustrate that after X-ray exposure, the absorption line intensities change at wavelengths of 946 nm (SiV<sup>0</sup>), 737 nm (SiV<sup>-</sup>), 575 nm (NV<sup>0</sup>), 637 nm (NV<sup>-</sup>) and 602 nm (GeV<sup>-</sup>), corresponding to color centers. In the sample with GeV, the appearance of new lines was observed, which can relate to GeV<sup>0</sup> and/or GeV<sup>+</sup> centers. A change in the SiV and NV centers was noted, the increase in the concentration of SiV<sup>0</sup> is proportional to the decrease in SiV<sup>-</sup>. A more complex interaction is observed between NV<sup>0</sup> and NV<sup>-</sup> because other charge states such as NV<sup>+</sup>, NV<sup>2+</sup> or unknown states may be involved in the process as the appearance of new lines after irradiation was found.

The result of research demonstrates that X-rays radiation can control the charge states of color centers in diamonds.

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