2nd International Conference on Physics
of Optical Materilas and Devices

BOOK OF ABSTRACTS

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2nd International Conference on Physics of Optical Materilas and Devices

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Herceg Novi, Montenegro

August 26th – September 31st, 2009

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FOREWORD

The 2009 International Conference on Physics of Optical Materials and Devices (ICOM2009) is the second conference jointly organized by the Institute of Nuclear Science "Vinča" (Republic of Serbia) and the École nationale supérieure de chimie de Paris (France).

Herceg-Novi in Montenegro is of course dedicated to tourism but also to enjoyable and useful discussions between scientists through several conferences every year.

This conference brings together scientists and technology users who are investigating or developing materials for optical applications. The conference will present the state of the art in preparation methods, optical characterization and usage of optical materials and devices in various photonic fields. The Workshop on low dimensional structures and materials will be held as a satellite meeting on ICOM2009 and will cover the advanced topics and subjects in the areas of bottom-up approaches to nanostructured materials. The conference will stress the value of a fundamental scientific understanding of optical materials and applications in lasers, scintillators, phosphors. The accent will be put on material elaboration and characterization.

The ICOM2009 Conference is organized in a workshop style, composed of several sessions, which will comprise 19 invited lectures by the leaders in the field, 50 contributed oral lectures and 156 poster presentations.

We are grateful for sponsorships which have assisted us by providing some financial support. We are grateful to Prof. G. Boulon, editor-in-chief, for the acceptance of some selected papers in the journal Optical Materials. We are grateful to Prof. M. Franko, associate editor, for the acceptance of some selected papers in the journal Acta Chimica Slovenica.

We wish to express our thanks to the members of the International committee for their suggestion of oral speakers and we are also grateful to the members of the local organising committee in Belgrade for their effort and time during preparation of the conference.

Chairpersons

Prof. Miroslav Dramićanin
Dr. Bruno Viana

List of contributions

ZnO NANOMATERIALS: OPTICAL PROPERTIES AND DEVICE APPLICATIONS

A. M. C. Ng,[1] X. Y. Chen,[1] F. Fang,[1] Y. F. Hsu,[1] A. B. Djurišić,[1*] W. K. Chan[2]

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Zinc oxide is a material of great interest for a variety of optoelectronic applications due to its wide band gap and high exciton binding energy [1,2]. In addition, ZnO can form a variety of nanostructured morphologies, which can be grown by different methods and which can exhibit very different optical properties [2]. ZnO nanorods fabricated by different methods are of interest for applications in light emitting diodes (LEDs) [3], as well as dye-sensitized solar cells (DSSCs) [4].

We have studied the influence of different fabrication methods (hydrothermal growth, vapor deposition, electrodeposition), as well as different post-fabrication treatments on the properties of ZnO nanorods (morphology and photoluminescence). Then, we have investigated the relationship between the nanorod optical properties and their performance in LEDs and DSSCs. There is a complex relationship between the native defects in the nanorods and their optical and electronic properties, and consequently device performance. In addition, factors affecting LED performance are interfacial states and energy band alignment which can be affected by the growth method, while for DSSC application the attachment of the dye may be affected by the surface properties of the nanorods. Various factors affecting light emitting and photovoltaic applications of ZnO nanorods with different properties are discussed in detail.

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INTERVALENCE CHARGE TRANSFER IN Pr^{3+} AND Tb^{3+}-DOPED DOUBLE TUNGSTATE CRYSTALS KRE $(WO_4)_2$ (RE = Y, Gd, Yb, Lu)

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First experimental evidences of intervalence charge transfer (IVCT) transitions in Pr^{3+} and Tb^{3+} doped double tungstate crystals $KRE(WO_4)_2$ (RE = Y, Gd, Yb, Lu) are reported. The IVCT bands are located nearly at the same energies for Pr^{3+} and Tb^{3+} in a given crystal and these energies are consistent with an empirical model recently developed for Pr^{3+} ions in titanates, vanadates niobates and tantalates [1-4] (see Fig. 1). These findings made it possible to locate the $4f^n$ states of trivalent lanthanides in KREW crystals by applying the Dorenbos "double seat" empirical model [5].

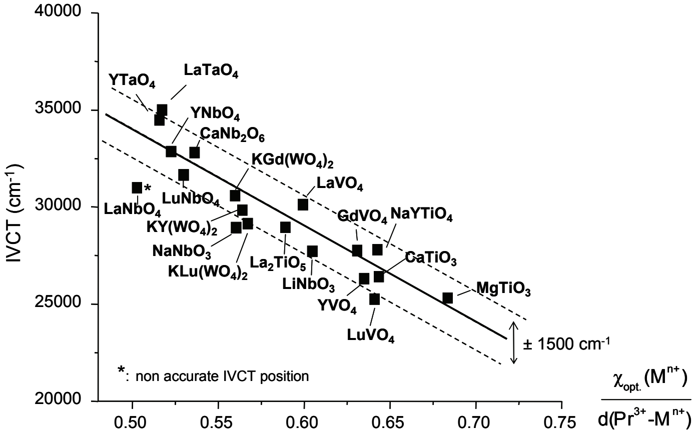

Fig. 1: Variation of the experimental IVCT energy vs. the ratio between the optical electronegativities of the d^0 M^{n+} lattice cations and the shortest Pr^{3+}–M^{n+} distances.

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LANTHANIDE LEVEL LOCATION IN TRANSITION METAL COMPLEX COMPOUNDS

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Luminescence quantum efficiency, preferred valence, charge carrier trapping, and energy transfer efficiency from the host to lanthanide impurities are often determined by the precise location of the relevant lanthanide impurity levels with respect to the conduction band and valence band of the hosting inorganic compound. Our knowledge, our experimental techniques, and our empirical and *ab initio* theoretical models are continually being improved to better understand and predict level location. With optical spectroscopy one can measure the energy of electron transfer from the valence band to the conduction band but also from the valence band to the open 4f shell of trivalent lanthanide impurities. This provides us with a method to position the divalent lanthanide ground state with respect to the top of the valence band [1]. With thermoluminescence techniques one may probe the trapping of electrons from the conduction band by the open 4f shell of trivalent lanthanide. This provides us with a method to position the divalent lanthanide ground state below the conduction band. The two complementary techniques give consistent results [2]. Those methods can not be used to determine the location of the ground state of trivalent lanthanide ions.

For the transition metal complex compounds (molybdates, tungstates, vanadates, niobates, tantalates, titanates) there appears another unique method to determine the location of the 4f ground state of trivalent lanthanides. The method is based on measuring the energy of electron transfer from the open 4f shell of a trivalent lanthanide ion to the transition metal cation. Boutinaud and co-workers studied this so-called Intervalence Charge Transfer (IVCT) by means of optical spectroscopy on many Pr^{3+} and Tb^{3+} doped transition metal complex compounds [3,4]. These type of compounds are characterized by a relatively low lying conduction band, and then the weak IVCT band can be observed at energies lower than the much stronger and otherwise overwhelming 4f-5d excitation bands. The energy of the IVCT band provides the location of the 4f ground state of trivalent lanthanide ions relative to the conduction band formed by the transition metal cation states.

In this work we will combine experimental information on the band gap, CT, and IVCT energies with empirical models on lanthanide level locations with the aim to determine the 4f ground state energies of all divalent and all trivalent lanthanides in a selection of molybdate, tungstate, vanadate, niobate, tantalate, and titanate compounds. Possible shortcomings of the method, and the implications of the found level locations on optical performance will be addressed.

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INVESTIGATION OF RARE-EARTH-DOPED AND DYE-DOPED LUMINESCENT SILICA NANOPARTICLES FOR DNA-MICROARRAY LABELING

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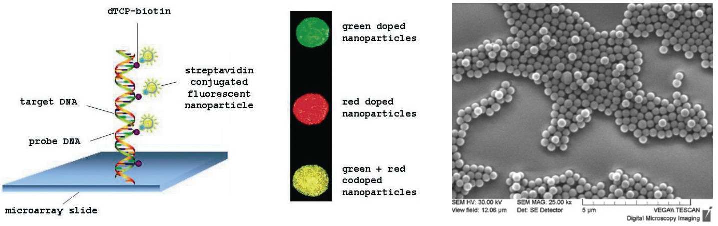
Luminescent nanoparticles are gaining more and more interest in bio-labeling and bio-imaging applications, like for example DNA microarray. This is a high-throughput technology that consists of an arrayed series of spots of ssDNA, called probes, each containing a specific nucleotide sequence. Probe molecules have the ability to hybridize a target sample and this event (probe-target interaction) is usually identified and quantified by means of optical, fluorescence-based detection. To improve the sensitivity of the microarray and to avoid limitations related to common dyes (i.e. photobleaching, chemical stability, etc…) the development of new and better biolabels is desiderable. In particular silica nanospheres are a promising and interesting solution because they can be uniform and well controlled in size, highly luminescent, non toxic and easily functionalized on their surface. The liquid synthesis of silica spheres can be obtained by hydrolysis and condensation of tetraethylortosilicate (TEOS) in basic environment. Luminescence of these spheres can be induced by the incorporation of organic or inorganic emission centres, such as rare earth ions, quantum dots or fluorescent dyes. In this talk the work done at the Civen/Nanofab laboratories about all these strategies is presented, pointing out the advantages and disadvantages of each. Rare earths exhibit narrow emission bands (easy identification), large Stokes shifts (efficient discrimination of excitation and emission), long luminescence lifetimes (possibility to perform time-delayed analysis) which can be efficiently used for the improvement of signal to noise ratio. On the other hand, luminescent dye-doped nanoparticles could be also excellent candidates for biological applications because they can be analyzed with the standard existing tools (microarray scanners, which are fitted for fluorophore excitation and emission curves), a large number of dye molecules can be incorporated in a single particle (increasing the optical signal) and the silica matrix provides a protective barrier minimizing photobleaching and photodegradation.

The synthesis and characterization of luminescent silica spheres either by rare-earth-doping or by organic dye-doping are investigated and reported. Moreover, their application in the DNA microarray technology in comparison to the use of standard molecular fluorophores or commercial quantum dots is discussed. Finally, trends for future developments are given. The cheap and easy synthesis of these luminescent particles, the stability in water, the surface functionalization and bio-compatibility makes them very promising for present and future applications in bio-labeling and bio-imaging.



Description of the DNA microarray technique (left), luminescence from spots containing silica spheres doped with different dyes (center) and SEM image of rare earth (Eu^{3+}) doped silica spheres (right)

POSSIBILITIES OFFERED BY HIGH-RESOLUTION FOURIER SPECTROSCOPY IN CHARACTERIZING OPTICAL MATERIALS: EXAMPLE OF $LiYF_4$ - Tm^{3+}

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Optical materials containing the rare-earth (RE) ions are widely used as laser media, luminophors, and scintillators. Currently, rare earth doped crystals attract great attention as promising systems for quantum information processing and storage. In this latter new field, particularly, one needs precise information on the positions, linewidths, hyperfine splittings, shapes of the RE spectral lines. Here, principal advantages of the Fourier-transform spectroscopy over other spectroscopic techniques offer unprecedented possibilities in characterizing such optical materials. To demonstrate this, examples of high-resolution optical spectra of $LiYF_4$ – Tm^{3+} single crystals are presented. Among other RE ions, the Tm^{3+} ion is of a special interest for quantum memory applications [1]. As for the $LiYF_4$ matrix, it is known to ensure a very narrow inhomogeneously broadened spectral line. The narrowest inhomogeneously broadened linewidth (0.001 cm^{-1}) ever reported for crystals was found in $LiYF_4$:Er [2].

The detailed energy level scheme for the Tm^{3+} ion in $LiYF_4$ is presented. Several crystal field transitions with low integral intensity were found that were not registered before by means of ordinary spectroscopy. Experimental data on the hyperfine and deformation splittings, isotopic effects, the spectra of the Tm – Tm pairs and of the Tm^{3+} ions in a vicinity of defects are discussed. Resonant enhancement of the intensity of some vibronics and an anomalous broadening of the Tm^{3+} ground state due to the resonant electron-phonon interaction is reported.

This work was supported by the RFBR (grant № 09-02-01067) and by the Russian Academy of Sciences under the Programs for Basic Research

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DESIGN OF LANTHANIDE-DOPED NANOMATERIALS FOR APPLICATION IN OPTICS AND CERAMICS

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The study of luminescent nanomaterials is largely motivated by the prospect of original specific applications such as electroluminescent devices[1], integrated optics[2], high efficiency and stable solid-state lasers[3], new sensors,[4] biological labels[5] or advanced ceramics[6]. Lanthanide ions are usually the species responsible for the optical properties of these materials because they exhibit a wide variety of luminescence phenomena (fluorescence, phosphorescence, up- and down-conversion, etc…), ranging from UV to infrared region, and a low impact for environment and human health.

The design of efficient materials for advanced applications require the development of novel synthetic strategies to prepare nanomaterials with a perfect control of parameters like size, morphology, crystalline phase, etc. and, of course, the optical properties. Among them, sol-gel methodology and solvothermal synthesis are two of the most successful procedures.

On the one hand, sol–gel technology offers an alternative way to prepare homogeneous and highly transparent materials at low temperatures, besides other facilities such as easy shaping, miniaturization, high purity of the precursors, possibility to combine organic and inorganic components providing the tunability of properties, etc. All these advantages are useful for integrated optical devices. On the other hand, solvothermal route allows to prepare nanocrystalline materials at low temperature with spherical morphology and controlled size (from nano to micro). These features are crucial to get stable dispersions of interest, for instance, in ink-jet ceramic technologies.

In this presentation, some outstanding examples of designing transparent inorganic and hybrid inorganic-organic nanomaterials for optics (Eu^{3+}-doped PDMS and Eu^{3+}:CdS/ZnS:SiO_2 materials) and inorganic materials for advanced ceramics (Eu^{2+}:$SrAl_2O_4$, $Ln_2Ti_2O_7$ with Ln: Er^{3+},Ce^{3+}/Ce^{4+} systems) will be shown. Special attention on the composition-synthesis-structure-properties relationship will be paid.

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IMPROVING SOLAR CELL EFFICIENCY: A CHALLENGE FOR THE TWENTY-FIRST CENTURY

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The solar energy which floods the Earth each year corresponds to 10,000 years of fossil energy to the rhythm of current worldwide consumption. However, to generate a significant fraction of the energy demand with solar cells, is a true challenge which implies to strongly increase the output of these while reducing their production costs. Currently one of the principal limits to the output of solar cells is the inadequacy between the spectrum of the incident radiation and the absorption spectrum of cells. Several solutions has been proposed to increase the solar cell efficiency that we will examine. Among the various possibilities suggested to obtain a better coupling between the spectrum of illumination and the absorption of solar cell, an approach, still little developed, consists in modifying the spectrum of illumination rather than to seek to adapt, as well as possible, solar cells to the sun spectrum. Accordingly, wavelength shifter materials are used to convert energy between various spectral ranges. Because of poor yield of currently known materials, the implementation of spectral conversion very often passes by a geometrical concentration of the light. For a direct application on solar cell, it is necessary to develop and optimize new luminescent materials which can be deposited as thin layers. Some of them will up-convert two infrared photons into one visible photon, others will down-convert UV-photons into less energetic photons. In both cases, the converted photons should fit better to the maximum of solar cell sensitivity. These latter "quantum cutter" materials in which emission of photons in cascade occurs, lead to a multiplication of photons in the active thin layer and should allow a rupture in terms of spectral conversion output. Their introduction appears as a very promising alternative. Potential candidates will be described.

CRYSTALLIZATION MEASUREMENTS ON TITANIA FILMS

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TiO_2 (titania) is an essential material component for many emerging nanoelectronic applications, including dye-sensitized solar cells, photocatalysis, and fuel cells. The metastable anatase phase of titania shows superior electrical properties to the equilibrium, rutile phase. As-deposited amorphous-titania thin films can be produced by either wet methods, using sol-gel chemistry, or dry methods, such as vacuum evaporation and RF sputtering. Post-deposition crystallization can then be performed to influence structural phase and promote desirable microstructural characteristics. Previous transmission electron microscopy (TEM) *in situ* studies of crystallization in titania thin films have used electron-beam irradiation to induce inhomogeneous nucleation [1], which allows direct observation and local control of grain formation. Crystallization of deposited layers by thermal annealing is a more common approach for device fabrication. During isothermal annealing of films on amorphous substrates, grains form via spontaneous, homogeneous nucleation, allowing measurement of intrinsic materials parameters. Using *in situ* TEM heating, we have observed and recorded the crystallization process in titania films deposited by both wet and dry methods, using amorphous-carbon support layers on molybdenum TEM grids as substrates. For samples synthesized under dry conditions, crystallization at 250 °C occurs with a characteristic time constant of less than 2 min [Fig. 1]. But, despite similar crystallization kinetics, we note dramatic differences between the consequent grain sizes and morphologies of material deposited by the different dry methods. The evolution of crystallinity in vacuum-evaporated films shows good agreement with classical predictions [2], but contrasts with results from solution-synthesized films, in which crystallization may be highly affected by nanoparticle coalescence [3].

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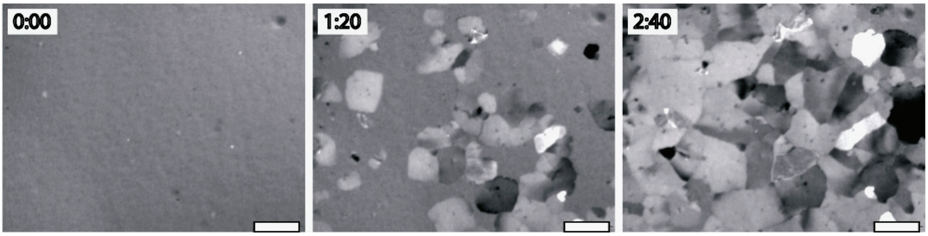

Fig. 1: Time-lapse TEM image series of evaporation-deposited titania films at various stages of crystallization. Time is given in min:sec. The scale bar is 500 nm.

TOWARDS MOLECULAR SCALE PHOTOPHYSICAL LOGIC CIRCUITS

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Charge and electronic energy transfer (ET and EET) are well-studied examples whereby different molecules can signal their state from one (the Donor, D) to the other (the Acceptor, A). This transfer is often studied as an intermolecular process but it can also occur intramolecularly, that is between two bridged parts of a molecule. In this communication we propose to use this transfer as a way of connecting between logical operations that are implemented on different molecules. With such a concatenation one can begin to think of the construction of larger scale integrated logic circuits, made up of many molecules. In particular, the already demonstrated EET in trichromophoric molecules assures us that a fanout operation, that is the communication of a given output as input to more than one circuit, will be possible. While we shall not make use of it, the scheme discussed in this presentation can exhibit a bi-directional transfer so that feedback is also possible.

We show, that one molecule can communicate its logic output as input to another molecule. This is achieved via an electronic energy transfer from a donor to an acceptor. We discuss a specific pair, the rhodamine 6G-azulene, for which there is considerable data, but the scheme is general enough to allow a wide choice of D and A pairs. We present results pertaining to a newly sythesized bicromophoric molecule based on this pair, in which a full adder is implemented, utilising intarmolecular electronic energy transfer between the two moieties.

NANO-ENGINEERED SILICON LIGHT EMITTING DIODES AND OPTICALLY ACTIVE WAVEGUIDES

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Silicon is the primary semiconductor material and represents around 90% of the semiconductor chip market. Ultra-large-scale-integration (ULSI) technology of silicon is the basis of microelectronics and drives the exponential growth (Moore's Law) in computer speed and power that underpins the whole information technology sector. Despite its predominance, silicon lacks a key semiconductor property. It has an indirect band-gap and is fundamentally unable to emit light! Nevertheless, it is increasingly clear that we need light emitting or light amplifying devices on silicon. In particular there is considerable interest in and need for wavelengths in the extended optical communications band from 1.2 to 1.8 μm for optical fibre communications and, in particular, an emitter at 1.3 μm is required in key applications such as Fibre-to-the-Home. One way to obtain these wavelengths is to use other optically active materials or centres in silicon for example the lanthanide rare earth elements - this approach has previously always failed to obtain efficient room temperature operation in bulk silicon due to the strong thermal quenching. We will show that nano-engineering a strain field in devices to provide spatial confinement of carriers can reduce, eliminate or even reverse thermal quenching in these devices [1]. We will report here on nano-engineered bulk silicon light emitting diodes incorporating the rare earth erbium operating at 1.5 μm. We will also report on diodes operating over the 1.2 to 1.35 μm range achieved by the implantation of the rare earth thulium, incorporated in the trivalent Tm^{3+} state, into silicon p-n junctions. We will then describe recent experiments [2] showing how rare earth implants combined with strain engineering can lead to optical gain in silicon-on-insulator waveguide structures. Gain is seen over a range of 150 nm, centred at 1550 nm, making it, unlike other recent approaches, ideally suited for dense wavelength division multiplexing over this most important wavelength range. Importantly, it can be electrically pumped unlike other approaches reported recently such as utilizing the Raman effect [3] and four wave mixing [4] which are purely optical effects and for fundamental reasons are not capable of being electrically pumped. Finally, the prospects of using the approach described here for achieving all silicon lasers and optical amplifiers will be discussed.

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NOVEL PROBES FOR BIPHOTONIC BIO-IMAGING

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We present here two different approaches for the design of novel fluorescent probes featuring high for two-photon absorption (TPA) cross-sections σ_{TPA}:

-using the unique luminescence properties of Ln^{III} ions (sharp emission, large Stockes shift, insensitivity to oxygen, and their long excited state lifetime ranging from µs to ms), which triggered the development of time-resolved microscopy for applications in biological imaging, we designed a new family of ligands-based chromophores able to induce lanthanides emission by two-photon antenna effect[1]. Tuning the strength of the donor as well as the length of the π-conjugated backbone (Fig.1, left) allowed to optimize the TPA cross-section[2].

The description of the first two-photon scanning microscopy bio-imaging experiments using these lanthanide complexes led to consider these complexes as a new generation of molecular probes (Fig. 1, right)[3].

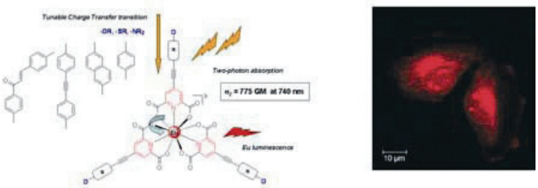

Fig. 1 Dipicolinic acid ligands based complexes with optimized cross-sections for the two-photon sensitized luminescence of europium (left); two-photon excited luminescence (right, λ_{ex}= 760 nm) and contrast phase (left) images of T24 cancer cell (right)

-in order to develop efficient probes combining both second-harmonic imaging and two-photon excited fluoresecence microscopies, we proposed a series of novel neutral push-pull probe molecules[4], fulfilling the right balance between hydrophobicity and hydrophilicity and for which a good membrane staining, compared to existing probes, could be observed, as shown in Figure 2[5].

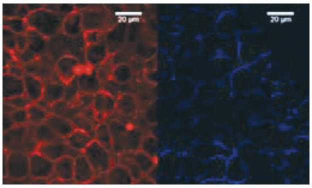

Fig. 2 Simultaneous TPEF (left) and second harmonic generation (right) images of F98 cells excited at 810 nm.

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OPTICAL PROPERTIES OF CR^{3+} ION IN TRANSPARENT NANOCERAMICS

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The synthesis of transparent nanoceramics from the Cr^{3+} doped $Y_3Al_5O_{12}$, $MgAlO_4$ and Al_2O_3 from nanocrystalline powders is presented. Their structure and morphology were determined.

The optical measurements (fluorescence, excitation and lifetimes) of Cr^{3+} in nanoceramics were performed. In particular it was noticed the emission and excitation spectra were strongly affected by the grain size of nanoceramics. The effect of applied sintering pressure on optical behavior of Cr^{3+} ion was observed. The effect of grain size and sintering pressure on electron-phonon coupling and crystal field strength were investigated.

NON LINEAR PROCESSES IN STRUCTURED SOLID STATE LASERS

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Structuring materials in the micro and sub-micrometer range constitutes an intense research field in photonics relevant from the fundamental point of view, but also from the increasing need of a spatial and spectral control of the electromagnetic radiation. In particular, when an appropriated structure is practised on a solid state laser crystal, new optical functions can be added.

The aim of our work is the extension of the functionality of laser materials to include new non-linear processes provided by a superstructure of ferroelectric domains on it. We will show how by using two-dimensional anti-ferroelectric micro-domain structures novel frequency conversion processes can be obtained.

Specifically, we will show how by means of the appropriated structure and configuration multiple-direction second harmonic generation can be continuously tuned in an extremely broad frequency range covering the whole visible spectrum.

The results are promising for novel optical multifunctional devices based on solid state lasers, which can simultaneously act as multiple harmonic generators, nonlinear prisms or all optical deflectors.

NEAR-INFARED MULTISPECTRAL IMAGING AS TECHNIQUE IN NANOMATERIALS: SYNTHESIS AND CHARECTERIZATIN OF SOL-GEL GLASS ENCAPSULATED FULLERENES

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We have recently developed a novel near-infrared multispectral imaging instrument (NIR-MSI), which employs an acousto-optic tunable filter (AOTF) for spectral scanning. This AOTF-based NIR-MSI has the combined advantages of a NIR spectrophotometer and a NIR imaging instrument, namely, it provides, for the first time, the means to noninvasively, sensitively (at single pixel resolution of about 10 μm/pixel in the NIR-MSI instrument and 0.6 μm/pixel in a NIR-MSI microscope), and rapidly (μsec) record, not at a single wavelength as in NIR imaging instruments, but an entire NIR absorption spectrum (as in a spectrophotometer), and not just one spectrum but tens of thousands of spectra at tens of thousands of different locations within a sample in a period as short as a few hundred microseconds. Chemical information derived from these spectra makes it possible to noninvasively and accurately detect and identify many different chemical species at many different positions within a sample. Using these unique capabilities, we have successfully used the instrument for studies and measurements which would otherwise have been impossible. Some applications of this imaging instrument including its use to characterize and determine molecular state and distribution of encapsulated fullerene molecules (C_{60}, C_{70} or their mixture) in newly synthesized sol-gel glass samples will be described in this seminar.

PHOTOACOUSTIC SPECTROSCOPY IN TRACE GAS SENSING

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In most applications of trace gas sensing high sensitivity, specificity, multi-component capability, minimal or no sample preparation, large dynamic range and good time resolution are important issues. Despite the availability of many instruments there is still a need for improvements or for developments of alternative techniques to meet above requirements. Optical and laser-based devices play an increasingly important role in this field as they offer some unique advantages. Often a tunable mid-infrared laser is used as light source. If less sensitivity is required, alternatives such as near-infrared diode lasers or even LEDs can be employed. With respect to sensitive detection, we focus here on the photoacoustic (PA) technique although other laser-based schemes such as direct absorption in multi-pass cells or cavity ringdown spectroscopy will also be introduced for comparison of performance.

Several examples will be discussed to illustrate the potential of photoacoustics. A first application concerns the monitoring of street traffic emission with a time resolution in the minute range. Even in a harsh and noisy environment we were able to record ppb-to-ppm concentrations of ethylene, ammonia and CO_2 with a time resolution of minutes with a mobile CO_2-laser based system incorporating a homebuilt multipass resonant PA cell with an array of 16 miniature electret microphones [1]. Another most recent example concerns the comparison of the generated PA signal by using either repetitively pulsed or CW modulated radiation incident on a resonant PA cell. In agreement with a theoretical model it was experimentally demonstrated that the pulsed radiation (pulsed at a repetition rate corresponding to an acoustic resonance frequency of the PA cell) yields a $\pi/2$-times higher PA signal amplitude than the modulated excitation at the same resonance frequency and average laser power. The experimental verification was performed for NO_2 buffered in argon with a pulsed and a chopper-modulated frequency-doubled CW Nd:YAG laser at 532 nm [2]. A further development is a self-normalizing PA gas sensor where the common intensity normalization (requiring a power detector) becomes obsolete. We introduced a novel scheme named dual-mode excitation and recently demonstrated its feasibility by successful humidity measurements with an LED-based sensor using this principle [3]. Further improvements with simultaneous excitation involving 4 LEDs are currently pursued.

If elevated temperatures are required (e.g. for studies on vapors) or if only low-power light sources are available, PA detection may not be the most appropriate sensing technique and other detection schemes like direct absorption in multi-pass cells can be employed as several other examples to be presented will demonstrate.

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OPTICAL NANO-ANTENNAS: CHARACTERIZATION AND CONTROL

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Optical antennas are elementary devices operating in the optical domain playing a major role in the manipulation of light on the nanometer scale. Optical antennas offer technological solutions for developing ultrasensitive biological and medical tools, for increasing the efficiency of photonic interactions and light extraction in solid state devices and for engineering radiation properties of single emitters. Although not strictly equivalent to radio-wave antennas (presence of losses), optical antennas are characterized by their spectral gain and their directional properties. This information is included in the description of the electromagnetic local density of states (LDOS) of the system. The LDOS uniquely demonstrates the available optical eigenmodes and is therefore central to the understanding and control of optical antennas. We will present spectroscopic LDOS measurements over different nano-antennas, and by comparaison to a reference radiator, quantitatively assess their gain and detuning from a given excitation wavelength (Fig. 1). Through a conoscopic and coranographic imaging techniques we will discuss the angular emission diagram of single nano-antennas as well as electromagnetically coupled elements.

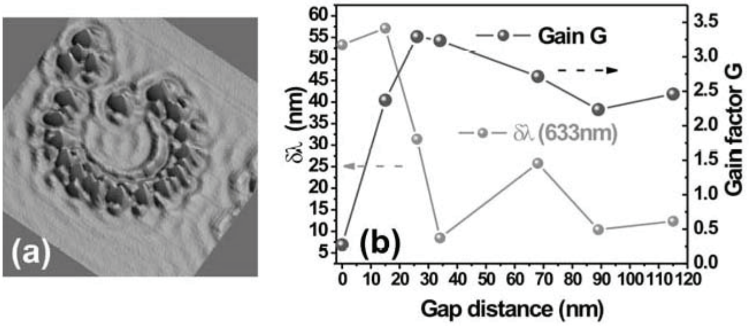

Figure 1: (a) Optical image of the LDOS of a corral in construction made of metal nanoparticle (optical antennas). (b) Gain G and detuning factor δλ for optical antenna dimers of varying gaps.

The use of optical antennas in functional integrated devices is strongly dependent on our ability to redirect electromagnetic radiation through the utilization of such element. Shape, size and materials constituting an optical antenna are all designed parameters that allow a form of passive control over the antenna response. Ultimate optical antenna-based devices will however require dynamic and active functionalities that will on-demand control the interfacing properties of individual optical antennas. In this presentation, we will show how to fine-tune antenna properties (detuning, gain, emission diagram, etc…) by a voltage-control of the surrounding dielectric medium. In particular, we will show that the coupling mechanisms between a single dimer-like antenna can be pitched on-demand.

RARE-EARTH-ACTIVATED GLASS CERAMIC WAVEGUIDES

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This work is focused on sol-gel-derived SiO_2–HfO_2 and SiO_2–SnO_2 glass-ceramic waveguides activated by Er^{3+} and Eu^{3+} ions. We demonstrate that with optimized fabrication protocols it is possible to succeed in preparation of low-loss GCs waveguides activated by rare-earth ions opening new potentialities for the development of smart and cheap integrated optical circuits.

Concerning sol-gel-derived Er^{3+}-activated HfO_2-based glass-ceramics the research activity has evidenced that: i) silica-hafnia glass ceramics allow to achieve an attenuation coefficient as low as 0.3 dB/cm at 1542 nm; ii) HfO_2 crystalline phase can efficiently enhance the spectroscopic properties of the embedded Er^{3+} ions; iii) Er^{3+} ions remain incorporated in tetragonal HfO_2 nanocrystals with dimensions of about 3-5 nm depending on the HfO_2 content. From a technological point of view patterning of photonic structures on the silica-hafnia film requires photolithography followed by CHF_3 reactive ion etching. A more simple approach consists in the exploitation of photorefractive properties. The inclusion of rare-earth elements, by allowing to combine photorefractive and active properties, may provide an effective route to the simple fabrication of integrated optics amplifiers and lasers. In this context we present SiO_2–SnO_2 glass-ceramic waveguides doped with Eu^{3+} ions with SnO_2 content as high as 25 mol %. Formation and growth of nanocrystals in the parent amorphous waveguides was induced by heat treatment. The formation of tetragonal rutile SnO_2 crystals in the films was confirmed by Raman spectra. Photoluminescence measurements indicate that most part of Eu^{3+} ions are embedded in SnO_2 nanocrystals. The excitation spectra clearly evidence the role of interband electronic transition of SnO_2 nanocrystals on the luminescence of Eu^{3+} ions. An attenuation coefficient a low as 0.8 ± 0.2 dB/cm at 632.8 nm was measured in the $75SiO_2$-$25SnO_2$ glass-ceramic waveguide. Preliminary measurements on the effect of exposure to the UV excimer laser irradiation have shown a modulation of the refractive index of the parent waveguide, suitable to realize optical Bragg gratings in these materials.

ELECTRONIC PROPERTIES AND MORPHOLOGY OF INTERFACES AND LAYERS IN ORGANIC SOLAR CELLS

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Organic solar cells are promising as relatively low-cost photovoltaic devices that would complement mature silicon-based solar cells in the area of flexible substrates and large-scale applications. One of the most promising approaches includes so called bulk heterojunction systems that comprise a blend of suitable polymer and acceptor material as layers for harvesting of solar energy. In the talk we will present basic principles of operation of bulk heterojunction solar cells that employ fullerenes as acceptors. We will also show how charge carrier mobility and recombination rate can be characterized by using short laser pulses and time-dependent transport measurements. Stability of metal/organic semiconductor contacts is affecting charge carrier transport across the interface, and represents one of the issues that preclude widespread commercialization of polymer-based organic solar cells. We will show that indium-related compounds diffuse through hudred-nanometer thick layers of polymers and give rise to additional electronic states in the polymer.

SOFT PROCESSING FOR CERAMICS: SINGLE-STEP FABRICATION OF NANO-STRUCTURED OXIDE CERAMICS (PARTICLES, FILMS, INTEGRATED LAYERS AND PATTERNS) FROM SOLUTION WITHOUT FIRING

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Since 1989 when we found a method to fabricate $BaTiO_3$ film on Ti substrate in a $Ba(OH)_2$ solution by Hydrothermal Electrochemical [HEC] methodat low temperatures of 60-200°C, we have proposed an innovative concept and technology, "Soft Processing" or "Soft Solution Processing," which aims low energetic (=environmentally benign) fabrication of shaped, sized, located, and oriented ceramic materials in/from solutions. It can be regarded as one of bio-inspired processing, green processing, or eco-processing.1,2) When we have activated/stimulated interfacial reactions locally and/or moved the reaction point dynamically, we can get patterned ceramic films directly in solution without any firing, masking or etching. Those Direct Patterning methods differ from previous patterning methods which consist of multi-step processes, for example: (1) synthesis of particles of compounds or precursors, [When this synthesis is done in a solution it is called"Soft Chemistry".] (2) dispersion of the particles into a liquid ("ink"), (3) patterning of the particles on a substrate by printing of the "ink", (4) consolidation and/or fixing of the particles' pattern by heating and/or firing at high temperatures. (5) Those processes would cause cracking and/or peeling of patterned films due to the shrincage of printed powders by sintering during heating and/or firing.

The notable feature of Direct Patterning is that each reactant reacts directly on site, at the interface with the substrate. Therefore, the chemical driving force of the reaction, A+B=AB, can be utilized not only for synthesis but also for crystallization and/or consolidation of the compound AB. It is rather contrasting to general patterning methods where thermal driving force of firing is mostly used for the consolidation of the particles.3)

We have developed the Direct Patterning of CdS, PbS, and $CaWO_4$ on papers by ink-jet reaction method and $LiCoO_2$ by electrochemically activated interfacial reactions.4) Furthermore, we have succeeded to fabricate $BaTiO_3$ patterns on Ti by a laser beam scanning and carbon patterns on Si by a needle electrode scanning directly in solutions.5) Recent success in TiO_2 and CeO_2 patterns by Ink-jet deposition, where nano-particles are nucleated and grown successively on the surface of substrate thus become dense even below 300°C, will be presented.6) Transparent films of several hundred nm thick can be oftained by 20 times of ink-jet scanning during 15-30 min.

As a development of Hydrothermal Electrochemical [HEC] method, we have proposed a new strategy:" Growing Integration Layer[GIL] method",which can provide well-adhered inte-grated/graded layers: Titanate/TiOx/Ti or Titanate/TiOx/Ti-alloys and/or metallic glass(es) at RT-150 C in a solution. This [GIL] strategy can be applied for many areas of functional ceramics.7-9) In addition,our recent results on mono-dispersed nano-particles of $CeO_2$10),(Hf,Eu)O_{2-x}11),$Fe_3O_4$12),etc. will be presented.

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NANOSIZE Tm^{3+}: Lu_2O_3 @ SiO_2 CORE-SHELL PARTICLES: SYNTHESIS AND CHARACTERIZATION

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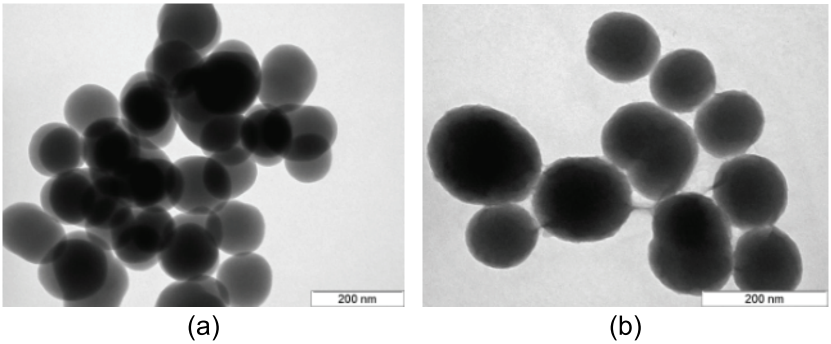
Nanosize Tm^{3+}:Lu_2O_3 @ SiO_2 core-shell powder (5 at. %) have been prepared by the modified Pechini method. The complex gel was prepared by the evaporation of the water solvent, from the aqueous solution of the rare earth nitrates and EDTA as chelating agent. Amorphous spheres of silica with a mean size of 100 nm (Alfa Aesar) were used as core. By the pyrolysis of the gel at 573 K and sintering process at 973 K we obtain the nanostructured powder. The morphology was studied by ESEM and TEM showing the formation of the surrounding layer, and X-ray powder diffraction pattern shows the crystallization of the Tm^{3+}:Lu_2O_3 and the expected cubic structure and $Ia\bar{3}$ space group. The increased value of unit cell parameter indicates the substitution of Thulium ion in Lutetium sites. Discussion of optical parameters will be presented from optical absorption spectra and infrared spectroscopy results.



(a) (b)

Figure 1 TEM graphs of silica nanospheres as obtained from the supplier (a), final core-shell structured nanoparticles (b).

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EPITAXIAL LAYERS OF $KY_{1-x-y}Gd_xLu_y(WO_4)_2$ DOPED WITH Er^{3+} AND Tm^{3+} FOR PLANAR WAVEGUIDE LASERS

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Since their demonstration in 1969, many materials have been studied to develop dielectric planar waveguide lasers (PWLs), such as oxides, fluorides, glasses [1], and more recently monoclinic double tungstates, $KRE(WO_4)_2$, [2,3]. The main advantages of using PWLs are i) the reduction of the cavity mode-volume due to the optical confinement in the active layer, ii) high optical gain, iii) low laser thresholds and iv) easy on-chip integration of these PWLs with other optical components.

Our first step towards the generation of PWLs based on $KRE(WO_4)_2$ was the careful optimization of a suitable chemical composition in the system $KY_{1-x-y}Gd_xLu_y(WO_4)_2$ to be grown on $KY(WO_4)_2$ substrates presenting high enough refractive index contrast and low lattice mismatch with the substrate. We showed that a passive guiding layer $KY_{0.59}Gd_{0.19}Lu_{0.22}(WO_4)_2$ epitaxially grown on **b** oriented $KY(WO_4)_2$ substrates behaves as a planar waveguide at $\lambda = 632.8$ nm and estimated upper limit for scattering losses amounting to 1 dB/cm [4].

Here we show the results we obtained up to now in the fabrication of planar waveguide lasers based on monoclinic double tungstates doped with Er^{3+} and Tm^{3+}. We have successfully introduced these ions in lattice matched $KY_{0.59}Gd_{0.19}Lu_{0.22}(WO_4)_2$ epilayers grown on $KY(WO_4)_2$ substrates without loss of optical quality and keeping a high refractive index contrast. We have characterized the waveguiding properties of these epitaxial layers at $\lambda = 632.8$ nm by dark modes spectroscopy, and we show that these waveguides can support up to three TE and TM modes. Spectroscopic characterization of the active lanthanide ions and waveguide laser experiments will also be presented.

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OPTICAL TRANSITION PROBABILITIES IN Er^{3+}- AND Tm^{3+}-DOPED $LiLa_9(SiO_4)_6O_2$ CRYSTALS

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Silicate crystals doped with trivalent lanthanide ions are promising candidates for the development of photonic devices due to their excellent thermal, optical and mechanical properties [1,2]. $LiLa_9(SiO_4)_6O_2$ (LLS) is a partially disordered silicate crystal, with apatite structure, that can be activated with optically active rare-earth ions to yield materials with attractive luminescent properties [3].

In this work LLS:Er^{3+} and LLS:Tm^{3+} crystals have been grown from a Li_2MoO_4 flux in the 1360–940 °C temperature range [3].

Optical absorption spectra have been measured to calculate the experimental oscillator strength from the ground state to the excited levels. Judd-Ofelt calculations were performed to estimate the Ω_2, Ω_4, and Ω_6 parameters, and therefore, the radiative lifetimes of the Er^{3+} and Tm^{3+} manifolds were calculated.

The different experimental luminescence lifetimes have been measured and, after comparing with the Judd-Ofelt predictions, the non-radiative probabilities, W_{nr}, have been obtained. They follow the classical dependence on the energy gap, ΔE, expressed by the "energy gap law" formulated by M. Weber [4]:

$$W_{nr} = \beta \exp(-\alpha \Delta E)$$

Following the corresponding least squares fit of the experimental data, the α and β parameters have been obtained.

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MAGNETORESISTIVE BEHAVIOUR OF NANO-PARTICLE $Fe_{1-x}Mn_xFe_2O_4$

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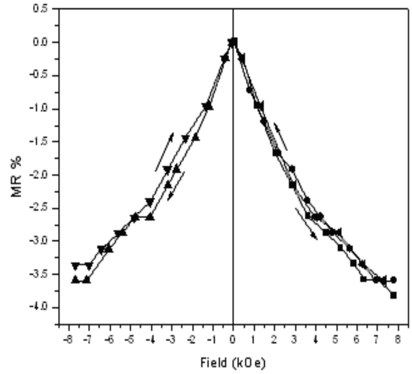
$Fe_{1-x}Mn_xFe_2O_4$ (Where x=0,1) have been prepared using a wet chemical method. Single crystalline phase nature of the prepared samples has been confirmed using x-ray diffraction measurements. The average particle sizes in the samples, estimated using x-ray diffraction line broadening and Debye Scherrer equation are x=0,1 are respectively 260 Å ,160Å . Electrical resistance has been measured, on sintered pellets of this sample, in the temperature range 20K – 300K and in fields upto 7.5 kOe, as the field is cycled from zero to +7.5 kOe, then to – 7.5 kOe. Hopping mechanism responsible for conduction in $Fe_{1-x}Mn_xFe_2O_4$ and the inter-granular tunneling in this nano-particle samples combine to impart an insulating/semi-conducting nature to $Fe_{1-x}Mn_xFe_2O_4$ samples at all temperatures till RT. Hysteresis in MR – H would owe to spin dependent charge accumulation.



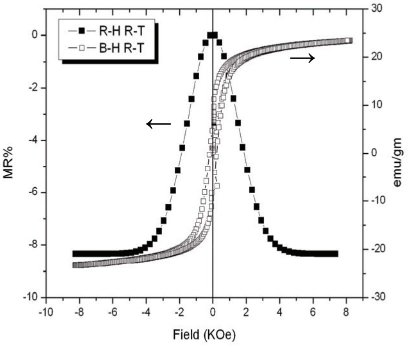


Fig. 1: MR – H plot for Fe_3O_4 (260 Å) sample.

Fig. 2: MR – H, M-H plot for $MnFe_2O_4$ (160Å) sample.

OPTICAL AND LUMINESCENCE PROPERTIES OF SI NANOCRYSTALS ENSEMBLES IN SILICON DIOXIDE STUDIED IN EXTENDED SPECTRAL RANGE

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While the properties of individual Si nanocrystals are well explained in terms of quantum confinement [1] and influence of defect states [2], the properties of ordered or assembled Si nanocrystals in a solid matrix are not well understood.

The results of the first study of luminescent properties of nc-Si superlattices (SL) consisting of alternating layers of Si nanocrystals and silicon dioxide (nc-Si/SiO2) in the excitation energy range up to 20 eV were reported at ICL2008. The approach for the fabrication of SL was based on nc-Si self-organization and, as a result, an excellent control over nc-Si size, shape and defect states in SiO_2 was achieved [3]. Investigation of optical and luminescence properties of nc-Si/SiO_2 SL in extended energy range including VUV can address both the effect of light scattering in dielectrically inhomogeneous medium and influence of the electronic states in the SiO_2 matrix on the excitation/de-excitation processes in nc-Si.

Samples were prepared by thermal crystallization of superlattices consisting of 40 pairs of layers SiO/SiO_2 on silicon substrate, for more details see [3]. Thickness of SiO_2 layers was set at 4 nm, that of SiO varied from 2 to 6 nm for different samples. Annealing at 1100 C in N_2 atmosphere for 1 h resulted in Si nanocrystals formation within SiO layers.

Luminescence spectra originating both from nc-Si and defects in SiO_2 at the excitation energies higher than 10 eV were measured. In the excitation spectra of nc-Si luminescence a steep rise of the quantum yield is observed in the region from 3 to 6 eV both at RT and LHeT. To clarify its origin absorption spectra were measured for SL on SiO_2 substrates. Comparison of the two types of spectra indicates that the increase in the quantum yield is due to the increase of the absorption. Possible reasons for the increase of the absorption in such an extended energy range are analysed, absorption of superlattices is compared to that of porous Si and SiO_2 films with Si-clusters.

Financial support of DFG grant 436 RUS 113/437 is gratefully acknowledged.

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WAVEGUIDING DEMONSTRATION ON Yb: Nb: $RbTiOPO_4$ / $RbTiOPO_4$ LAYERS GROWN BY LIQUID PHASE EPITAXY

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Rubidium Titanyl Phosphate, $RbTiOPO_4$, (RTP), crystallize in the orthorhombic system, with space group of symmetry $Pna2_1$. This material has important applications in nonlinear optics due to its high nonlinear optical an electrooptical coefficients. It has been demonstrated that RTP can be doped with Yb^{3+} with low distribution coefficient, and the Yb^{3+} concentration in RTP is not enough for laser operation. The distribution coefficient of Yb^{3+} can be increased by codoping with Nb^{5+} and laser operation of Nb:Yb:RTP has been demonstrated in 2007[1]. With the aim to guide the light with a doped RTP nonlinear optical material, we have grown epitaxial films of Nb:Yb:RTP on RTP substrates by liquid phase epitaxy. All epitaxies were grown on the (001) crystallographic plane to try to obtain in a future periodic inversion domains. To choose the basical solution composition in the Rb_2O-P_2O_5-TiO_2 system and the mol % of TiO_2 substituted by Nb_2O_5 and Yb_2O_3, we used previous results related with the study of the critical concentration of Nb_2O_5 and Yb_2O_5 which allows to obtain the Nb:Yb:RTP phase[2]. We have also studied the rate of growth as a function of the time and the effect of the angular velocity of rotation. The Yb^{3+} concentration in the crystal was measured by Electron Probe Microanalysis (EPMA) and its concentration is $0.1876.10^{20}$ atm/cm^3. The unit cell parameters were refined, and then the lattice mismatch between the epitaxy and substrate were calculated. To study the guiding light, we have applied the prism coupler method[3] with a He-Ne laser emiting at 632.8 nm. We calculate theoretically the thickness required by the sample to obtain five propagation modes, with TM polarization, and oscillating along the ***c*** crystallographic direction. Then, the epitaxial film was polished up to the thickness required. The propagation modes obtained are shown in Figure 1.a), and an optical microscope photograph is shown in Figure 1.b).

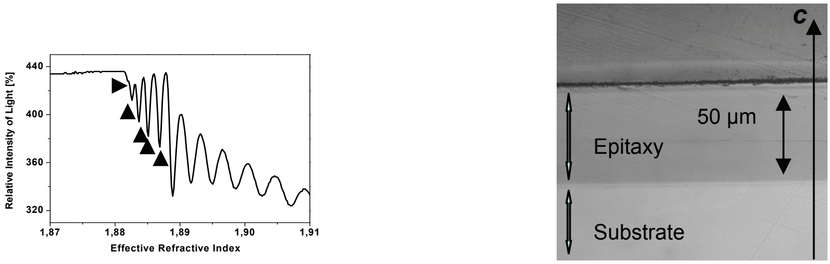

Figure 1: a) Reflected intensity of light versus the effective refractive index, b) Optical microscope photograph of Yb:Nb:$RbTiOPO_4$ / $RbTiOPO_4$ epitaxy.

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OPTICAL AND PHYSICAL PROPERTIES OF SODA GLASS BASED ON THAILAND QUARTZ SANDS DOPED WITH IRON OXIDE

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Soda glass samples were fabricated in the laboratory scale using local quartz sand from Tak province, northern Thailand, and 25 wt% of Na_2CO_3 as the main compositions. Fe_2O_3 was doped with various concentrations (0.1-10.0 wt%). Well-mixed and dried powders mixtures were melted in a ceramic crucible, in an electric furnace, at the maximum temperature of 1250 °C for 4 hr. Transparent and bubbles-free glass samples were yielded after cooling down. Physical and optical properties of the glass samples were studied. It was found that the glass color was changed from colorless to dark brown. The density, refractive index and dielectric constant were increased as the increase of Fe_2O_3 contents. UV-Visible-Near Infrared spectra were detected. X-ray absorption spectroscopy (XAS) was also discussed.

TAILORING OPTICAL PROPERTIES OF HYBRID MATERIALS FOR OPTOELECTRONIC APPLICATIONS

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Optoelectronic devices based upon hybrid materials made of semiconducting polymers doped with inorganic nanoparticles are increasing the interest of studies on optical properties of these materials [1,2]. In particular, those hybrid materials processed from solution that can be cast by simple techniques, such as different printing technologies, drop-casting or spin-coating among others.

We have synthesized PbS nanocrystals directly in poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) semiconducting polymer. This hybrid material is prepared in solution of 80% toluene and 20% di-methylsulfoxide (DMSO). A series of hybrid solutions with different concentrations of PbS with respect to the polymer has been prepared and characterized first in solution and then as thin film deposited on quartz sustrates by spin-coating.

The formation of PbS nanocrystals has been verified by transmission electron microscopy. The mean particle diameter has been estimated to be 4nm.

An optical spectroscopic study of this series of hybrid materials has been performed. Absorption spectra of the pure MDMO-PPV reference sample and the series containing different PbS nanocrystals concentration has been measured. Also, the evolution of photoluminescence of the series is presented and analyzed.

The study shows that the optical behaviour of this hybrid material can be tailored changing the ratio between the polymer and the nanoparticles synthesized inside it. An enhancement of the absorption at wavelengths below 400nm is observed with increasing PbS nanoparticles concentration. This result suggests that this MDMO-PPV:PbS hybrid material can be a worthy candidate as active layer in organic photodetectors and photovoltaic devices.

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SYNTHESIS AND CHARACTERIZATION OF Ho_x:$Lu_{2-x}O_3$ NANOCRYSTALS TO PERFORM LASER CERAMICS

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The synthesis of lanthanide-doped nanocrystals has created a great interest as a first step for ceramic lasers preparation, being an alternative to classic bulk single crystals due to their improved thermal and mechanical properties. The rare earth sesquioxide materials are known as an excellent laser host materials due to its good physical properties such as low thermal expansion[1], and higher conductivity and larger ground state splitting than YAG, when are doped with rare earths[2].

In the present study, the modified Pechini method has been used to obtain Ho_x:$Lu_{2-x}O_3$ nanocrystals because of its several advantages such as low temperature process, low cost and simplicity[3,4]. Trivalent holmium is used as an active ion, which emission near 2μm is interesting because it belongs to eye-safe spectral region, the water absorption at this wavelength and medical applications involving coagulative cutting and tissue welding. The structural characterization of Ho_x:$Lu_{2-x}O_3$ nanocrystals was carried out by X-ray diffraction powder, TEM studies and electron diffraction. Synthesized Ho_x:$Lu_{2-x}O_3$ nanocrystals belong to the cubic system with space group $Ia\bar{3}$ and the particle size was estimated by Scherrer's equation around 15nm.

Figure 1a shows a characteristic TEM image, where it can be observed the interplanar lattice indicating the high crystallinity degree. To study the possible orientation of the observed nanocrystals, it was performed their FFT pattern (fig.1b) and the nanobeam electron diffraction (fig. 1c). The reflections were indexed as {200}, {211} and {400}. Moreover, the spectroscopic properties of Ho^{3+} have been studied at room- and low-temperature. The ceramics experiments will be performed in the future.

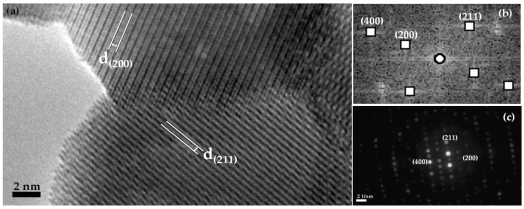

Fig.1 (a) TEM image of Ho_x:$Lu_{2-x}O_3$ nanocrystals, (b) FFT pattern of (a), (c) Nanobeam electron diffraction pattern.

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THE KERR EFFECT IN 1-D PHOTONIC CRYSTALS WITH A THIN TBFECO MAGNETIC LAYER

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In this study, we have analyzed magneto-optical Kerr effect (MOKE) in amorphous TbFeCo as a defect layer in magneto-photonic crystal (MPC) structures. The target application of this rare earth-transition metal alloy is magneto-optical data storage. By formation of an optical microcavity which partially traps the incident light at the position of TbFeCo, the MOKE enhancement in the amorphous film has been demonstrated. We have shown that despite of a large extinction coefficient at short visible wavelengths, TbFeCo can be utilized effectively as a recording medium. This has been done through efficient design of MPC in order to simultaneously obtain desired values for light reflectivity and Kerr rotation. To determine the most favorable structure, we have studied theoretically the effects of the magnetic layer in various MPC structures using a 4×4 matrix method [1]. We have also computed the distribution of light intensity in the interior of the structure [2]. This computation has confirmed that light localization would occur for some specially designed structures. Figure 1 illustrates the light distribution and refractive index modulation in such a structure which is found to exhibit suitable magneto-optic behavior. This figure clearly shows partial localization of light at the position of the thin TbFeCo defect layer. The reflectivity spectrum of this device with the designed resonance wavelength of 405 nm, has been depicted in the inset of figure 1, too.

We have also studied the effect of light incident angle on the resonance conditions and photonic band gap of MPCs. The results of this later study would be useful for applications which require oblique incidence of light on magnetic structures.

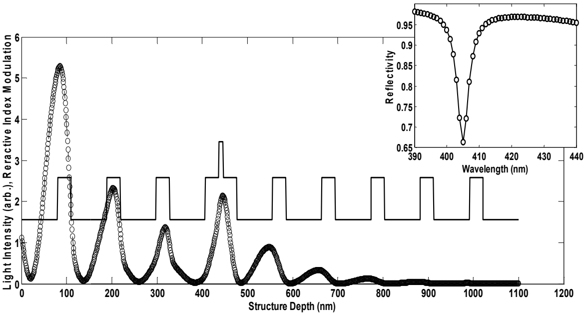

Fig. 1: Light intensity distribution and refractive index modulation of the MPC structure including a thin TbFeCo defect layer. The inset shows the corresponding reflectivity spectrum.

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THE MORPHOLOGY AND MOLECULAR STRUCTURE OF POLYFLUORENE THIN FILMS SYNTHESIZED BY A NOVEL PLASMA POLYMERIZATION METHOD

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As a π conjugated polymers, polyfluorene (PF) and its derivatives have emerged as the dominant class of polymers for LED and photovoltaic cells applications due to their easy processability, high luminescence efficiency and excellent electronic-semiconducting properties. The way of producing organic thin film has a strong influence on the morphology and molecular structures. The synthesis of PF thin films by superposing simultaneously a continuous and pulsed discharge and the characterizations of these samples are presented. The double discharge plasma system is constructed by superposing two discharges namely low pressure dc glow one and a high current pulsed one. The PF thin films are synthesized for the first time by such technique. The flourene monomers have been used as plasma precursors, at 0.5 mbar operating pressure. The substrates were silicon wafer and quartz glass plates and placed at two different locations at the reactor.

The molecular structure of the films was investigated by XPS, UV-visible, FTIR and the morphological studies carried out by XRD and SEM. The XPS, UV-visible and FTIR results reveal that the molecular structures of the synthesized thin films are different from that of the conventional techniques due to the fragmentation of the monomer during the film formation at plasma processes. Upon the iodine doping, the optical energy band gab (E_g) drops down from 3.4 eV to 2.3 eV. The morphology of the synthesized PF thin films has some fractional crystallinity and having granular structures with different size depending on the location of the substrate.

CRYSTAL GROWTH AND CHARACTERIZATION OF Ho^{3+}:$KRE(WO_4)_2$ (RE = Y, Gd, Lu)

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Development of eye safe solid state lasers around 2 μm based on holmium (Ho^{3+}) ion has received considerable interest in recent years due to their potential applications in the field of medicine, since it is absorbed by water of human tissues due to the strong absorption bands of water in this spectral range, lidar for military application, radar for remote sensing application and in optical parametric oscillator (OPO) systems for frequency conversion. Moreover Ho^{3+} doped crystals offer high gain cross section and long life time [1] in the $^5I_7 \rightarrow {}^5I_8$ transition that generates the 2 μm emission.

On the other hand, potassium rare earth double tungstates $KRE(WO_4)_2$ (RE =Y, Gd, Lu) as host for active ions induce high values of absorption and emission cross sections and relative broad absorption and emission bands [2]. This enables the use of diode lasers as pump sources. Another advantage of $KRE(WO_4)_2$ crystals is that they can be highly doped reducing the thickness necessary to reach a good absorption of the laser crystal. This minimizes the problem of reabsorption in quasi three level lasers as the 2 μm laser emission of Ho^{3+}.

Taking into account the above mentioned advantages and potentialities of Ho^{3+} and $KRE(WO_4)_2$ crystals, our work is focussed on doping $KRE(WO_4)_2$ with Ho^{3+} as laser crystals for diode pumped solid state laser (DPSSL). Here we present the results obtained from crystal growth of different doping ratios, structure and spectroscopic properties of Ho^{3+} among three hosts. This comparative study serves to correlate with the laser efficiency. All the experiments were done under similar conditions. The crystal growth experiments ware carried out by Top Seeded Solution Growth Slow cooling method (TSSG-SC). The structure was characterized by X-ray powder diffraction. The spectroscopic characterisation of these materials were performed in terms of polarized optical absorption at room and low temperature (6K) and photo luminescence around 2 μm which is of our interest. In order to optimize the best host with Ho^{3+} among these three hosts the laser generation experiments are planned.

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INTRINSIC EXCITATIONS IN THE PERFORMANCE OF OPTICAL FUNCTIONAL MATERIALS BASED ON YAG

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Yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG) being an extremely well-studied material from the standpoint of its luminescent properties related to its applications as a laser material (when doped by Yb^{3+}) and as a scintillator (when doped by Ce^{3+}), provides an excellent basis for the study of the role of intrinsic excitations, including excitonic type excitations, inherent defects and typical inadvertent impurities, in the energy transfer to the dopant ions and in the energy relaxation. Such processes affect the performance both of the laser material and of the scintillator. Here we compare luminescent properties of single crystalline YAGs grown by different techniques, those of films and those of ceramics fabricated by vacuum sintering and nanocrystalline (VSN) technology. Study of intrinsic luminescence of complex oxide crystals has a long-lasting history. Widely accepted interpretation of its properties, attributing two intrinsic luminescence bands of oxide materials to the coexisting self-trapped holes and self-trapped excitons ([1] and references therein), was developed for single crystals; extending the study to film materials resulted in another model emphasizing the role of anti-site type defects [2] (chronologically not the first paper on the subject but contains a lot of references) to account for two pairs of excitation-luminescence bands. Here we add to the discussion recent data including that for ceramics intending to complete the picture and to provide further insight into excitation relaxation in complex oxides.

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ENERGY STORAGE AND TRANSFER IN RARE GAS SOLIDS

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The widest band gap insulators - rare gas solids (RGS) - are excellent model objects for studying the processes of energy and charge transfer in solids irradiated with some kind of ionizing radiation. Exposure of RGS to ionizing radiation results in generation of electron-hole pairs, followed by a sequence of relaxation processes involving a variety of radiation induced defects – defects of structure, self-trapped/trapped holes, electrons trapped at some lattice imperfections or by impurities with positive electron affinity. These centers are capable to store a part of the energy absorbed during excitation for quite a long time at low temperatures. To understand the radiation effects one has to study different channels of relaxation processes. Up to very recently there were not so many publications on the activation spectroscopy study of RGS. Method of thermally stimulated luminescence (TSL) is in most common use. In the case of doped RGS or RGS containing some impurity centers TSL may originate both from recombination of charged particles and from recombination of neutral atoms. New radiative mechanism of energy transfer from atomic to electronic subsystem in pre-irradiated rare gas solids (RGS) was revealed in [1]. To study the whole set of relaxation channels and their interconnection there is a clear need to combine optical and current spectroscopy methods e.g. TSL and thermally stimulated exoelectron emission (TSEE). Such a combination of activation spectroscopy methods is a highly efficient tool for studying channels of energy relaxation in pre-irradiated solids and for probing defect energy levels. We developed a low temperature modification of correlation spectroscopy – synchronous measurements of TSL, TSEE and desorption of neutral atoms [2] from pre-irradiated RGS. Thermally stimulated techniques were complemented by photon-stimulated luminescence (PSL) and photon-stimulated exoelectron emission (PSEE) methods. Activation spectroscopy methods were used to probe relaxation processes in RGS pre-irradiated with an electron beam. We have found that a presence of dopants in RGS significantly changes the energy transfer processes and affects TSL and TSEE yields. Three relaxation channels were revealed: i) recombination of charged particles and ii) recombination of neutral ones both followed by photon emission in VUV and visible range correspondingly and (iii) emission of exoelectrons. A correlation in the positions of TSL and TSEE peaks observed in our experiments pointed to the common primary process – electron detrapping from the same kind of traps. A competition between branching relaxation channels (i) and (iii) was demonstrated. Recombination of neutral atoms (ii) is considered to play the role of stimulating factor triggering (i) and (iii) channels.

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OPTICAL PROPERTIES OF CdTe/ZnTe CORE/SHELL QUANTUM DOTS SUITABLE FOR TARGETED BIOIMAGING

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In this work we present results of our calculations of CdTe/ZnTe core/shell quantum dots (QDs) of very small size capable for targeted bioimaging. The transition energy of the electron and hole system confined in a CdTe/ZnTe core/shell sphere is obtained by the effective-mass approximation. Optical properties are analyzed as function of QD size and spatial composition and compared to already known experimental results. CdTe/ZnTe core/shell-structured QDs are perspective to their use in biomedical applications because: they exhibit strong luminescence and low toxicity (compared to the CdTe QD); shell of wide-gap semiconductor protects core from degradation; they have long-term colloidal and optical stability; their surface can be passivated with biocompatible functional molecules; they can be produced in small size, less than 5 nm. These properties enables their use for targeted bioimiging.

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SPECTROSCOPIC PROPERTIES OF ZnWO4: Li, F CRYSTALS

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Zinc tungstate ($ZnWO_4$) is a perspective scintillating material for X-ray tomography, detection of ionizing radiation and for double beta processes searching though its light yield is slightly lower comparing to that of the well-known scintillating material cadmium tungstate. Recently it was shown that co-doping with univalent metals and fluorine ions improves transparency and scintillation yield of $ZnWO_4$ (Nagornaya, 2008).

The pure and doped with lithium and fluorine $ZnWO_4$ single crystals of high quality were studied. All crystals were grown using Czochralski method in the Institute for Single Crystals, Kharkov and Institute of Chemistry and Mechanics, Moscow. Measurements were performed at the Superlumi station (DESY, Germany) and at the laboratory set-up.

In this work we discuss the origin of the absorption and luminescence bands in the undoped zinc tungstate as well as in the crystals doped with lithium and fluorine ions. Intrinsic luminescence of $ZnWO_4$ is generally acknowledged to be that of the self-trapped exciton on the WO_6 complex. In the fundamental absorption region the yield of this type of luminescence is controlled by the competition with the alternative relaxation channels. Since, the dependence of the probability for the separated electrons and holes to be bound into the exciton on its kinetic energy and temperature is also discussed for the investigated crystals of $ZnWO_4$.

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FABRICATION AND CHARACTERIZATION OF ONE DIMENSIONAL DIFFRACTION GRATINGS ON THE NONLINEAR OPTICAR CRYSTAL RbTiOPO4 BY ULTRA FAST LASER ABLATION

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In recent years, diffraction gratings of nonlinear optical materials are attracting an increasing interest in photonic science and technology due to the interesting peculiarities that they provide in nonlinear optical phenomena. However, only few studies have been devoted up to now on diffraction gratings of nonlinear optical materials, despite the efficiency of the enhanced frequency conversion processes proved in these structures when compared to bulk crystals [1].

We report here that we fabricated one dimensional diffraction gratings on the (010) surface of $RbTiOPO_4$ nonlinear optical crystals by the ultra fast laser ablation technique. This material crystallizes in the orthorhombic system, $Pna2_1$ space group. We followed the fabrication of these 1D diffraction gratings by an analysis of the linear and nonlinear diffraction properties and characterization of their morphology. The linear optical diffraction by FT-IR results in a very good agreement between the lattice parameter obtained by optical microscopy observation with the simulation of diffraction performed with the FT-IR data. The one dimensional grating structures generate enhanced second harmonics when illuminated with a pulsed Nd: YAG laser, when compared to non-structural surfaces of the same material. We observed that the ratio between the lattice parameter of the diffraction grating and the depth of the grooves play a major role on the intensity of the second harmonic generated by nonlinear optical material [2].

These diffraction gratings with a 1D photonic structure might have potential applications in the field of photonic crystals. These devices can be opened the way to control light like modulators, narrow bandwidth filters, and for telecommunication such as demultiplexing.

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Yb/Er CO-DOPED GADOLINIUM OXIDE UPCONVERSION MULTI WAVELENGTH FLUORESCENT NANOCRYSTALS

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The Yb/Er combination is of great importance for fiber amplifiers in dense wavelength division multiplexing (DWDM) technology. The Yb^{3+} ions have a 10 times higher absorption cross section at 980 nm acting as Er^{3+} sensitizers enhancing the near-infrared (NIR) at 1.5 μm $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. Moreover, the possibility of achieving visible emission arising from upconversion luminescence Er^{3+} ions is also of great interest for application in efficient visible lasers, colour displays, and undersea optical transmission. [1-[4]

In this work, luminescent Er^{3+} and Yb^{3+} (Yb/Er) co-doped gadolinium oxide (Gd_2O_3) nanophosphors were prepared through optimized hydrothermal route using nitrates. The nanocrystals are NIR emitters and display upconversion visible emission. Under excitation at 980 nm several upconversion emission bands at 408, 523–548 and 667 nm ascribed to the $^4G_{11/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions from Er^{3+} ions respectively, are observed in the temperature interval 11-300 K. Still under 980 nm, the nanocrystals displays the NIR infrared emission at Er^{3+} 1.55 mm. The emission spectrum reveals the presence of two distinct Er^{3+}-local environments attributed to different crystallographic sites with C_2 or S_6 local symmetry groups. Input excitation power dependence has been studied for different transitions, at low input pump energies the relation $Iupc\ \alpha\ (Iexc)^n$ seems to hold well with n equal to 2, indicating that two incident NIR photons are needed for each emitted photon. The influence on the emission features of the Yb/Er concentration ratio and the calcination temperature will be further investigated.

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3,4,9,10-PERYLENETETRACARBOXYLICDIIMIDE/ZnO HYBRID NANOMATERIALS

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There is a considerable interest in studying organic/inorganic hybrid structures for various applications in optoelectronic devices. We have recently demonstrated fabrication of 3,4,9,10-perylenetetracarboxylicdiimide (PTCDI) nanostructures and hybrid PTCDI/ZnO nanorod structures and studied their optical properties [1]. We have found that PTCDI nanostructures exhibited significantly different emission compared to PTCDI films and powder, and we also demonstrated efficient energy transfer between ZnO nanorods fabricated by a hydrothermal method and PTCDI nanostructures.

ZnO nanorods can be fabricated by a variety of methods resulting in different optical properties [2]. Therefore, we have studied the influence of ZnO nanorod growth method and post-growth annealing in oxygen atmosphere at different temperatures on the energy transfer to PTCDI nanostructures by photoluminescence measurements. In addition, we have also deposited PTCDI nanostructures on ZnO bulk samples (single crystal and/or thin films) and studied their optical properties. Fabricated structures have been investigated using scanning electron microscopy, transmission electron microscopy and photoluminescence measurements, and the obtained results are discussed.

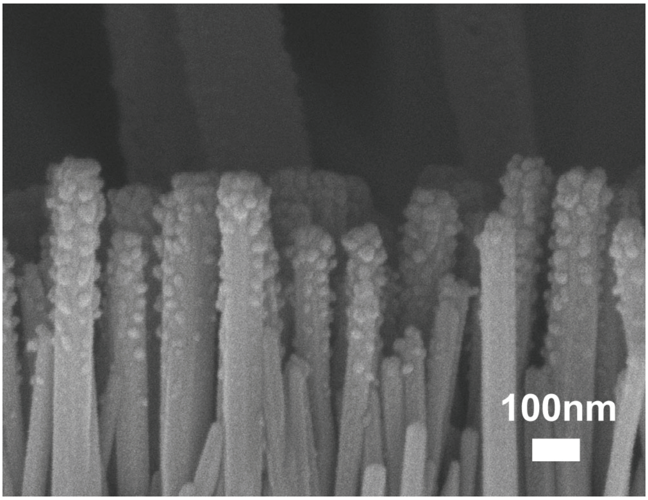

Figure 1 SEM image of PTCDI clusters on ZnO nanorods

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SPATIAL LASER BEAM PROFILE DETERMINATION BY PULSED PHOTOACOUSTICS: DETECTION RADIUS/WAVELENGTH APPROXIMATION

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Utilizing a mathematical algorithm developed for photoacoustic tomography it is possible to deduce the laser beam spatial profile within the pulsed photoacoustic measurements. This method is based on the temporal shape of the photoacoustic signal analysis. The exact solution for the laser beam spatial profile obtained with this method involves summation of a series and may take much time to compute. Sometimes the simplification of this solution can be done if the detection radius is much larger than the photoacoustic signal wavelength. This simplification is, so called, detection radius/signal wavelength approximation. Our results obtained with this approximation are presented here. The experimental photoacoustic signals used in our numerical analysis are obtained after the multiphoton absorption in SF_6-Ar mixtures. Together with the laser beam spatial profile molecular vibrational to relaxational time of the excited molecules are calculated simultaneously.

QUANTUM EFFICIENCY OF BROAD-BAND EMISSION IN VANADIUM OXIDES

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Vanadium oxides showed broad-band photoluminescence due to the charge transfer transition in the VO_4 tetrahedra[1,2]. Recently, we have revealed that the AVO_3 (A: Rb and Cs) has very large internal quantum efficiency[3]. In addition, the broad-band emission (400–800 nm) of these materials realized white light luminescence by themselves The vanadium oxides with the V^{5+} have various crystal structures in terms of coordination of VO_4 tetrahedra. In the AVO_3, the VO_4 tetrahedra link one-dimensionally at two corner oxygen atoms each other, and the one-dimensional VO_4 chains are two-dimensionally arrayed. The VO_4 sheets and the A-cation layers are alternately stacked. On the other hand, the $M_3V_2O_8$ (M: divalent cations) has a three-dimensional orthorombic structure, and the VO_4 tetrahedra are isolated with each other. In the $M_2V_2O_7$ (M: divalent cations), the VO_4 tetrahedra show dimerization. These structural features would affect their luminescent efficiency.

The AVO_3 showed the broad band emission from 380 to 800 nm, and the □ for the KVO_3, $RbVO_3$ and $CsVO_3$ were 4, 79 and 87%, respectively. The CIE colour coordinates are located at white region on the chromaticity diagram. The $M_3V_2O_8$ (A: Mg, and Zn) also exhibited a quite broad band emission between 410 and 900nm, indicating yellow luminescent colour. The $Zn_3V_2O_8$ showed high □ value, 52%, compared to that of the $Mg_3V_2O_8$ (□ = 6%). This enhancement of □ in the $Zn_3V_2O_8$ could be due to the increasing exciton diffusion assisted by the hybridizations of Zn 3*d* and O 2*p* orbitals for the valence band, and Zn 4*s* and Ti 3*d* orbitals for the conduction band. In the presentation, we will report the quantum efficiency of photoluminescence in the vanadium oxides by focusing on their crystal structures.

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RADIATIVE TRANSITIONS IN NANOCRYSTALS

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It is known that the radiative lifetimes of the excited states of rare earth ions contained in nanocrystalline dielectric are different compared to their values in crystallographically equivalent bulk crystals. Their lifetimes depend on the effective index of refraction of the media consisting of nanoparticles (n_{eff}), and the substance filling the space between them [1]. Here we present results of the theoretical study of the optical characteristics for the small-radius optical centers in the subwavelength ellipsoidal nanocrystals embedded in a dielectric medium. Some results for simplest case of the spherical nanoparticles are listed below.

The ratio of the probability of the electric-dipole transition in the nanoparticle (A_{nano}^{ed}) to that in the bulk sample (A_{bulk}^{ed}) was found to be [2]

$$A_{nano}^{ed} \big/ A_{bulk}^{ed} = \left(n_{eff} \big/ n_{cr}\right)\eta^{2} . \tag{1}$$

where $\eta = 3 \big/ \left[2+\varepsilon - c(\varepsilon - 1\right]$; c is the volume fraction of nanocrystals in the medium (filling-factor); $\varepsilon = \varepsilon_{cr} / \varepsilon_{med} = n_{cr}^{2} / n_{med}^{2}$; n_{cr} and n_{med} are refractive indices of crystal and medium, respectively.

The similar ratio for electric-quadrupole transition is found to be

$$A_{nano}^{eq} \big/ A_{bulk}^{eq} = \left(n_{eff} \big/ n_{cr}\right)^{3} \eta^{2} . \tag{2}$$

It is clear also that the ratio for magnetic- dipole transition is equal to

$$A_{nano}^{md} \big/ A_{bulk}^{md} = \left(n_{eff} \big/ n_{cr}\right)^{3} . \tag{3}$$

As it follows from expressions (1)-(3) the radiative rates are decreasing (are increasing) if $\varepsilon = \varepsilon_{cr} / \varepsilon_{med} > 1$ ($\varepsilon = \varepsilon_{cr} / \varepsilon_{med} < 1$) for all type transitions. However, the relative contributions to the radiative lifetime are changing in nanoparticles as compared to the bulk sample.

The ratio of the IR absorption coefficient in the nanocomposite due to IR absorption in nanoparticles (k_{nano}^{IR}) to IR absorption coefficient in the bulk sample (k_{bulk}^{IR}) is found to be

$$k_{nano}^{IR} \big/ k_{bulk}^{IR} = c\left(n_{eff} \big/ n_{cr}\right)\eta^{2} . \tag{4}$$

The other optical characteristics of nanoparticles (the two-photon absorption, the Raman scattering intensity, the Raman gain coefficient etc.) are discussed.

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LOW-COST EXPERIMENTAL APPARATUS FOR SOLID STATE PHOTOACOUSTIC MEASUREMENTS

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The aim of this study is the development of a laser diode-based low-cost photoacoustic device which is able to measure the heat-transmission and thermoelastic effects in various solid samples. Our low-cost device has an advantage to the conventional one using a sound card as a dual-phase lock-in amplifier in the modulation frequency range from 10Hz to 10kHz. Such advantage allows us to satisfy some of desirable apparatus properties like the simplicity of design and use, reasonable weight and portability. The presented results show that our device satisfies the main criteria for solid sample photoacoustic investigations: the reliability and reproducibility of the amplitude and phase measurements. We have tested our device and showed that it provides the results very similar to those obtained by conventional one. All of the results presented here are obtained with Al, Si and Sigradur K samples.

IN VIVO MICROVASCULAR BLOOD PERFUSION MAPPING USING THE SELF-MIXING EFFECT IN A PROTON-IMPLANTED VCSEL

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Vertical-Cavity Surface-Emitting Lasers (VCSELs) are mass-produced for high-speed optical communication applications. They provide a circular, anastigmatic beam that can be formed by simple optics. In this work, we demonstrate how an off-the-shelf proton-implanted VCSEL can be used to sense fluid flow through a highly scattering tissue phantom. The VCSEL is used as a self-mixing sensor whereby some of the light exiting the VCSEL is reflected from particles moving in the fluid and re-enters the laser cavity. The motion of the particles impart a Doppler shift on the light [1] and when this light re-enters the laser cavity it causes changes in the carrier density that in turn causes small perturbations in the laser junction voltage. Processing this voltage signal allows the extraction of the fluid flow parameters. This allows a compact, low-power system to be implemented to create a flow map of a tissue phantom. The tissue phantom consists of a glass capillary tube supplied with a constant flow rate and is surrounded by a highly scattering medium to simulate the effects of the highly scattering biological tissue (Fig. 1). This allows the experimental characterisation and verification of the system before it is used to measure blood flow of real tissue. The effect of the highly scattering medium is to randomise the direction the Doppler shifted light [2] producing a broad signal spectrum (Fig. 2) with certain statistical properties. It is possible to extract the average flow velocity and flow density from the spectrum [3]. This system is suitable for medical imaging and investigation into skin disorders such as burns and malignancies. This research was supported under Australian Research Council's Discovery Projects funding scheme (DP0988072), and The Commonwealth of Australia International Science Linkages programme (FR090026).

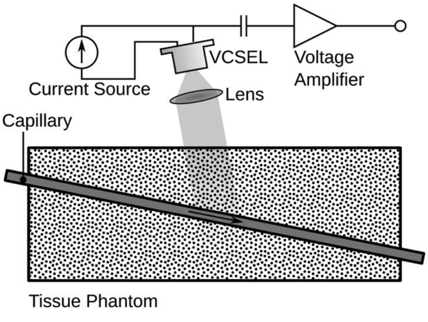

Fig. 1. Diagram of experimental setup.

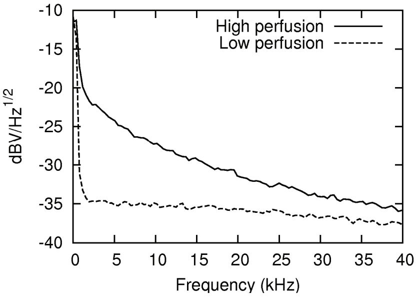

Fig. 2. Typical VCSEL junction voltage spectra for different perfusion levels.

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HIGH Tm^{3+} DOPING IN $KLu_{1-X}Tm_x(WO_4)_2/KLu(WO_4)_2$ COMPOSITES FOR THIN-DISK LASERS

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In recent years, the thin-disk laser design has taken special interest in developing high power diode pumped solid state lasers (DPSSL). The thin-disk configuration ensures both a high efficiency and better beam quality compared with the bulk configurations. Due to the the thickness of the active medium (100 – 200 μm) thermal effects are reduced and the heat management is very efficient [1].

Concerning the laser material, the most common laser crystal is Yb:YAG for thin-disk configuration. More recently, the monoclinic potassium lutetium double tungstates $KLu(WO_4)_2$ or KLuW doped with lanthanides, have became interesting for solid state lasers [2]. Among the advantages of these crystals are: i) the use of KLuW as host induces interesting spectroscopic properties to Ln^{3+} so that the laser efficiency is very high, ii) it allows the radiation to be polarized, and iii) the use of diodes as pump sources is of great value because of the reduction of both economical cost and the physical size of the equipment. Previous works, demonstrated the first Yb:KLuW thin disk laser with very high efficiency [3]. In addition, CW laser operation of Tm-doped KLuW (bulk [4] and epitaxial layers [5]) were achieved around 2 μm spectral range showing the suitability of these material for thin-disk lasers.

In this work we present the extended epitaxial growth of layers of $KLu_{1-x}Tm_x(WO_4)_2$ on $KLu(WO_4)_2$ subtrates oriented perpendicular to the **b** direction, were grown by the Liquid Phase Epitaxy (LPE) method, with 5, 7.5, 10 and 15 mol % of Tm, and thicknesses between 20 – 400 μm. The samples are of high quality, homogeneous Tm^{3+} distribution, no diffusivity of Tm^{3+} in the composite, and film/substrate interface free from macroscopic defects. The realization of a thin disk laser is planned.

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THE CONTROL OF SPONTANEOUS PATTERN FORMATION ON AZO POLYMER FILM

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We report the control of spontaneous pattern formation on the surface of an azo polymer film under a single uniform laser polarized light beam illumination. The translational wormlike diffusion caused by the photoisomerization of the azobenzene chromophores upon the light irradiation plays a key role in this all optical process. The diffusion direction is parallel to the polarization of writing beam. Periodic structures with a variety of topography are inscribed through different experimental conditions. Diffraction efficiency of the recorded gratings has been measured. Atomic force microscope measurements confirm the presence of complex structures. For linearly polarized light with normal incidence stripes oriented perpendicular to the polarization direction are observed. The topology, pitch and amplitude of this self-organized surface relief grating (SRG) are depended to the polarizations state, wavelength and intensity of the recording beam and the thickness of the azo-polymer film. The self-organized SRG formation rate is increased by writing beam intensity. For p polarized light only the pitch and amplitude of grating change with incidence angle. Off-normal incidence for s polarized light inscribed complex pattern configurations (square and hexagonal). Circular polarized light produced relief spots and some nanometric holes on the surface of azo polymer films. The experimental results are in good agreement with a simple theoretical model based on the stimulated Wood anomalies. The surface patterns obtained through this all-optical process can be erased by thermal or optical methods and the writing–erasing process is completely reversible. In most cases, the writing and erasing cycle can be repeated for many times without causing damage to surfaces.

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VACUUM MULTIPHOTON UPCONVERSION FOR LANTHANIDE OXIDES

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Under a vacuum of ~10^{-2} torr, the neat and high purity lanthanide sesquioxide powders Nd_2O_3, Yb_2O_3, Er_2O_3 and Tm_2O_3 have been excited by an unfocussed 975 nm diode laser at powers up to 1 W. The excitation leads to the production of charge carriers which can then undergo reaction or trapping. Broad band emission is observed over the visible spectral region which is characterized by multiphoton excitation quanta of between 3 and 4. The broad emission band is assigned to emission from a self-trapped exciton state below the conduction band. Emission is also detected from the divalent lanthanide ion species Tm^{2+}, showing that electron trapping occurs, as well as from intraconfigurational $4f^N$ -$4f^N$ transitions. The emissions are characterized by rise times of several seconds, depending upon the laser power. The emission intensity is several orders of magnitude greater than that for the doped lanthanide species Y_2O_3:Yb^{3+}, Er^{3+} in air. Moreover, the colour purity of emission from neat Yb_2O_3 is close to that of white light, with CIE coordinates (0.329, 0.335).

Fig. 1(a) shows the upconversion spectrum for Yb_2O_3 under various excitation powers, as well as the log-log plot of emission intensity and excitation power. Note the saturation at higher powers. Fig. 1(b) shows the corresponding plot for Nd_2O_3.

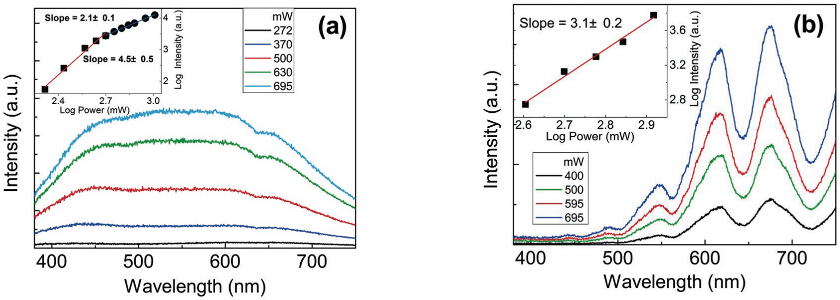

Figure 1. 975 nm upconversion of lanthanide sesquioxide powders between 380-720 nm with powers as marked, under 10^{-2} torr: (a) Yb_2O_3; (b) Nd_2O_3. The figure insets are log-log plots of upconversion emission intensity versus laser power, with the slopes marked.

Acknowledgement

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PROPERTIES OF SnS THIN FILMS OBTAINED BY ELECTROCHEMICAL DEPOSITION AND THEIR APPLIATION IN SOLAR CELLS

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Thin films of SnS with thickness of 1.5 μm were obtained by electrochemical deposition, from aqueous solution of $SnCl_2$ and $Na_2S_2O_3$. The SnS thin films were prepared on the glass substrate, with layer of conductive tin oxide. Cyclic voltammetry was performed to determine the optimum potential for electrodeposition and structure analysis. Obtained thin films of SnS are nanoctrystals, whose composition, morphology and structure were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX). The direct band gap of 1.18 eV was estimated from the optical transmission spectra. Also, the thin films of SnS were electrodeposited on the SnO_2-CdS layers, where they showed good adherence, without pin holes. The *I-V* characteristics of the obtained SnO_2-CdS-SnS- graphite photoelectrochemical solar cells were studied, so that the open-circuit voltage V_{oc}=600 mV and I_{sc}=200 μA/cm^2, were determined.

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PHOTOACOUSTIC ELASTIC BENDING METHOD: STUDY OF THE ION-IMPLANTED Au-Si SYSTEM

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The influence of thermal, elastic and electronic transport parameters for an Au – Si system was investigated by a photoacoustic frequency transmission technique. The amplitude and phase photoacoustic spectra were measured in dependence on the modulation frequency of the excitation optical beam. The influence of the ion-modification process to the experimental photoacoustic signal was analyzed. Such influence can be an indicator of the degree of modification. The analysis was based on a theoretical model adopted for a metal-semiconductor system. This model includes the space-charge region on the semiconductor surface, and thermodiffusion, thermoelastic, and electronic deformation effects. All mentioned parameters presented in this paper are obtained comparing the experimental and theoretical photoacoustic signals.

PREPARATION OF THE NEW SPHERICAL NANO-SIZED X-RAY PHOSPHORS ON THE BASIS OF Lu_2O_3:Eu^{3+}

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It is known that lutetium oxide is the effective host for rare-earth dopants. Nowadays nano-sized Lu_2O_3 doped with Eu^{3+} ions is considered as one of the most perspective materials for X-ray detection and imaging and also new X-ray phosphors creation due to its high density (ρ=9.42 g/cm^3) and high effective atomic number $Z_{eff.}$=71. However, preparation of Lu_2O_3 spherical particles with narrow size distribution by conventional soft chemistry methods meets some difficulties, which is limited of the nanostructured scintillation materials creation on the lutetium oxide basis. Development of the method of the spherical Lu_2O_3:Eu^{3+} particles preparation with the given sizes and heterostructures on their basis opens up the possibilities of the creation of the effective X-ray screens, high-resolution displays with improved characteristics and also photonic matrixes preparation with the diffraction enhancement of the luminescence light. Monosized Lu_2O_3:Eu^{3+} spherical particles (diameter range from 60 to 300 nm) and core-shell heterostructures on their basis (Lu_2O_3:Eu^{3+}/SiO_2, SiO_2/Lu_2O_3:Eu^{3+}/Lu_2O_3) were prepared for a first time. The structure, morphology and X-ray luminescent properties were studied in this work. Lu_2O_3:Eu^{3+} spherical particles were prepared by the co-precipitation technique from water solutions with subsequent heat treatment. Europium content in the samples was ranged from 1 to 10 at. %. Lu_2O_3:Eu^{3+}/SiO_2 core-shell heterostructures were synthesized according to Stober method. Lu_2O_3:Eu^{3+} coverings of the controlled thickness (10-50 nm) were formed on the surface of the SiO_2 spheres by the sol-gel technique from water solutions. The shape, sizes, phase composition of the heterostructures prepared were studied by means of electron microscopy methods, X-ray diffraction, X-ray photoelectron and FT-IR spectroscopy. The temperature conditions of the crystallization and morphology properties of the Lu_2O_3:Eu^{3+} solid-state solutions in the form of spherical particles and nanolayers onto SiO_2 spheres were investigated. Lu_2O_3:$Eu^{3+} \rightarrow$ Lu_2SiO_5:$Eu^{3+} \rightarrow$ $Lu_2Si_2O_7$:Eu^{3+} structural transformations in the heterostrucrures prepared in the 900 – 1200 ºC temperature range were observed. The features of Eu^{3+} entering in the low dimensional systems were also discussed. The X-ray luminescent properties of the Lu_2O_3:Eu^{3+} spherical particles and Lu_2O_3:Eu^{3+}/SiO_2, SiO_2/Lu_2O_3:Eu^{3+}/Lu_2O_3 heterostructures were studied. Under X-ray excitation europium-doped nanophosphors obtained are characterized by effective luminescence in the λ=575–725 nm range corresponding to $^5D_0 \rightarrow ^7F_J$ transitions (J=0÷4) of Eu^{3+} ions in the crystalline host. It has been shown that radioluminescence intensity of the heterostructures strongly depends on the phase composition, shells thickness and Eu^{3+} dopant concentration.

MULTISCALE MODELLING OF EXCITON DYNAMICS IN POLYMERIC SYSTEMS CONCERNING THE EFFECT OF POLYMER MOLECULAR PROPERTIES AND MORFOLOGY

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In our days is already recognize the huge potential of using polymer semiconducting materials in optoelectronic devices such as solar cells, light emitting diodes or photodetectors. Nevertheless, the advance of the research to understand the physics that is behind the functioning of these devices reveal that the morphology of the organic semiconductor plays a major roll on the device optical properties. For the case of semiconducting polymer-based devices, the morphology of the semiconductor at nanoscale can influence the optical phenomena present in these devices, since the packing of the long conjugated polymer chains leads to the disruption of the conjugation forming rigid segments with different lengths and orientations that work like chromophores, which strongly influence exciton dynamics in such systems. By using a multiscale modelling we performed a study to understand the influence of the polymer morphology at nanoscale on exciton dynamics, namely singlet excitons since they are the main excited species produced in polymer-based solar cells and photodetectors and those which are responsible for the fluorescence in polymer light-emitting diodes. In this communication we will present an overview of our latest results were we use quantum molecular dynamic calculations to understand the effect of polymer molecular properties on singlet exciton formation in polymeric devices and dynamic Monte Carlo simulations to understand the influence of the polymer morphology on exciton dynamics within the device. Our results clearly show that the chromophore molecular structure influences the intramolecular singlet exciton energy and, as a consequence, it will influence not only the exciton diffusion process in the polymer network that depends on the polymer morphology, but also exciton quenching near the electrodes.

FORSTER-LIKE NONEXPONENTIAL ENERGY TRANSFER DECAY IN DOPED NANOPARTICLES

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Computer simulation of static donor-acceptor energy transfer in a sample of equal-size impurity-doped nanoparticles and in a corresponding bulk crystal was performed, analyzed, and compared. For the nanoparticles, a new double nonexponential decay was observed and explained by the two-stage bulk and surface-bulk quenching law. For the fitting computer simulated decay curves, simple analytical expression was proposed in the form $N_D(t)=n_1(0)\exp(-W_1t)^{d/S}+n_2(0)\exp(-W_2t)^{d/S}$, where the first term is the same as in bulk materials with dimensions d = 1, 2, 3 and multipolarity S=6, 8, 10.... The decay rate of the second term $W_2=(1/2)^{S/d}W_1$ is at least four times smaller than the bulk Forster average decay rate W_1. This results in a higher total fluorescence quantum yield in nanopaticles compared to bulk crystals.

NONEQUIVALENT Yb^{3+} CENTERS IN $R_xYb_{1-x}Al_3(BO_3)_4$, R=Y, Tm, Lu, Yb SINGLE CRYSTALS.

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Nowadays, much attention is given to nonlinear laser crystals, in particular yttrium aluminum borate doped with ytterbium ions. A drawback of these crystals is that they can be grown only by the flux method, giving rise to a variety of defects, such as twinning, uncontrollable impurity substitution, etc. Such defects have a significant effect on laser properties of crystals and are, therefore, worthy of serious investigation.

Up to now, only a few investigations have been carried out in this direction. The existence of the second Yb^{3+} center, Yb2 in $Yb_xY_{1-x}Al_3(BO_3)_4$ was reported and the dependence of the concentration of Yb2 on x was investigated [1]. Also, multiple Yb^{3+} centers in the stoichiometric optical single crystal $YbAl_3(BO_3)_4$ were found and investigated using high-resolution optical Fourier-transform spectroscopy [2].

In the present work, we investigate a series of $RAl_3(BO_3)_4$ (R=Y, Tm, Lu, Yb) crystals doped with various amounts of ytterbium ions, grown in two different laboratories using different fluxes. High-resolution polarized absorption spectra of the single crystals were measured at low temperature (down to 3.5 K). The crystals were analyzed to determine the presence of possible impurities. The absorption spectra of crystals grown using $K_2Mo_3O_{10}$ or $Bi_2Mo_3O_{12}$ based fluxes were compared. The positions and intensities of the satellite spectral lines corresponding to additional Yb centers are different for the samples prepared by different techniques. We propose that the satellite spectral lines come from Yb^{3+} ions in regular crystallographic positions situated in the vicinity of some defects that deform their nearest surrounding. These defects are, mainly, atomic impurities coming from the flux. We try to relate spectral satellites to particular defects.

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AB-INITIO CALCULATIONS OF THE OPTICAL PROPERTIES OF PURE AND Sm^{3+}-DOPED ANATASE AND RUTILE TiO$_2$

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Titanium dioxide (TiO$_2$) is a wide-gap (3.0–3.2 eV) semiconductor that has been found suitable for doping with several rare earth ions. Sm-doped (nanocrystalline) titania is one of the most promising combination with intense host-sensitized emission of possible interest in a LED phosphor [1, 2], low-temperature luminescence-based gas sensors [3], enhanced photocatalytic processes [4]. In the present work we report on detailed *ab initio* studies of the band structure, density of states (DOS) and optical properties of pure and Sm^{3+}-doped rutile and anatase. All calculations were performed using the CASTEP module of Materials Studio 4.0. The calculated properties were as follows: optimised geometry of the unit cell; total and partial DOS; real and imaginary parts of the dielectric function for different polarizations; absorption, reflection and transmission spectra from IR to UV; dependence of the refractive index on the wavelength (approximated by the Sellmeier equation $n = A + \frac{B\lambda^2}{\lambda^2 - C^2} - D\lambda^2$).

Fig. 1 visualizes a part of the obtained results for pure anatase.

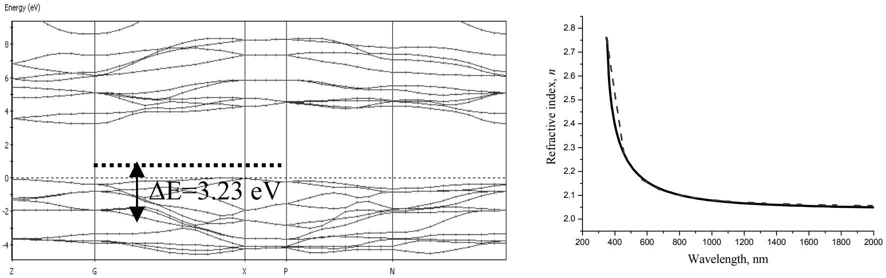

Fig. 1. Calculated band structure (left) and dependence of the refractive index on the wavelength (right) for pure anatase TiO$_2$. The calculated refractive index values are shown by a solid line, and Sellmeier approximation by a dashed line with the following values of the coefficients: $A = 1.72238 \pm 0.00892$; $B = 0.32868 \pm 0.00775$; $C = 288.23543 \pm 1.19044$ nm; $D = 4.1107 \times 10^{-10} \pm 1.3680 \times 10^{-10}$ nm^{-2}.

The obtained resutls are compared with the experimental data and other calculations; influence of impurity ions on the optical properties is discussed.

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NEW APPROACHES FOR THE SYNTHESIS OF Eu^{3+}: La_2O_3 NANOPARTICLES AND THEIR SPECTROSCOPIC CHARACTERIZATION

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Lanthanum oxide is a semiconductor material with the largest band gap among rare earth sesquioxides with a value of 4.3eV. This compound has numerous applications in various fields of industry: as a component of catalyst supports and ceramics. Its synthesis in a form of fine dispersion represents now an exciting area of research [1].

When doping La_2O_3 with luminescent active Ln ions, such as Eu^{3+}, will allow combining the semiconductor properties of La_2O_3 with the red emission of Eu^{3+}. Such red phosphors have been previously investigated under the form of bulk and nanoparticle materials [2,3]. Due to quantum confinement effect and surface effect, nanosized materials with particle sizes of 100 nm or less may show electrical, optical and luminescent properties more efficient than the corresponding bulk materials. Up to now, nanoparticles of Eu-doped La_2O_3 have been synthesized by means of solution combustion synthesis [2], and nitrate decomposition procedures [3]. Such nanoparticles showed emissions centered in the red region of the electromagnetic spectrum, at around 626 nm.

In the present work we developed the synthesis of Eu doped La_2O_3 nanoparticles by several synthesis methods such as: the modified Pechini method, which is an alternative to the conventional sol-gel method, the precipitation method and a hydrothermal process.

The nanoparticles obtained have been characterized by X-ray diffraction (XRD) to determine their crystalline structure and average grain sizes. Their morphology, homogeneity, distribution and particle size, ranging between 10 and 300 nm depending on the synthesis method, have been investigated by electronic microscopy. Finally, the photoluminescence (PL) and cathodoluminescence (CL) properties of the Eu doped La_2O_3 nanoparticles obtained have been analyzed, obtaining emission at ~626 nm, indicating that Eu^{3+} ions have been successfully incorporated in the structure of La_2O_3.

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SPECTROSCOPIC STUDIES OF THE MIXED SYSTEM $Nd_xGd_{1-x}Fe_3(BO_3)_4$

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Multiferroic features of the trigonal huntite-type borates $GdFe_3(BO_3)_4$ and $NdFe_3(BO_3)_4$ have been shown in the studies of their magnetoelectric properties [1, 2]. It was found that $NdFe_3(BO_3)_4$ compound demonstrates appreciably greater than $GdFe_3(BO_3)_4$ magnetic-field-dependent electric polarization and a giant quadratic magnetoelectric effect. To understand a mechanism of the magnetoelectric effect in these compounds it is important to know the peculiarities of the crystal structure and to have information on the crystal field for the rare-earth ion. $GdFe_3(BO_3)_4$ is known to undergo the structural phase transition at 156 K from the D_3^7 structure into the D_3^4 one, accompanied by the antiferroelectric ordering; at T_N =37 K it orders antiferromagnetically into the easy-plane structure; finally, at T_R =9 K a spin-reorientation phase transition occurs. As for $NdFe_3(BO_3)_4$, this compound preserves the D_3^7 crystal structure, at least down to 3K, and orders antiferromagnetically into the easy-plane structure at T_N =33 K. In our earlier work [3], we have performed the optical absorption study of $NdFe_3(BO_3)_4$. From the crystal-field (CF) calculations a set of six real crystal-field parameters, the wave functions, magnetic *g*-factors and the values of the local effective magnetic field at the Nd^{3+} site were obtained. Crystal field calculations for the $P3_121$ structure are more complicated (15 crystal-field parameters). The mixed Gd-Nd system $Nd_xGd_{1-x}Fe_3(BO_3)_4$ is interesting for studying a gradual change of structural and magnetic properties and the crystal field for the Nd^{3+} ion.

In this work, we present broad-band (1500-25000 cm^{-1}) high-resolution (down to 0.1 cm^{-1}), temperature-dependent (3.5-300 K) spectral measurements of $Nd_xGd_{1-x}Fe_3(BO_3)_4$ (x=0, 0.01, 0.04, 0.25, 0.5, 0.75, 1.0) single crystals grown in a bismuth trimolibdate $Bi_2Mo_3O_{12}$ based flux. High-temperature structural phase transitions were registered for the compounds with x=0.01, 0.04, and 0.25. When the concentration x increases the temperature T_R decreases. The analysis of the temperature-dependent spectra revealed the energy of the Nd^{3+} Kramers doublets. The crystal-field parameters, wave functions and magnetic *g*-factors were obtained as a result of CF calculations.

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THEORETICAL STUDY OF THE INFLUENCE OF DEFECTS ON EXCITON FORMATION IN SEMICONDUCTING POLYMERS

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Polymeric films present an amorphous structure, compared to the inorganic counterparts, which is mainly due to the very weak coupling of adjacent polymer chains compared with the strong interatomic coupling of conventional semiconductors. During the polymerization process or even after the polymer film formation, the polymer semiconductor can present several defects, with different origin and concentration that can strongly influence the optical behavior of the devices where they are used. These defects can create not only deep energetic sites that work like traps for excitons where they can relax during their migration inside the polymeric system, reducing exciton diffusion and even decreasing the fluorescence effect, but they can also function like quenching sites by allowing easy exciton dissociation into a pair of charges of opposite signs which reduces also the fluorescence process. It is well known from the literature the existence of these defects, which are related to the decrease of the optoelectronic efficiency of the device due to their presence on the polymer network. However, it is necessary to understand how these defects work at molecular level on exciton formation and their effect on the exciton energy in polymer chromophores if we want to improve organic devices efficiency. By performing a theoretical study of the influence of these defects on exciton formation by using a self-consistent quantum molecular dynamics method, we will present in this communication our latest results in the understanding of the effect of such defects on energetic disorder in polymeric systems and assess the consequences for exciton dynamics on those systems. Our results show that depending on the type of defect, exciton formation in polymer chromophores with defects leads to changes on intramolecular exciton localization as well as exciton energy.

METAMATERIALS BASED ON QUANTUM CASCADE LASER STRUCTURES IN STRONG MAGNETIC FIELD

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We analyze the possibilities of constructing a novel metamaterial with the arrangement of structural layers as in quantum cascade lasers. The starting point is the Lorentz model of atomic electrical susceptibility. Within this model the total permittivity has two parts: the first part is the averaged permittivity of the background material, while the second one is proportional to the difference of electron occupation densities of corresponding energy levels. In case of a passive configuration (where upper levels are less occupied than the lower ones) the second part of permittivity is positive (both the real and the imaginary part). However, if the occupation of levels is inverse (active configuration), the total permittivity could be made negative, hence this configuration would possess the property of negative-refraction materials, i.e. left-handedness.

A favorable candidate for illustration of these effects is the quantum cascade laser in strong magnetic field. Considerable values of the second part of the permittivity may be achieved by large charge sheet densities (of the order of 10^{13} cm^{-2}), owing to narrow absorption linewidths and large matrix elements. Numerical results obtained for AlGaAs quantum cascade lasers illustrate strong tuning capabilities, of the sign and magnitude of the real and the imaginary part of the total permittivity, with magnetic field.

OPTOMAGNETIC FINGERPRINT OF CONTACT LENSES: LIGHT INFLUENCE ON BRAIN ACTIVITY

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Light has influence on brain activity with very complex pathway (Fig.1). Since, light is composed of electrical and magnetic spectra it is very important to know how light interact with contact lenses. The orbital velocity of valence electron in atoms of polymers is about 10^6 m/s what gives ratio between magnetic force (FM) and electrical force (FE) in contact lenses of about $FM/FE \approx 10^{-4}$. Since force related directly to quantum action (Planck action, $h=F\times d\times t = 6.626 \times 10^{-34}\ Js$) it means that magnetic force is four of order closer to quantum phenomena than electrical.

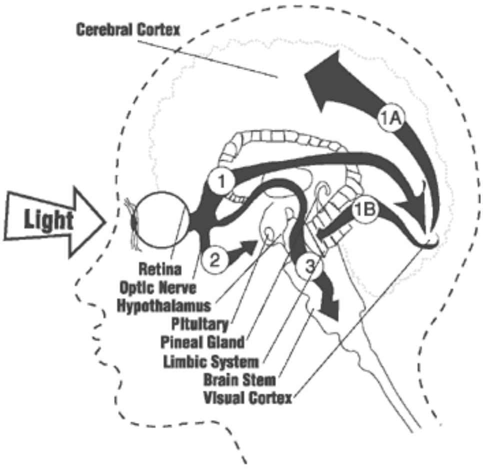

Fig.1. Nerve pathways from the eyes to the brain goes not only to the visual cortex, but also to deeper brain areas, concerned with neurotransmiters, neurohormones, emotions, etc.

Polymers of contact lenses surface are changing their conformation states during contact lenses production. Since, conformation change of polymer molecules generates quantum effects it may have influence on magnetic component of light. We investigated contact lenses samples from optomagnetic approach to see is there significant difference between them after production.

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MAGNETIC PROPERTIES OF CONTACT LENSES: CHARACTERISATION BY MAGNETIC FORCE MICROSCOPY

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Visual perception is the ability to interpret information from visible light reaching the eye. The act of seeing starts when the lens of the eye focuses an image of its surroundings onto a light-sensitive membrane in the back of the eye, called the retina. Since, visible light is composed of electrical and magnetic spectra, which have different influence on brain activity (EEG and MEG signals, Fig.1), we investigated magnetic property of contact lenses, as optical material, which have influence on electrical and magnetic light signals properties.

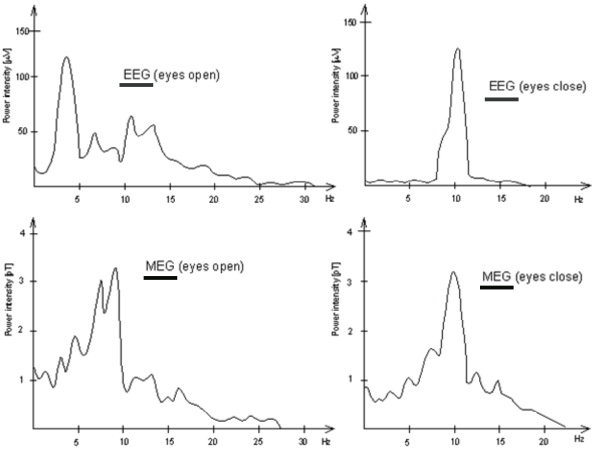

Fig.1. Brain activity (EEG and MEG) under light influence when eyes are open and close

To characterize magnetic properties of contact lenses we use JR-5 spinner magnetometer and MFM (magnetic force microscopy) to measure remanent magnetism and magnetic gradient, respectively, before and after light influence.

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UPCONVERTING $LiNbO_3$: Er/Yb NANOPARTICLES

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Marina Villegas[b], Amador C. Caballero[b]

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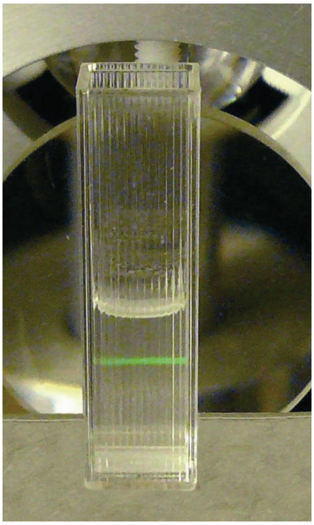
In this work we present the fabrication and optical characterization of micro- and nano-particles of Er/Yb co-doped lithium niobate ($LiNbO_3$). The nano-particles have been prepared by attrition milling of precursor monocrystals and the distribution of particle sizes is studied as function the milling parameters.

The optical properties of the particles, with special emphasis on the IR to visible up-conversion have been studied. After IR excitation of Yb^{3+} ions with an AlGaAs laser ($\lambda = 980$ nm) the characteristic green & red emissions from Er^{3+} ions is observed, indicating the occurrence of energy-transfer-up-conversion.

The luminescence characteristics of the nanocrystalline particles, both in solid phase or in suspension, are studied and compared to the bulk emissions.



Up-conversion luminescence of $LiNbO_3$ nano-particles in water suspension

[1] J.R. Schwesyg, H.A. Eggert, K. Buse, E. Sliwinska, S. Khalil, M. Kaiser, K Meerholz, Appl. Phys. B 89 (2007), p. 15 .

[2] E. Cantelar and F. Cussó, J. Lumin. 102 (2003), p. 525.

NEW SYNTHESIS AND STRUCTURES OF $Na_2Mo_2O_7$ AND $Na_2W_2O_7$ USING THERMODINAMICALLY STABLE MOLYBDENUM AND TUNGSTEN (VI) OXIDE CLUSTERS AS PRECURSORS

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A new method for the synthesis of disodium dimolybdate ($Na_2Mo_2O_7$) and disodium ditungstate ($Na_2W_2O_7$) in the process of ultrasonic spray pyrolysis using acidified aqueous solutions of thermodynamically stable molybdenum and tungsten (VI) oxide clusters as precursor is described. $Na_2Mo_2O_7$ and $Na_2W_2O_7$ particles were collected in isobutyl alcohol and ultra-centrifugation was employed to isolate solid materials from solution. The scanning electron microscopy revealed formation of uniform spherical $Na_2Mo_2O_7$ particles with average diameter of about 0.25 μm, and plate/shelf like $Na_2W_2O_7$ particles with average thickness of about 1.2 μm. The X-ray diffraction analysis undoubtedly confirmed formation of orthorhombic $Na_2Mo_2O_7$ as for $Na_2W_2O_7$ and the refinement of the diffraction data showed that those powders belongs to the base-centered orthorhombic type of structure with 64 space group Cmca. It was found that the basic units of the octahedral WO_6 precursor complexes in the both cases remain preserved in the powder structures. The tetrahedral WO_4 building units that coexist together with octahedral units joined in infinite chains in the powder structures are the most likely developed by termination of the weak octahedral bonds and by placement of the molybdenum or tungsten atom in the center of tetrahedra.

EPR AND VIBRATIONAL STUDIES OF SOME TUGSTATES AND MOLYBDATES SINGLE CRYSTALS

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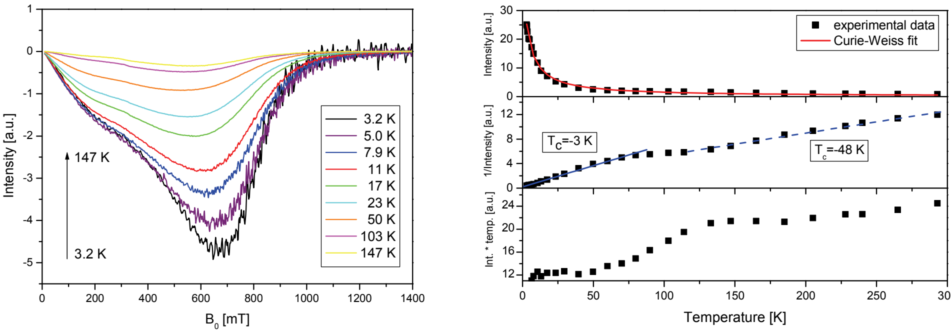
$CsDy(MoO_4)_2$, $KY(MoO_4)_2$, $KCe(WO_4)_2$, $KDy(WO_4)_2$, $KGd(WO_4)_2$ $KLa_{0.25}Pr_{0.75}(MoO_4)_2$, $KLa_{0.25}Pr_{0.75}(WO_4)_2$ molybdates and tungstates single crystals, have been investigated using the Raman and EPR techniques.

The EPR spectra were recorded using Bruker E 500 X-band spectrometer (~ 9.4 GHz) at temperatures between 3-300 K. Paramagnetic ions, present in the above potential laser matrices, show mainly antiferromagnetic kind of interactions below ~70 K, with some anomalies at higher temperature range. g-factor shows, sometimes, anomalous increase in low temperature range suggesting the existence of some internal magnetic fields. Total magnetic moment shows complex behavior giving evidence on the simultaneous presence of different kinds of spin systems in the compounds.

The temperature dependence of Raman spectra show no anomalies in the 10 – 300K range indicating that no structural phase transition is observed in this range.



EPR spectra for several temperatures and temperature dependence of the integral intensity, reciprocal of the intensity and the product of the intensity and temperature for $KGd(WO_4)_2$ single crystal.

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EFFECTS RELATED WITH PHOTOCONDUCTIVITY AND MOBILITY IN TlBr

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Thallium Bromide (TlBr), due to its wide bandgap, high density and high atomic numbers, is a promising material for X- and γ-ray detection. Though, presence of the ionic conductivity is still preventing it from the practical application.

We had investigated photoelectrical and current transient properties of TlBr from 100 K up to 300 K, where the effect of the ionic conductivity changes notably. TlBr crystals were grown by the Bridgman–Stockbarger method.

Current peculiarities were revealed that could stand for both electronic and ionic conductivities. Non-monotonous conductivity variation with temperature was identified, demonstrating mobility-related maximum that was superimposed on an intrinsic conductivity growth. This maximum could be caused by the recharge of the scattering centre at about 1.65 eV.

From the spectral dependencies several defect-related transitions at 0.55; 0.83, 1.1; 1.32 and 1.65 eV were identified, being dependent on sample prehistory, i.e., its excitation by light and/or voltage. The defect-related shoulders at about 0.83 and 1.1 eV used to intensify if the spectra were scanned from the higher quantum energies. Meanwhile influence of the levels at 1.32 and 1.65 eV used to decrease if the sample was kept biased for several hours.

The photocurrent kinetics had demonstrated a complex structure in which its decrease was changed by the growth. The thermal activation energy of the time constants of both processes was found to be 0.24 – 0.27 eV. Such complex behaviour could be explained either by the combined trapping and/or recombination of light-generated carriers to the defect centres, followed by the growing ionic conduction or by the variation in time of the ion diffusion-related scattering.

Our results demonstrate that ionic conductivity in TlBr is pronounced down to about 250 K. Moreover, even low intensity intrinsic light excitation might be effective in capacitating ionic conductivity.

The results obtained before degradation are compared with that in degraded devices.

Acknowledgements. This work was supported by the Lithuanian and Ukrainian Ministries of Education and Science and Lithuanian State Studies and Science Foundation (project No V-18/2009). The samples were kindly provided by Brucker Baltic (dr. V. Gostilo and dr. M. Shorohov).

CHARGE CARRIER MOBILITY AND AGEING OF ZnPc/C60 SOLAR CELLS

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Cu and Zn Phtalocyanines (CuPc and ZnPc), and C60 are materials frequently used for organic Solar cell engineering. Their energy levels are suitably located to form a donor-acceptor junction. Such systems have high absorption coefficients and a complementary absorption for the Sun spectrum.

We have investigated ageing properties of ZnPc/C60 Solar cells as they are influenced by the charge carrier mobility. The test Solar cell structures were formed on the glass plates covered with ozone treated Indium Tin Oxide (ITO). The sample structure is ITO/ZnPc (18 nm)/C60 (52 nm)/AOB doped C60 (5 nm)/Al (100 nm). A ZnPc buffer is used instead of the usual phenanthroline derivatives due to its higher thermal stability, while the overall device behavior should be the same. The devices were encapsulated. The simple device structure provides a reasonable conversion efficiency of η~1.5%.

The samples were aged for 1300 hours upon illumination with blue LED, with peak emission at 475 nm, incident light power density of 10 mW/cm^2. The devices aged under light showed a strong and fast degradation of the short circuit current and of the fill factor after several hours followed by an almost constant behavior of these values. The reference samples kept in the dark at the room temperature did show only very small changes in their I-V curves.

Carrier mobility dependencies on electric field strength at different temperatures were measured by the Charge Extraction by Linearly Increasing Voltage (CELIV) method. It was demonstrated that mobility values decrease during degradation as compared to the reference samples. Nevertheless only mobility changes cannot explain the observed drop of device current. Probably this is due to the enhanced recombination in devices caused by their morphology changes leading to the decrease of the effective carrier density.

Acknowledgements. R. Lessmann acknowledges CAPES/Brazil and DAAD for the scholarship. Part of this work was performed within the EC FP6 project OrgaPVNet.

OPTIMIZING ALL OPTICAL SWITCHES IN SEMICONDUCTOR MICRORESONATORS USING CARRIER BEHAVIOR

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An important component of high-speed optical communication networks is an all-optical switch, where an incoming switching beam redirects other beams through light-by-light scattering in a nonlinear optical material [1]. An other favourable property of all-optical switches is that the output beams are controlled by a weaker switching beam [2].
Recently, a switching technique that is based on sensitivity of transverse optical patterns have been developed in both atomic and semiconductor systems [2, 3]. A transverse optical pattern is the spatial structure of the electromagnetic field in the plane perpendicular to the propagation direction [2]. Optical patterns emerge from the coupling of the nonlinear medium response, diffraction, and the feedback action of mirrors [4]. For switching they present a non-feedback technique, which allows to select the orientation of spatial patterns in system, also this method is based on injecting a weak perturbation into the system [3].
Kheradmand et al. presented an all-optical switch in semiconductor microresonators [3] that had a rise time of sub-nanosecond scale but in that work they focused on behavior of filed while we know the importance of carriers in semiconductor microresonators. Here carriers have substantial role in behavior of switching thus we studied behavior of carriers for optimize switching. First of all, we considered the steady state by using a model characterized by two dynamical equations for field and carriers and studied the homogeneous stationary state of carriers. We found some parametric regions where behavior of carriers is bistable (see Fig. 1). As it has shown in Fig. 1, by choosing proper physical parameters Ns-EI curve will be bistable. The homogeneous stationary state of carriers leads us to study and simulate dynamical properties of carriers in optical switch and optimizing the parameters to get high speed optical switches.

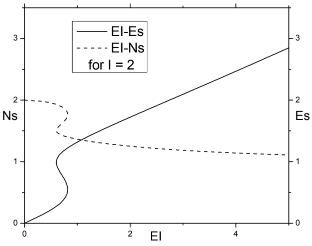

Figure 1: steady-state curve of the homogeneous solution for carriers and field

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DISORDERING EFFECT OF PERIODICALLY POLEDNONLINEAR CRYSTALS0N PARAMETRIC DOWN CONVERSION

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Recently it has been shown [1,2] that periodically poled nonlinear crystals are leading to quasi phase- Matching in photonic conversion processes and particularly are also highly promising for generation of nonclassical states of light and open interesting view for applied Quantum information.

A particularly effective structure in (PPNC) is one in which the sign of the nonlinear susceptibility $X^{(2)}$ is periodically invert through the medium.

We investigate spectral properties and multimode structure of joint states of photon pair produced by pulsed parametric down conversion in (PPNC) with adding random length to each domain.

The initial manner to this approach is the idea manipulating overall group delay mismatches between various fields in structured materials for syntheses of twin photon state [3]

Most of experimental arrangements consist of the periodic assembly of $NX^{(2)}$ crystals of length l with positive and negative susceptibility. In this work we assume that the mismatch functions and lengths are not the same in each domain and vary randomly. While $l=l(l+\varepsilon)$, where ε is random number and is less than one.

We investigate that, in this system the two-photon spectral Amplitude will be

$$\Phi = E_0 L X e^{\frac{-iL\Delta k}{2}} \sum_{n=1}^{N} \frac{(-1)^{n+1}}{i\delta}\left[1 - e^{-i\delta(1+\varepsilon_{n+1})}\right]\left[e^{-i\delta\sum_{j=1}^{n} j(1+\varepsilon_j)}\right]$$

Where E_0=pump envelope function $L = Nl$ X= susceptibility ε= random number

As it has shown in Figure (1), $|\phi|^2$ has extremum values for ε=0 and it thrown down by increasing ε. It means that, perturbation in periodic structure – length vanishes the amplitude of output.

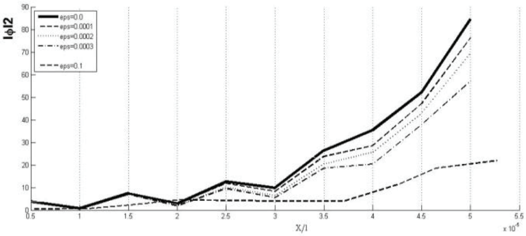

Fig1: Two photon spectral as a number of layers in periodically poled nonlinear crystal with different values of perturbation coefficient ε.

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MODIFICATION OF WTi/Si SYSTEM BY 1064 nm PICOSECOND Nd:YAG LASER PULSES

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The WTi alloy as a refractory material possesses very good physicochemical characteristics such as thermochemical stability and high melting temperature. Conventional processing of this material is extremely difficult because of its hardness and brittleness, and the use of a laser is a possible solution. In this work interaction of Nd:YAG laser with tungsten-titanium (WTi) alloy deposited on single Si (100) substrate is considered. During WTi system irradiation with picosecond laser pulses the main part of the absorbed energy was rapidly transformed into heat thus the intensive modifications on the target surface was occurred. The WTi thin film (thickness of 190 nm) was deposited by sputtering process. Various analytical techniques were used for characterization of the samples. The phase composition and crystallite structure of WTi/Si sample were determined by X-ray diffraction method. Surface morphology was monitored, by optical microscopy (OM), by scanning electron microscopy (SEM) and by profilometer. In the experiment typical laser output parameters were: wavelength 1064 nm, pulse duration 40 ps and laser pulse energy density (fluence) 5.7 J/cm^2. Multi-pulse laser irradiation was conducted in air atmosphere. Modification of WTi can be summarized as: (i) partial ablation/exfoliation of the WTi thin film, (ii) partial modification of the silicon substrate with formation of mosaic structure, (iii) appearance of hydrodynamic features including nano globules.

CAVITY SOLITONS IN VCSEL’S BEYOND THE RATE EQUATION APPROXIMATION

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Cavity solitons have been theoretically predicted and recently experimentally demonstrated in broad area, vertical cavity, driven semiconductor lasers (VCSEL) slightly below the lasing threshold[1,2]. Above threshold, the simple adiabatic elimination of the polarization variable is not correct, leading to oscillatory instabilities with a spuriously high critical wave-number, to achieve real insight on the complete dynamical problem; we considered also the steady state, material polarization dynamics, by using a model introduced by Agrawal, characterized by five dynamical equations. We studied the homogeneous stationary state and their instabilities, both stationary (Turing) and dynamical (Hopf). We found some parametric regions where the homogeneous state is bistable, with the lower branch unstable for a Hopf instability, and the upper branch unstable for Turing instability.

The model which we used in this paper differs from the two level Maxwell-Bloch equation for the macroscopic polarization **P** where, as in[3,4] ,the right hand side of the equation is multiplied by a complex term where two real parameters Γ and Δ appear and determine the shape of the effective susceptibility . The two parameters are assumed to depend on the population variable D, and the dependence can be phenomenologically derived by a quadratic fitting of the gain curves calculated with a microscopic model.

In this work, we just point out that a standard adiabatic elimination of P allows to recover straightforwardly the rate equation model [1], which makes the physical comparison with the amplifier configuration more straightforward. The numerical results obtained by integration of the dynamical equations using Split-Step method show that stable CSs are possible in this regime, even if they sit on an unstable background (see Fig. 1). Despite the instability affecting the background, it turns out to be perfectly possible to write and erase CSs in the usual manner. A writing beam (WB) is injected into the cavity, with the same phase as the holding field, for a certain time (ranging from half to several nanoseconds), then it is removed. The CS grows up and remains fixed at the location where the WB was injected.

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EXPERIMENTAL INVESTIGATION OF DYNAMIC BEHAVIOR OF HOLOGRAPHIC GRATING IN AZO-DYE DOPED NEMATIC LIQUID CRYSTAL

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In this experimental work the dynamic of laser induced holographic grating formation and relaxation is studied when one or both of the writing beams are switched on/off in different thickness of cells filled with Dispersed Red 1 azo-dye doped E7 nematic liquid crystal. The results are used to extract the diffusion parameters of dye molecules in the nematic LC host for two different geometries (when diffusion direction was parallel or perpendicular to the LC director). According to the results, two different mechanisms are suggested for the grating formation in this guest-host system. Comparing the grating relaxation times for the cells when light intensity modulation direction is perpendicular or parallel to the director, indicates that diffusion of excited dye molecules from the regions that have been illuminated is dominant mechanism for relaxation of grating. The relaxation time investigation for various grating periods yields diffusion constants. Also, the observed difference in dynamic behaviors of grating formation, as an overshoot, when one or both of the writing beams are switched on for the thinner sample is explained using the diffusion of guest molecules.

CHARACTERIZATION OF OPTICAL NONLINEARITY IN AZO DYE DOPED NOVEL NEMATIC LIQUID CRYSTAL

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We report the formation of photo-induced refractive index grating in a planar aligned 50 micron cell contains a novel nematic liquid crystal mixture (1294-1b) doped with well known Azo dye DR1 at concentration 0.5% wt. Two pump beams (Ar+ laser at 514 nm) were set to be s-polarized and intersect in the sample at a small angle. Then the diffraction efficiency of the refractive index grating was measured using a probe beam (He-Ne laser at 633nm, far enough from sample absorption) in various intersecting angles of writing beams at room temperature. Using another pump-probe setup, the absorption coefficients of trans and cis isomers of dye molecules investigated experimentally too. The results used to explain the mechanisms of photo-induced refractive index grating formation in the sample. According to the results higher absorption coefficient observed for trans isomers than cis isomers. Also the quantum efficiency for trans-cis transition obtained which was higher than cis-trans transition. The highest diffraction efficiency is achieved for the optimum intersect angle 0.5 degree and its related nonlinear refractive index, n2, is obtained about 2.8 x 10E-3 Cm2/W.

TEMPERATURE DEPENDENCE OF THE THRESHOLD CURRET DENSITY OF A GaN BASED QUANTUM DOT LASER

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Group III nitride-based optoelectronic devices are used in a wide range of applications due to their large band gap energies. III nitride-based heterostructures form the active layer in blue–green LED's and laser diodes commercially available today [1]. Quantum dot (QD) structures could still improve their performance enormously [2]. In particular, III nitride-based QD lasers are expected to have low threshold current densities and better temperature stability compared with conventional blue lasers with III nitride-based quantum wells (QW) [3].

In this work, a detailed theoretical analysis of the temperature dependence of threshold current density of a GaN based semiconductor quantum dot laser (QDL) is given. Temperature dependences of the threshold current density components associated with the radiative recombination in QD's and in the optical confinement layer (OCL) is calculated. Temperature dependences of the optimum surface density of QD's and the optimum thickness of the OCL, minimizing the threshold current density, are obtained.

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CHARGE TRANSPORT MODEL OF GATE SOLUTION AlGaN/GaN HIGH ELECTRON MOBILITY TRANSISTORS

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The wide band gap III-Nitride semiconductor materials have been the subject of intensive investigation, both theoretical and experimental, in view of their applications in electronic and optoelectronic devices. In this article, a transport model of gate solution AlGaN/GaN high electron mobility transistor has been developed that is capable of accurately predicting the sensitivity of the drain current as well as small-signal parameters such as drain conductance, device transconductance and cutoff frequency to pH values of the electrolyte and to charged adsorbates at the semiconductor–electrolyte interface. This model built up with incorporation of fully and partially occupied sub-bands in the interface quantum well, combined with a numerically self-consistent solution of the Schrödinger and Poisson equations. In addition, the polarization effects, and self-heating are also taken into account. In comparison with exist experiment data, our results shows good agreement.

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LUMINESCENT PROPERTIES OF SILVER COMPLEXES IN SOLID SOLUTIONS OF INORGANIC COMPOUNDS

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The present work is devoted to a consideration of the spectral properties of haloid and oxygen-containing solid solutions, activated with silver complexes.
The absorption, photoluminescence, and photoexcitation spectra of those solutions with a silver ion impurity have been investigated in the temperature range of 4.2 – 290K.
The observed spectra are conditioned by electron transitions between the energy levels of Ag^+ ion which are deformed due to the interaction with environment.
The study of silver impurity in examined solid solutions allowed to elucidate the energy structure of absorption end emission centers in those solutions.
The analysis of spectral characteristics of silver ions in solutions of inorganic compounds allows to develop the high-sensitivity luminescent techniques of testing of microimpurity of silver in those solutions.
The mechanism of luminescence of Ag^+ impurity in investigated solutions and phosphors with the same composition will be discussed.

THE SCATTERING OF HOT ELECTRONS BY PHONONS IN AlGaN/GaN QUANTUM WELLS

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The wide band gap III-N semiconductor materials have been the subject of intensive investigation, both theoretical and experimental, in view of their applications in electronic and optoelectronic devices. A detailed study of the energy and momentum relaxation together with the determination of the dominant scattering mechanisms in these materials are crucial for obtaining a comprehensive understanding of the carrier dynamics, especially at high operating electric fields [1-4].

In this work we study an undoped AlGaN/GaN quantum wells. The energy loss rate of the quantum well are calculated as a function of the external controllable parameters such as ns (electrons density), L (well width), T_L (lattice temperature), Te (electron temperature), x (percent Al alloy) and numbers of wells for the interaction of the charge carriers with acoustic (deformation potential and piezoelectric) and optical phonons.

Our results indicate in AlGaN/GaN QW, for T_e lower than 75K, the dominant scattering mechanism is acoustic phonon scattering and for the higher temperature than 120K the optical phonon is overcome. For the low temperatures (Te < 20) unlike GaAs based QW, the predominant mechanism is piezoelectric scattering which emphasize strong piezoelectric effects in GaN [5]. Also, our results show that the increasing of well width decrease the energy relaxation rate whereas it increases by increasing the alloy percent.

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MECHANOLUMINESCENT SMART MATERIALS AND THEIR APPLICATIONS

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Mechanoluminescence (ML) is the phenomenon of light emission from a solid as a response to mechanical stimulus given to it. The light emissions induced by elastic deformation, plastic deformation, and fracture of solids are called elastico ML, plastico ML, and fracto ML, respectively. The light emission induced by rubbing a solid or separation of two solids in contact is known as tribo ML or triboluminescence. Whereas, nearly 50% of all inorganic salts and organic molecular solids show ML during their fracture, only a few solids show ML during their elastic and plastic deformation. In recent past, several materials have been investigated whose ML intensity is so intense that it can be seen in day light with naked eye. Depending on the prevailing conditions, ML spectra that resemble the spectra of another type of luminescence of a solid or light emission that comes from a gas discharge or that combine characteristics of both may be obtained. The important requirement for exploring applications of ML is the development of materials with strong non-destructive ML intensity. In recent years, systematic materials research has resulted in producing a variety of materials that emit an intensive and reproducible ML during elastic deformation without destruction. So far ZnS:Mn nanocrystals and $SrAl_2O_4$: Eu, Dy microcrystals have been found to be the most promising mechanoluminescent smart materials for various mechano-optical devices. The elastico and plastico ML in ZnS: Mn nanocrystals arises due to the piezoelectrically-induced electroluminescence, and the elastico and plastico ML in $SrAl_2O_4$: Eu, Dy crystals arises because of the piezoelectrically-induced detrapping of charge carriers. The fracto ML appears because of the intense electric field created near the charged surfaces produced during fracture of solids. The mechanoluminescence of ZnS: Mn films and $SrAl_2O_4$: Eu, Dy mixed in epoxy resin have been found to be suitable to fabricate artificial skin for sensing stress. The visualization of stress distribution in solids can be made using the ML from $SrAl_2O_4$: Eu, Dy as their ML intensity is higher for higher stress. Such ML materials are either mixed in the target sample or coated on to the surface to sense stress distribution by emitting light. The mechanoluminescent paint of $SrAl_2O_4$: Eu can also be used to visualize the invisible defects in structures. By mixing $SrAl_2O_4$:Eu,Dy in the composite or by coating the paint of this phosphor mixed in resin or by coating thin film to the surface of solids, the quasidynamic crack propagation in solids can be visualized. Using the ML technique, the crack–growth resistance curve (R–curve), crack velocity, bridging stress distribution, crack–tip stress field, wake width, etc. can be determined. An intense fracto-mechanoluminescent material embedded in or attached in to a composite structure acts as a real-time damage sensor. In this technique, each location of the structure either comprises different ML materials or all locations use the same ML material in which different fluorescent dyes are mixed for different wavelengths-shifting at different locations. When an impact fractures the ML material, it sends a flash of light through optical fibres to the detector, whereby the intensity of light gives directly the magnitude of the damage and the wavelength of the light emitted indicates the location of damage caused by the dynamic events. The intense fracto mechanoluminescent materials such as Eu, Tb or Mn complexes have been found suitable for the mechanoluminescent damage sensor. Further studies related to the preparation of new intense mechanoluminescence materials and new applications of ML are needed. Furthermore, it would be interesting if the mechanoluminescent sensors could find application in giving prior information to the occurrence of earthquakes.

SYNTHESIS OF TRANSITION METAL AND RARE EARTH DOPED MIXED OXIDE NANOPOWDERS

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The synthesis of organic precursors and the development of flame spray pyrolysis equipment for laboratory scale production of nanocrystalline aluminate materials is described in this article. Synthesized materials are pure and doped Al_2O_3 and $MgAl_2O_4$ nanopowders. The powders are characterized by X-ray diffraction analysis, surface area analysis and scanning electron microscopy. The purpose of the research is to find the applications of nanomaterials in fluorescent sensor research and in the production of transparent polycrystalline ceramic materials for laser and optical industry.

CLEAVAGE MECHANOLUMINESCENCE IN POLYMERS

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The present paper report the theory of mechanoluminescence (ML) produced during cleavage of polymers, when the polymers like polyethylene (PE), polyvinylidenefluoride (PVDF), polypropylene (PP), polystyrene (PS), polymethylmethacrylate (PMMA), and polyethylmethacrylate (PEMA) are cleaved, initially the ML intensity increases with time, attains a peak value then it decreases with time. The peak of ML intensity versus time curve shifts towards shorter time value with increasing thickness of the polymers. No significant change in ML intensity was observed with impact velocity. It is found that there is good correlation between ML intensity and area of newly created surfaces. The total ML intensity (I_T) is found to be increased directly with area of newly created surfaces. The ML emission may be due to the piezoelectrification of newly created surfaces, dielectric breakdown of intervening gases and dielectric breakdown of the material caused by intense electric field produced between the newly created surfaces.

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LIGHT EMISSION PRODUCED DURING IMPULSIVE DEFORMATION OF POLYMERS

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When Polymers like polyvinylidene fluoride (PVF_2), Polyethylene (PE), Ploymethylmethacrylate (PMMA), Polyethylmethacrylate (PEMA), Polypropylene(PP) and polysterene are deformed by dropping a load from different heights, then initially the mechanoluminescence (ML) intensity increases with time, attains a maximum value at a particular time and then decreases with time. The peak of ML intensity versus time curve increases in intensity and shifts towards shorter time values with increasing impact velocities. However, the total ML intensity I_T, initially increases with time and then it attains a saturation value. It is shown that the charging of the newly created surface is responsible for the light emission produced during fracture of the polymers. In piezoelectric polymers, the surface charging may take place due to the piezoelectrification. However, in non piezoelectric polymers surface charging may take place due to barro-diffusion of charged defects near the tips of the moving cracks.

STRUCTURAL, ELECTRONIC AND OPTICAL ASPECTS OF THE CHROMIUM DOPING OF THE BGO: AB-INITIO STUDY

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The $Bi_4Ge_3O_{12}$ (BGO) has been the subject of numerous studies due to its excellent scintillation properties suitable for technological applications. In a pure form it is utilized as scintillator in scientific research, non-linear optical devices and nuclear medicine [1]. When doped with Cr, the BGO exhibits enhanced photorefractive response [2] and shows potential to be used as a near infrared (NIR) solid state laser host [3]. Several experimental studies have been performed on this system so far, investigating its optical properties and the possible Cr accommodation within the lattice. It was not unambiguously determined which position the Cr impurity occupies in the BGO: the octahedral Bi^{3+} or tetrahedral Ge^{4+} site. The EPR study of Bravo et al [3] indicates the Cr presence in both sites. The Cherney et al [4] however concluded that Cr substitutes just the Ge site, and the same conclusion was drawn from the optical absorption analysis of Mello et al [5]. In this work we used the density-functional theory based, linear augmented plane wave method to calculate structural, electronic and optical properties of doped BGO crystal with substitutional Cr impurity situated either at the Ge^{4+} or the Bi^{3+} site. The crystal structure of doped systems was computationally optimized: all atoms around the impurity were allowed to relax, while the unit cell parameter was taken from the theoretical study of the pure BGO [6]. The results of energetic balance do not strongly indicate which site, Bi or Ge, should be preferable for substitution. The defect formation energy in the case when Cr substitutes the Bi is just 0,039 eV lower in comparison with the case when Cr substitutes the Ge. When situated at the Ge site, the Cr maintains the bond lengths with the neighboring O's practically unchanged. When substitutes the Bi, however, it strongly deforms its octahedral environment, additionally suffering large off-site departure along the C_3 axis. The electronic structure calculations show that the Cr modifies the band offset of the pure BGO introducing its states within the band gap: two deep and one shallow band if it resides at the Ge position and two shallow bands if it resides at the Bi position. In the first case the Cr magnetic moment is calculated to be $+1.58\mu_B$, while in the second $-2.44\mu_B$. The optical absorption spectra were calculated as functions of the incident radiation energy up to 40 eV. The absorption peaks caused by the Cr presence were identified and interpreted in terms of calculated electronic structure, for both possible positions of the Cr impurity. Our results compared with the existing experimental data indicate that the Cr doped BGO should contain the Cr atoms at both Ge and Bi substitution sites, confirming thus the conclusions of the work of Bravo et al [3].

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CRYSTALLOGRAPHYC ORIENTATION OF SUBSTRATE AS THE KEY POINT FOR ZnO@Si, ZnO@SiO_2 MORPHOLOGY AND LASING CHARACTERISTICS

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Zinc oxide is a promising wide band gap semiconductor (3.37 eV) for ultraviolet optoelectronic applications which attracts the attention of researchers in various fields of knowledge. This work presents the results of the investigation on synthesis, morphology and spectroscopic characteristics of nano- and microcrystalline ZnO deposited on various crystalline substrates.

Nanocomposites ZnO@Si, ZnO@SiO_2 were prepared by soft low-temperature hydrothermal synthesis. Single-crystalline Si and SiO_2 plates with various crystallographic orientations (for Si (100) and (111), for SiO_2 (0001), $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$) were used as substrates. During hydrothermal treatment, ZnO polycrystalline coatings were formed onto substrates. Such coatings had high optical quality and specific growth morphology depending on growth parameters. The ZnO@Si, ZnO@SiO_2 nanocomposites demonstrated intensive exciton luminescence and lasing (excitation by 3th harmonics of YAG:Nd^{3+}, 355 nm).

Earlier [1] we have shown that the laser action in disordered media may be divided into two types (random laser and microlaser) in accordance with the formation of random cavities or regular cavities in excited active media. Morphology of crystallites is responsible for the appearance of the lasing type mentioned above. Analysis of lasing spectra of synthesized ZnO-based nanocomposites had shown that lasing parameters were better for ZnO@Si(111) composite then for ZnO@Si(100). For SiO_2 substrates, the best results were obtained for substrates oriented parallel to small rhombohedron $r\{10\bar{1}1\}$ and large rhombohedron $z\{01\bar{1}1\}$ in comparison with *c*(0001) orientation.

Observed features of zinc oxide lasing parameters confirm the connection between the lasing action and morphological types of ZnO crystallites which in turn are supervised by the basic physical and chemical characteristics and structure-forming elements of growth systems. Lasing parameters of hydrothermally grown nanocomposited are discussed taking into account the type of substrate, crystallographic orientation and growth morphology.

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MORPHOLOGY AND PROPERTIES OF SOL-GEL PREPARED LDPE-SILICA NANOCOMPOSITES

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This project involved the preparation of sol-gel derived silica nanocomposites prepared with LDPE and LDPE-g-MA as matrices in the absence and presence of an oxidized Fischer-Tropsch paraffin wax as possible compatibilizer. The silica was prepared using a previously published sol-gel based method [1-3] and mixed with LDPE and LDPE-g-MA, as well as LDPE/oxidized wax and LDPE-g-MA/oxidized wax blends. The morphology and interactions were investigated using FTIR, SEM and TEM, while the thermal and mechanical properties were investigated using DSC, TGA, DMA and tensile testing.

The FTIR results clearly indicate interactions between the functional groups of the LDPE-g-MA and the wax, and the –OH groups on the silica. It is, however, difficult to establish the exact nature of these interactions. The SEM photos of the surfaces of the nanocomposite samples more clearly show the nanoparticle distribution than either the SEM photos of the fractured surfaces or the TEM photos. The DSC results show a very definite influence of the presence of nanoparticles and wax on the crystallization behaviour of the polymers, and the TGA results show a fairly small influence of the nanoparticles on the composite degradation in the absence and presence of wax. The mechanical and dynamic mechanical properties of the composites were significantly influenced by the presence of wax and nano-silica.

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PHOTOLUMINESCENT PROPERTIES OF NANOSTRUCTURED $Y_2O_3:Eu^{3+}$ AND $(Y_{1-x}Gd_x)_2O_3:Eu^{3+}$ POWDERS OBTAINED BY AEROSOL SYNTHESIS

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The nanostructured phosphor particles of $Y_2O_3:Eu^{3+}$ and $(Y_{1-x}Gd_x)_2O_3:Eu^{3+}$ (x=0.25, 0.50, 0.75) systems were synthesized through aerosol method. The corresponding nitrate solutions were ultrasonically atomized (1.3MHz) and the obtained aerosol was decomposed at 900°C. The as-prepared powders were thermally treated at 1000-1200°C/12h. The employed synthesis method assured formation of spherical, full, non-agglomerated and polycrystalline materials with crystallite size around 20nm. Powders structural and morphological features were investigated by means of XRD, SEM, TEM/SAED and HRTEM/FFT methods. Functional properties were examined through photoluminescent analysis. A detail study of the emission spectra after excitation with 393nm wavelength and of the decay lifetimes for Eu^{3+} ion $^5D_0$ and $^5D_1$ levels gave an insight into improved luminescent properties of the obtained powders. The emission spectra showed typical Eu^{3+} $^5D_0 \rightarrow {}^7F_i$ (i=1, 2, 3, 4) transitions with dominant red emission at 611nm, while the lifetime measurements gave an insight into the effect of dopant concentration (5 and 10 at%) and its distribution into host lattice according to the applied thermal treatment. Additionally, luminescent properties were correlated with the obtained structural and morphological features of the synthesized powders.

CORRELATION OF STRUCTURAL AND OPTICAL PROPERTIES OF SPUTTERED $FeSi_2$ THIN FILMS

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Iron-disilicide is an interesting optoelectronic material, being a narrow band gap direct semiconductor (E_g=0.85–0.95 eV) both in its crystalline β-phase and in amorphous phase, as well as in the form of very fine (3–5 nm) β-$FeSi_2$ nano-crystals. Furthermore, it has a high photo-absorption coefficient, good thermal stability, corrosion resistance, and consists of non-toxic materials, which make it a promising material for potential applications in large area electronics and for fabrication of solar cells. In these experiments $FeSi_2$ films were deposited on Si (100) wafers by ion sputtering, at substrate temperatures ranging from room temperature (RT) to 700°C, to a thickness from 300-400 nm. Samples deposited at RT were additionally heat-treated, for 30 min at 200-700°C. The structures were characterized by Rutherford backscattering spectrometry (RBS), transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDX), and we also performed photo-absorption (PA) measurements on the samples. Compositional analyses verified the $FeSi_2$ stoichiometry in all as-deposited and heat-treated films. For deposition temperatures from RT to 300°C the grown films had an amorphous structure, while those deposited at 400-700°C had a crystalline β-$FeSi_2$ structure. In the later case the mean grain size increased with the deposition temperature. On the other hand, the heat-treated films remained amorphous up to 400°C, and at 500°C and higher temperatures they transformed to crystalline β-$FeSi_2$. There is also a marked difference in the structure of as-deposited crystalline films, which is controlled by surface diffusion, compared to the structure of crystallized amorphous films, which is controlled by bulk diffusion. The PA measurements showed a semiconductor nature for both amorphous and crystalline $FeSi_2$ films. However, these measurements indicate a different behavior with respect to the short to medium range order in amorphous structures, and different concentration of defects in crystalline structures.

OPTICAL PROPERTIES OF BETANIN SENSITIZED GELATIN FILM

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Gelatin sensitized with betanin dye produces a film which can be deposited on microscope glass plates by simple technique. Optical properties of betanin sensitized gelatin film were analyzed. This mixture shows good photosensitivity in the green part of spectrum.

Betanin is reddish-purple natural, water soluble pigment, from red beet roots, with maximum absorption at 535 nm. It is a commercially available food dye (E 162) which is used without further purification. Commercial quality gelatin (edible gelatin) was used. The material is cheap, nonpoisonous and used for microstructure fabrication by Nd:YAG laser operating at 532 nm. The long term stability of betanin sensitized gelatin film was obtained without additional chemical processing.

LUMINESCENT ANALYSIS OF LILAC ALPHA SPODUMENE

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In search of new materials for optical applications due to wide variety of crystals available, one should focus on some positive characteristics of crystals. The spodumene, which is a natural silicate relatively abundant in nature, in its purple variety shows thermoluminescent peaks in temperatures at wavelengths suitable for use in dosimetry. Besides, there are evidences that it produces intense visible radioluminescence which could be used in radiation detectors or other optical application. Thus, the radioluminescence and thermoluminescence samples of alpha-purple natural spodumene excited with X, gamma and beta rays were examined. The material showed very intense orange light emission in all forms of excitement and for both types of luminescent phenomena studied. The results led to the conclusion that the mechanism of charge capture by traps during irradiation is the same for both types of radiation, electromagnetic or beta-rays. Preliminary results of radioluminescence confirm that lilac spodumene may have application as a radiation detector.

OUT OF EQUILIBRIUM SYNTHESIS OF MODEL UNCAPPED ZnO NANOPARTICLES

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Among wide-bandgap semiconductors for optoelectronic applications, ZnO has come to the forefront in the present decade primarily because of the large value of its exciton binding energy (60meV). In order to obtain high efficiency UV nano-source, many techniques like MBE, CVD, chemical synthesis or PLD have been used to synthesize ZnO nanoparticles. But the nanoparticles synthesized are often affected by an oxygen lack which is responsible for a green visible luminescence leading to a poor UV efficiency [1].

In this work, we report a simple and effective technique of synthesizing uncapped ZnO nanoclusters which are well crystallized, faceted, controlled in stoichiometry and crystallinity, deposited, and analyzed in ultra high vacuum (UHV). Different from the conventional chemical vapor deposition or other chemical routes, the low energy clusters beam deposition technique (LECBD) involves neither catalytic processes nor specific substrates and is carried out in non steady state [2].

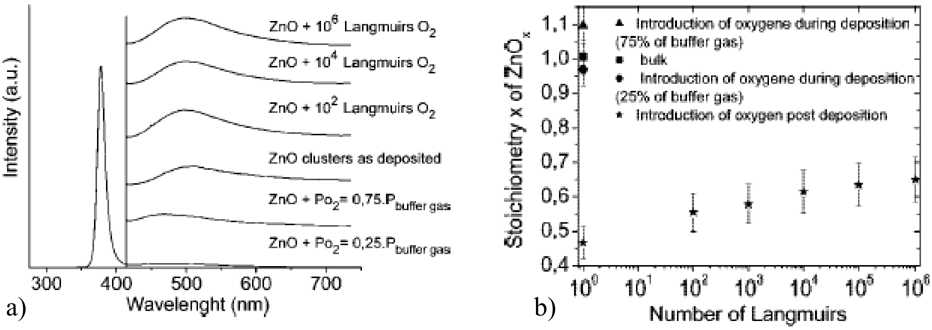

Figure 1: Photoluminescence (a.) and stoichiometry (b.) of variously treated ZnO NPs.

The introduction of controlled quantity of oxygen in UHV after clusters deposition or during the nucleation has been studied to further improve the quality of ZnO NPs. The analysis of X-ray photoelectrons, nanometric EDX probe, Auger lines and luminescence spectra of the cluster assembled films reveals a clear difference between these two ways on the crystallinity and stoichiometry of the clusters (Fig 1). Depending on the process of incorporation of oxygen in the clusters network, particles with identical stoichiometry exhibit quite dissimilar luminescence properties. This proves that the green luminescence does not originate directly from a lack of oxygen but by the crystalline defects caused by this lack. [3]

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ORIGIN OF THE A BAND IN ZnO: A VUV APPROACH

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The main barrier to overcome in order to industrialize ZnO optoelectronic compounds is the control of p-doping [1]. One proposed way to confirm p doping is the observation of a low temperature emission at 3.31 eV (called A band) resulting from the trapping of excitons at acceptor defects. However, this band is often present in undoped nanostructures and its energy is closed to the 1LO replica of the free exciton (FX). Therefore, the assignment of this band is controversial [2].

In order to study the origin of the A band we have made a systematic study of the temperature dependence of the excitonic luminescence of three kinds of ZnO structures under near band gap and VUV excitation. The three samples used are a monocrystal (MC), microcrystals (μC) and an assembly of nanoparticles (NP) which are uncapped, controlled in stoichiometry and cristallinity and deposited in Ultra High Vacuum [3]. The VUV excitation allows us to favour the exciton trapping by defects to the detriment of the FX related emissions [2].

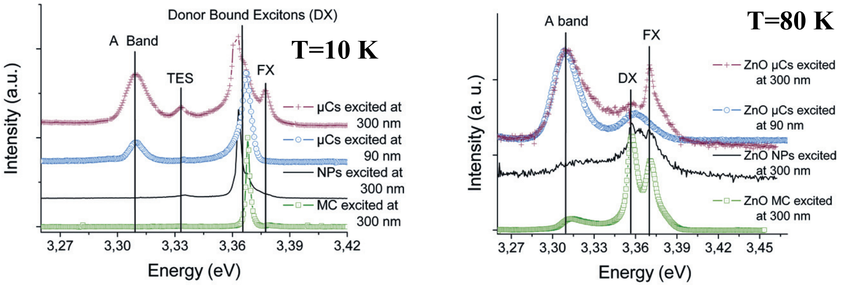

Figure 1: Emission spectra of three samples recorded at 10K and 80K for different excitations

Our study, relying on comparisons of spectra obtained with a VUV excitation or a near band gap one for all three samples, reveals that two mechanisms evoked in the literature are alternatively involved. Below 80K, the contribution of the defects is prominent (fig 1). The temperature dependence of this band for μC follows a kT/2 variation, characteristic of a free to bound transition probably localized on extended crystal defects [4].

At temperatures higher then 80 K, a second contribution is added, stemming from 1LO phonon replica of the FX. This is confirmed both by the modelling of the spectra by a Maxwellian distribution and the appearance of the A band for the NP and MC samples (fig 1).

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ESR STUDY OF Mn^{2+} RED EMISSION IN $CaGa_2S_4$ CODOPED WITH A REE

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$CaGa_2S_4$ and $SrGa_2S_4$ have been extensively studied as the candidates for host materials of phosphors. In these compounds, we have found that the Mn^{2+} ion exhibits a red emission. This emission could be enhanced by co-doping with a Rare Earth Element. Especially, in La co-doping case, the Mn^{2+} red emission was enhanced by approximately 14 times [1]. To make clear the mechanism of this effect, a theoretical calculation has been done using a cluster model [2]. However, to get the concrete evidence, the substitutional site of a Mn^{2+} ion should be clarified; which site of the two, i.e, the Ca or Ga site does it occupy? The purpose of this study is to determine the Mn^{2+} site through ESR measurement.

Single crystal of $CaGa_2S_4$:Mn(0.1mol%) was prepared by the horizontal Bridgman method. A sample cut out from one of the crystals was oriented by the reflection Laue method and mounted at one end of a quartz rod. ESR spectra were measured at room temperature using an X-band microwave by applying the magnetic field perpendicular to the b crystal-axis and rotating the sample around the same axis every two degrees.

If a Mn^{2+} ion (S=5/2) occupies a single identical site in a crystal, it generally gives 30 ESR lines including the hyper fine structure due to its nuclear spin (I=5/2). In our measurement, more than 60 (30×2) lines were observed. Therefore, it is considered that there should be at least two substitutional sites in a crystal of the above compounds for Mn^{2+} ions to occupy. From the angular dependence of the ESR signals, they can be classified into 3 groups. One is well explained using ESR parameters, g=2.018 (isotropic), $D=d_{zz}=0.016cm^{-1}$, $E=d_{xx}-d_{yy}= -0.012cm^{-1}$, assuming the axis of D tensor to the c-axis (z-axis). For the other two sets of the signals, however, the angular dependences seem to obey the effective spin Hamiltonian assuming the axes of D tensor along the a- and b-axes of the crystal, respectively. Based on the results obtained up to now, the Mn^{2+} ion is expected to occupy the Ga site. To obtain the further evidence of the Mn^{2+} site occupation, we are now trying to do ESR measurements by rotating a sample along the other crystal directions.

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$Sn_2P_2S_6$ CRYSTALS – NEW HIGH EFFICIENT ACOUSTO-AND MAGNETOOPTIC MATERIALS

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In the present work we have studied the acoustic, acoustooptic, magnetooptic and thermomechanic properties of $Sn_2P_2S_6$ crystals.

For the first time all the acoustic wave velocities for the promising acoustooptic material, $Sn_2P_2S_6$ crystals was determined, and on this basis the acoustic slowness surfaces in both the crystallographic system and the eigen coordinate system of their elastic stiffness tensor have been constructed. The complete matrices of the elastic stiffness and compliance coefficients have been determined. Following from the quantitative analysis of the acoustic and elastic properties of these crystals, we have determined the directions of propagation and polarization of the slowest eigen acoustic waves, with accounting consistently the acoustic obliquity and the deviation of acoustic polarization direction from the states corresponding to purely transverse and longitudinal ones. In the directions of propagation of the latter waves there is no acoustic obliquity, while the deviation of their polarizations from the purely transverse and purely longitudinal types is negligibly small. The acoustooptic interaction with these acoustic waves should be most efficient, when compare with that typical for any other waves, owing to essentially increased acoustooptic figure of merit. It has been found that the acoustooptic figure of merit for these crystals achieves a large value, $M_2 = (1.7 \pm 0.4) \times 10^{-12}$ s^3/kg . To our knowledge, this is one of the highest acoustooptic figure of merit known for the acoustooptic materials operating in the visible spectral range. The consequence is that the acoustic powers as low as $P_a = (1.5 \pm 0.3) \times 10^{-3}$ W would be enough for gaining high diffraction efficiencies (e.g., $\eta = (16.0 \pm 3.2)\%$).

We have revealed large Faraday rotation in $Sn_2P_2S_6$ crystals, which makes this material promising for magnetooptics. The effective Faraday tensor component and the Verdet constant for the direction of optic axis have been determined at the normal conditions and the wavelength of 632.8 nm. The effective Verdet constant is found to be equal to 115 rad/T×m .

We have determined all the components of thermal expansion tensor in the temperature range of ferroelectric phase transition in both the crystallographic system and the coordinate system linked to the eigen vectors of this tensor. The temperature evolution of the indicative surface of the expansion tensor has been studied, too. It has been found that all the components of thermal expansion tensor tend to zero in the vicinity of the room temperature. This feature is promising when considering possible applications of these crystals.

THERMO-OPTICAL INVESTIGATIONS OF MULTILAYER BST/PZT THIN FILMS BY SPECTROSCOPIC ELLIPSOMETRY

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Significant development in the micro and nano-electronics caused a new rise of interest to the structure, state and properties of the surfaces of solids. A great increase of interest in the last few years has been developed in the multilayer thin films having thin layers of different compositions thin films [1]; bilayer structure, due to their enhanced dielectric, ferroelectric and pyroelectric properties [2-5], is a promising material combination for applications. The study of phase transitions (PT) in the systems with low-dimensions such as surfaces, thin films and multilayers is not only fascinating from a fundamental point of view, but also has technological significance for nanostructures, where interfaces and surfaces play an increasingly important and sometimes prevalent role. There are just few methods giving opportunity to investigate PT in ultra thin film, and some of them demand very specific sample preparation and even destruction of the sample, and complex data analyzes. One of the possibilities to detect or invest PT in non-destructive way in films, it is using of the optical methods.

In this work the nanocomposite materials consisted of alternating layers of $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) and $PbZrTiO_3$ (PZT) deposited by pulsed ablation technetium on to obtain complex heterostructure $Si/SiO_2/Ti/Pt/SrRuO_3$/BST/PZT/…/BST. The optical studies were made by J.A. WOOLLAM spectral ellipsometer. Main ellipsometric angles ψ and Δ were measured in the wavelength range of 280 - 1700 nm, at the incident angles of 60° - 75° (step 5°) and in the temperature range of 293 - 673 K. Dynamic measurements of ψ and Δ at the high temperatures was provided by self-maid PC controlled heating stage. Analysis of the room temperature and dynamic experimental data were accomplished by the licensed VWASE32 program.

High values of refractive index and optical band gap energy was found for the multilayer structure. Increase of refractive index till 65°C and then decrease was evaluated for BST/PZT multilayer, what corresponds to ferroelectric - paraelectric PT of BST. The complexity of the fitting, interpretation of the room temperature and dynamic optical data in terms of possible conductivity, interface and free Pb existence [7] in the film will be discussed.

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DEPENDENCE OF CRYSTAL FIELD EFFECTS ON VARIATION OF INTERIONIC DISTANCES IN ZnS:V^{2+} AND MgO:Cr^{3+}

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Optical spectra of transition metal ions in crystals can be modified by applying external pressure [1]. From the computational point of view, pressure effects can be modeled by changing interionic distances around impurities. Microscopic studies of crystal field effects are a useful tool for the analysis of optical properties of 3d ions in crystals [2,3]. In the present work we analyze the energy level schemes of two isoelectronic ions (V^{2+} and Cr^{3+}) in the 4-fold (ZnS) and 6-fold (MgO) coordination, respectively. The exchange charge model of crystal field [4] was used to diagonalize the crystal field Hamiltonians of both ions for different "impurity ion – ligand" distances. Fig. 1 shows how the 10*Dq* parameter depends on distance in both systems.

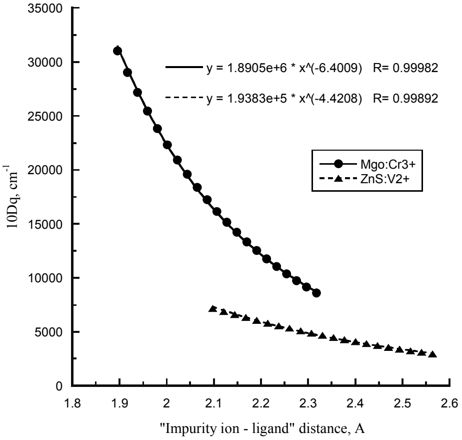

Fig. 1. Dependence of 10*Dq* on distance for MgO:Cr^{3+} (circles) and ZnS:V^{2+} (triangles). Approximating lines and their equations (power laws) are shown in the figure. Note that $10Dq \sim 1/x^{n}$, $n = 6.4009$ for MgO:Cr^{3+} and 4.4208 for ZnS:V^{2+}.

The obtained 10*Dq* dependencies were used to estimate the parameters of the electron-vibrational interaction for Cr^{3+} and V^{2+} ions in these crystals.

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PHOTOLUMINESCENT PROPERTIES OF Zn-Mn-O

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Photoluminescent spectra of polycrystalline Zn-Mn-O samples with nominal manganese concentration x = 0.01, 0.04 and 0.10 thermally treated in air at 400, 500 and 900 °C were investigated. Two emission bands are observed, an emission band in the UV region, and a broad visible emission band. It has been found that the UV emission band consists of free exciton luminescence and two acceptor-related emissions. The energy level of the first acceptor state is located at 140 meV, whereas the position of the second acceptor state is estimated to be 200 – 300 meV above the valence band maximum of the zinc oxide crystal lattice. It appears that the intensities of both the acceptor related- emissions in the samples thermally treated in air at higher temperature (900 °C) are much smaller than those originated from the acceptor transitions in the samples with the same manganese concentration, but thermally treated in air at low temperatures (400, 500 °C). It is known from earlier studies that the Zn-Mn-O samples with x = 0.01 and 0.04 thermally treated in air at low temperatures (400, 500 °C) exhibit room temperature ferromagnetism, and lose their high-temperature ferromagnetic properties when they are thermally treated at 900 °C.

OPTICAL SPECTRA OF FLUX GROWN Cr-DOPED SILICATE CRYSTALS

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Single crystals of Cr-doped Zn_2SiO_4 (willemite), Mg_2SiO_4 (forsterite) and $LiScSiO_4$ (forsterite) have been grown by the flux growth method. Their optical spectra have been measured at different temperatures, evidencing that the chromium dopant is present as Cr^{4+} in the willemite and as both Cr^{3+} and Cr^{4+} in the forsterite crystals, consistently with the structural properties of the host matrices. The electronic structure of Cr^{4+} replacing Si^{4+} in these lattices has been discussed in the framework of the exchange charge model. The crystal field parameters have been evaluated using the structural data as the only input information, and the correspondence between the calculated and the experimental energy levels deduced from the 10 K absorption spectra has been verified. These results have then been applied to the analysis of the luminescence properties of the investigated compounds. As an example of our analysis, we show in Fig. 1 the polarized experimental absorption spectrum of Cr-doped forsterite. The calculated energy levels of Cr^{4+} are shown by the vertical lines at the top. The Cr^{3+} absorption bands at about 650 and 450 nm also contribute to the total absorption.

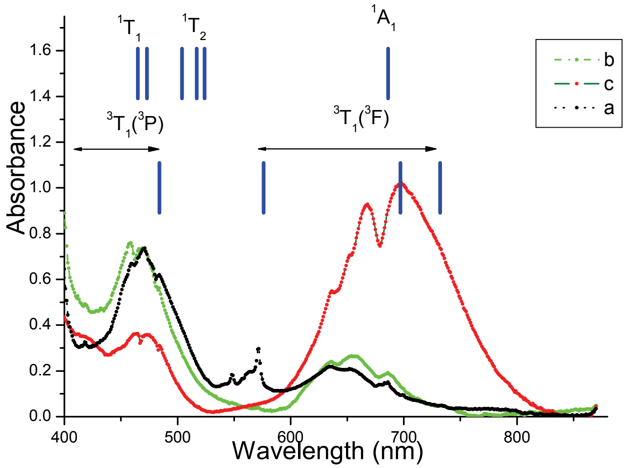

Fig. 1. Absorption spectrum of Mg_2SiO_4:Cr.

SPECTROSCOPIC STUDIES OF 38PbO-62SiO$_2$:Nd^{3+} GLASS

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Glasses activated with trivalent lanthanide ions emitting in the near infrared have been of interest for a long time due to their potentialities as materials for high power lasers and optical amplifiers for telecommunications. The application of these glasses requires the evaluation of spectroscopic properties, such as the Judd-Ofelt intensity parameters, luminescence branching ratios and radiative lifetimes of the excited states. Among the oxide hosts, lead silicate glasses have received great attention in the past due to their good chemical and physical properties. The optical spectroscopy and excited state dynamics of trivalent lanthanide ions in these materials, in particular with the molar composition 38PbO-62SiO$_2$, has been reported for several doping ions, such as Eu^{3+}, Tb^{3+}, Tm^{3+}, Ho^{3+} and Er^{3+} [1-4]. We have found it interesting to extend these investigations to the Nd^{3+} ion, which is considered as the most important dopant for laser applications.

In this work we report on the optical spectroscopy of a 38PbO-62SiO$_2$ glass doped with Nd^{3+}. From the analysis of the RT absorption spectrum, the Judd-Ofelt intensity parameters have been evaluated and used to calculate the radiative lifetime of the $^4F_{3/2}$ excited level. These quantities are used in the analysis of the luminescence spectrum and decay curves. The values of the intensity parameters are compared to the ones relative to other oxide hosts doped with Nd^{3+}, in particular containing lead as a major component of the glass.

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LiF SINGLE CRYSTAL FOR YAG:Nd LASER Q-SWITCH

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The LiF single crystals with small diameters are interesting because of their optical properties. In our previous works our target was to obtain crystal with length at least 50 mm and 8 mm diameter with good optical transmission in vis-nir domain.

For Q- switch applications [1], LiF crystals must have a structure without any kind of defects as other authors report [2]. We can not obtain controlled color centers with gamma or electron irradiation inside the crystal when starting crystal has imperfect structure due to improper growth conditions [3].

All experiments were performed using the growth installation which has an original design. The component parts of installation represent practically, individual systems for: automatically temperature control, vacuum control and speed of crucible control. Optical grade polycrystalline LiF used as raw material for single crystal growth was obtained by chemical synthesis, followed by vacuum distillation.

Using experimental data we can establish optimal working conditions for obtaining LiF single crystal taking into account simple or multiple regression analysis function of number and type of variables.

The paper deals with the analysis of LiF single crystals growth conditions in order to establish the main parameters which are involved in the crystal quality (Fig.1).Taking into account experimental data, correlations between growing conditions and the single crystals quality used as active media or Q-switches were made. The dependence of crystals length, fixed as driving property function of growth process independent variables was achieved.

Figure 1 LiF single crystal

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Fe- AND Co-DOPED SnO_2 THIN FILMS PREPARED BY ELECTRON BEAM EVAPORATION

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Tin oxide (SnO_2) compounds with metal-like conductivity, excellent optical transparency and high chemical stability, have been recognized as very promising materials with large technological applicabilities [1]. In this work we have investigated the structural, optical and electrical aspects of Fe- and Co-doped SnO_2 thin films deposited onto glass substrates using the electron beam evaporation technique. The produced samples were transparent, amorphous and highly resistive. The investigation of structural properties was carried out by X-ray diffraction pattern. After annealing, the films tend to become polycrystalline and conductive. In addition to structural transformation, the presence of oxygen vacancies effectively decreases the resistance [2]. Furthermore, as can be seen from figure 1, the optical transparency and band gap of the samples increases after annealing and formation of crystallites.

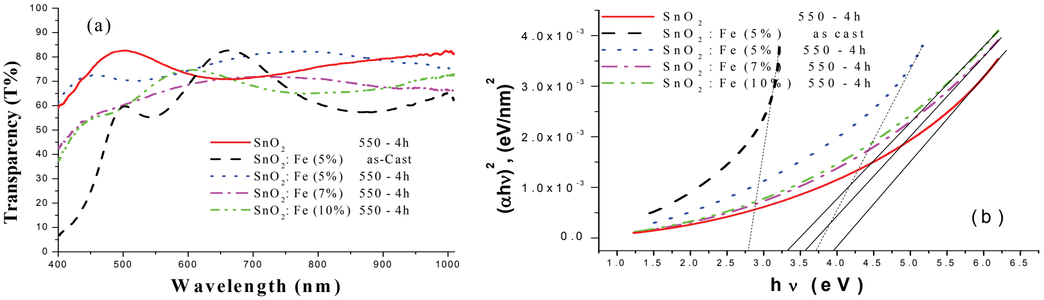

Fig. 1: (a) Optical transparency of various Fe-doped SnO2 films annealed at 550° C for 4 hours. (b) Plots of (αhν)2 versus hν (photon energy) for undoped and Fe-doped SnO_2 films. The cross-points of the lines with photon energy (hν) axis show the value of the optical band gap.

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CHANGES OF PROPERTIES OF CURED AND UNCURED DISILOXANE BISBENZOCYCLOBUTENE THIN FILMS UNDER IRRADIATION

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Due to the unique combination of properties induced by stable aromatic, and reactive, strained cyclobutene rings, the low dielectric constant BCB based dielectric polymers have found numerous applications in micro and optoelectronics, as interlayer dielectric materials, wafer-level adhesive bonding materials, gate materials for organic field effect transistors, and as the materials for biosensors components. Low optical losses, high transparency, up to 1.7 μm, and refractive index (n=1.549 at λ=838 nm) qualify them as suitable dielectric materials for optical applications in integrated circuits. The main challenge for the large-scale commercial applications of BCB polymers is to perform their curing rapidly and efficiently at low temperatures, and in the same time, to obtain large area, high quality, pinhole free dielectric thin films. For that purpose we investigated numerous uncured and cured BCB films, approximately 2 μm thick, spin-coated on glass/ITO surface, using optical and AFM microscopy, infrared (IR) and Raman spectroscopy and changes of their properties under α-particles and photons irradiation. We relate the microscopic molecular changes induced by irradiation to modifications of macroscopic properties of the cured and uncured BCB polymer films, which could be important, both for the process of curing, and some of their practical applications.

CZOCHRALSKI GROWTH OF β-$Na_xV_2O_5$ SINGLE CRYSTALS

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Recently a new technique for formation nanostructures from separate atoms with the use of a needle–probe made from a bronze oxide single crystal has been offered. The structural peculiarities of oxide vanadium bronze allow to emit interstitial atoms from channels of V-O skeleton on a substrate or, on the contrary, to remove atoms from a substrate and introduce them into the structural channels of the needle- probe. On the other hand tunnel microscopy allows to control such adsorption-desorption processes. Different configurations of nanosize surface layers can be created by variations of such conditions as probe chemical composition, scanning parameters, temperature and type of substrate. Here we present the growth of β-$Na_xV_2O_5$ single crystals by Czochralski method. The peculiarities of growth processes are considered. Single crystals were grown in the air from platinum crucible using r.f. heating. Charge of $Na_{0.28}V_2O_5$ was prepared from vanadium pentaoxide and sodium carbonate in molar ratio (1.0:0.14). The melting process is characterized by strong oxygen absorption from chamber atmosphere. The melting point depends on oxidation velocity. In our growth conditions melting temperature of $Na_{0.28}V_2O_5$ was measured as 674±5°C on melt surface and under melt surface of 1.0 cm being 728±5°C. A seed was grown by spontaneous crystallization method and oriented along the “b” monoclinic axis. For Czochralski method pulling rate was 1-2 mm/h and rotation rate - 7.0 rpm, vertical thermal gradient - 120°C/cm. In typical growth process polycrystalline boule was formed as a result of the presence of numerous cleavage planes containing “b” axis. It was estimated that melt crystallization initiates quick oxygen evaporation and, consequently, strong increasing of volume of crystalline bronze in crucible. The supercooling degree depends on content of interstitial metal. At temperature decreasing rate of 2.5°C/min the supercooling value was measured as 90°C for $Na_{0.28}V_2O_5$. The special growth conditions to obtain monocrystalline needles of sodium vanadium oxide bronze are developed. Some examples of nanostructures formation using $Na_{0.33}V_2O_5$ probe in scanning tunnel microscope will be presented.

STUDIES ON Al DOPPED ZnO FILMS SPUTTERED AT VERY LOW PRESSURE FOR PHOTOVOLTAIC APPLICATION

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Al_2O_3-dopped ZnO films (AZO) have been widely studied for a substitution of ITO films in thin film solar cell system. AZO films sputtered at elevated temperature have better properties than the films sputtered at lower temperature. This means sufficient energy should be supplied during growth of the films. Therefore AZO films would be affected by the kinetic energy of incident particles. In this study the kinetic energy of the particle was controlled by varying sputtering pressure. Mean free path of the sputtered particles increases with decreasing sputtering pressure so that the sputtered particle with sufficient kinetic energy can arrive at the growing surface of the films when a sputtering pressure is lower than 1 mtorr. However, most studies on AZO films were perfomed at relatively high pressure [1,2]. 150 nm AZO films were fabricated from a 2 inch diameter target on glass substrate at room temperature with an rf magnetron source. Resistivity and transmittance of the films were measured with four point probe and spectrophotometer, respectively.

With decreasing sputter pressure, film growth rate increased. However, at very low sputter pressure the rate decreased because of very low concentration of Ar ions (Fig.1). Fig. 2 shows variation of XRD patterns of AZO films with different sputter pressure. Intensity of (002) peak were high in films sputtered at low sputter pressure. The resistivity of the films sputtered at lower pressure was lower than that of the films sputtered at higher pressure. More detailed properties and discussion will be presented.

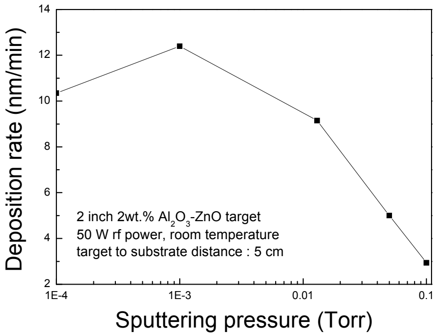

Fig. 1 Variation of AZO film depostion rate with pressure.

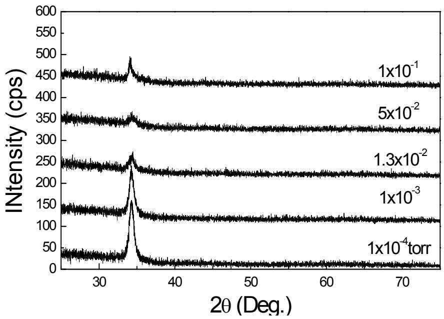

Fig. 2 Variation of XRD patterns of AZO films.

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X-CHROMIC MATERIALS WITH POTENTIAL APPLICATIONS AS FRIENDLY INDICATORS FOR TEMPERATURE, PRESSURE AND UV DOSE

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X-chromic materials are compounds which color changes under an external stimulus. Namely, thermo-chromism, tribo-chromism and photo-chromism refer to the ability of a material to undergo a color change with respect to the temperature, the application of a pressure, and the light illumination, respectively. Nowadays, this kind of materials receives much attention due to their potential applications as user friendly temperature, pressure and UV indicators. In this framework, we will report first on the unprecedented "one finger push" induced phase transition of $CuMo_{0.9}W_{0.1}O_4$ which goes along with a drastic color change of the material, the pristine color being recovered by heating at about 100°C. [1-3] Second, we will discuss the exceptional photo-chromic properties of some organic-polyoxomolybdate hybrid materials and examine the involved mechanism at the light of diffuse reflectance measurements and ab-initio calculations. [4-6]

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SYNTHESYS AND CHARACTERIZATION OF BISMUTH SULPHIDE NANOSTRUCTURES IN W/O MICROEMULSIONS

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Two different morphologies of bismuth sulphide (Bi_2S_3) nanocrystals including faceted nanoparticles and nanorods were prepared in W/O microemulsions by using cyclohexane /Triton X–100/n-pentanol/water as a reaction system. The difference in morphology was achieved by adjusting reactant concentrations. The faceted nanoparticles of Bi_2S_3 with an average edge dimension of about 25 nm were synthesized for the first time, while a nanorods had diameter in between 5 and 20 nm and length from 150 to 400 nm. X-ray diffraction analysis revealed that obtained samples have pure orthorhombic phase of bismuth sulphide with Pnma space group ($a = 11.2983$ Å, $b = 3.9854$ Å and $c = 11.1447$ Å). Base on optical measurements of both samples, band gap value was estimated to be 1.5 eV indicating quantum confinements due to reduced dimensionality.

DYNAMICAL ANDERSON LOCALIZATION OF COUNTERPROPAGATING BEAMS IN OPTICALY INDUCED PHOTONIC LATTICES

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In a numerical study, we report the first observation of transverse Anderson localization of mutually incoherent counterpropagating beams in optically induced disordered two-dimensional photonic lattices, recorded in a photorefractive crystal. We consider a system of two counterpropagating broad probe beams propagating through the fixed photonic lattice. We demonstrate Anderson localization of the probe beams, by adding random disorder to the lattice. Changing the disorder we observe the localization effect on the probe beams.

STRUCTURAL CHARACTERIZATION OF ULTRA-THIN P(VDF-TrFE) FILMS

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For many decades, intensive studies have been made on the fabrication of nonlinear optical (NLO) polymer materials which exhibit large E/O coefficient and long term stability. Currently, the most widely used fabrication technique for E/O materials is solvent casting and spin coating method. However, because of the spontaneous relaxation behavior of aligned dipoles, the performance using this technique is not high enough to satisfy the industrial requirement.

Recently, the Langmuir-Blodgett (LB) method was successfully applied for the fabrication of highly ordered non-centrosymmetric films for the optical applications. Our previous study [1] also demonstrated that the LB films based on P(VDF-TrFE) copolymer exhibit gigantic E/O coefficient and excellent long term stability.

In order to understand the origin of NLO performance, in this work, we focused our attention on the characterization of non-centrosymmetric crystal structure of the P(VDF-TrFE) films.

The meta-stable nature (Fig.1) of the Langmuir film was discussed in terms of the remanent ratio of the molecules on the water surface. The rigidity of the Langmuir film was also studied with the surface morphology observed by Brewster angle microscope.

LB films were made by subsequently transferring the Langmuir layers onto a solid substrate. With the help of excellent nanometer scale resolution of AFM, the structures and structure changes of LB films were successfully investigated.

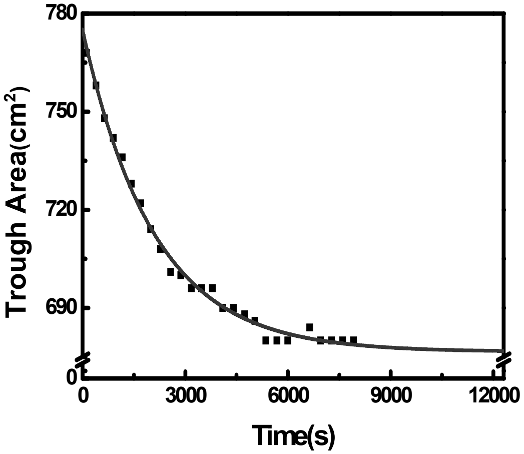

Fig1. Time dependence of the remanent polymer molecules on the water surface

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NONLINEAR OPTICAL PROPERTIES OF P(VDF-TrFE) COPOLYMER FILMS.

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Second order nonlinear optic properties(NLO) of copolymer of vinylidene fluoride with trifluoroethylene P(VDF-TrFE) in the forms of spun-cast and Langmuir-Blodgett (LB) films were studied by optical second harmonic generation(SHG). Since the SHG intensity is proportional to the square of nonlinear quadratic polarization, SHG method can be used as a specific tool for probing the crystal structure of the films.

For both films, second order NLO coefficients were measured by using Maker fringe method. Typical patterns of both samples are shown in Fig.1.and Fig.2. Theoretical fit in Fig.1. could be obtained from $d_{33}=5.263\times10^{-9}$esu and $d_{31}=1.766\times10^{-9}$esu for the spun film, and best fit in Fig.2 could be obtained from $d_{33}= 4.283\times10^{-7}$esu and $d_{31}=1.448\times10^{-7}$ esu for the LB film.

The NLO properties are analyzed in terms of polymer composition and applied poling voltage. Formation of **β** phase for both samples were clearly confirmed from XRD peak of 2θ=19.7°.

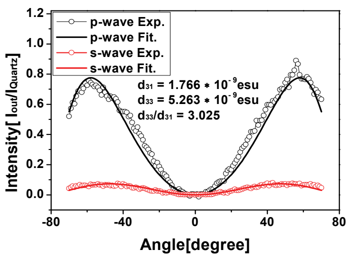

Fig.1 Typical Maker fringe patterns of the spun-poled film poled at 10 kV/cm

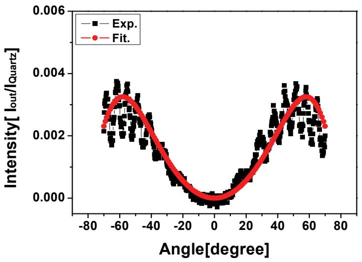

Fig.2 Typical Maker fringe patterns of LB films

NEW CADMIUM AND RARE-EARTH METAL MOLYBDATES WITH SCHEELITE TYPE STRUCTURE

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The development of new solid-state lasers requires crystals with very high stability of emission, high efficiency, long lifetime and low excitation threshold. Double molybdates and tungstates containing rare-earth ions are known as promising host materials for laser applications. The diode pumped solid-state lasers based on these compounds demonstrate the emission of nanosecond and sub-nanosecond pulses with high peak power. These lasers are used for optical and undersea communications, medical and eye-safe detecting, scientific researches and military.

It was reported that cadmium tungstate ($CdWO_4$, the wolframite type structure) reacted with rare-earth metal tungstates ($RE_2(WO_4)_3$ where RE=Pr-Ho) to give two families of double tungstates with the following formulas: $Cd_2RE_2(WO_4)_5$ and $CdRE_2(WO_4)_4$ [1-3]. The compounds of the first group crystallize in the scheelite type structure, while the second group in the monoclinic system, in a structure very similar to the scheelite type structure [1-3].

In the present work, new cadmium and rare-earth metal molybdates with the formula $CdRE_2(MoO_4)_4$ where RE=Pr-Ho have been prepared by the high-temperature solid-state reaction according to the following equation:

$$CdMoO_{4(s)} + RE_2(MoO_4)_{3(s)} = CdRE_2(MoO_4)_{4(s)}$$

The obtained compounds crystallize in the scheelite type structure. It was ascertained that at the concentration range above 50.00 mol % of $CdMoO_4$ in initial $CdMoO_4/RE_2(MoO_4)_3$ mixtures new cadmium and rare-earth molybdates with $CdMoO_4$ form substitutional solid solutions with the scheelite type structure. The $CdRE_2(MoO_4)_4$ melt at the temperature range of 900°-1100°C. The melting point of these compounds increases from Pr to Ho. IR spectra of cadmium and rare-earth metal molybdates confirm presence of isolated MoO_4 tetrahedra in their structure.

EPR method has been used to identify paramagnetic centers in $CdRE_2(MoO_4)_4$ (RE=Nd, Sm, Gd and Dy), their local crystal environment and magnetic interactions. The resonance EPR line observed for all the samples could be ascribed to Re^{3+} complex magnetic centers, i.e. clusters or low dimensional chains with antiferromagnetic type of interactions. E.g., for $CdGd_2(MoO_4)_4$ compound we have identified more than one type of gadolinium centers, including the isolated Gd^{3+} ions.

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ELECTRICAL AND OPTICAL PROPERTIES OF THIN FILMS OF DNA: PEDOT

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Nucleic acids and their derivatives are known because of their important biological role. At the same time DNA, which exhibits a charge migration, is a subject of interest for its physical properties, and particularly for a great potential of application in photonics and in molecular electronics. However, pure DNA is electrically passive material. In order to render it active one has to functionalize it with PEDOT molecules.
We report investigations of DNA-PEDOT thin films. After sonication of DNA in deionized water, DNA solution was added to PEDOT (PEDT/PSS) aqueous solution with different ratios 1:0.2 and 1:0.5 of DNA:PEDOT. The solutions of polymers were spin-coated on the ITO glass substrates. The thickness of the obtained films was 0.3-1.5 μm. The semi-transparent aluminum contacts were evaporated on the top. The films were characterized by the UV and visible spectroscopy. Their conductivity temperature dependencies were measured from 77 K up to 300 K depending on the light excitation. Sample conductivity at room temperature was in average about $(1\text{-}5)\times10^{-10}\ \Omega^{-1}\text{cm}^{-1}$, though it could deviate by up to two orders of magnitude even in the samples produced on the same glass substrate indicating sensitivity of their properties to the technological conditions. IV curves were linear and symmetrical down to LN temperature. The thermal activation energy of the dark conduction near the room temperature was about 0.033 eV, and it did not depend on the applied bias.
We did not identify any carrier trapping by the Thermally Stimulated Current method, what proves the fast recombination of light-generated carriers. Though, by constant light excitation a “bistable” photoconduction below the room temperature was evidenced. I.e., upon excitation by light from the spectral region ~ 500-800 nm a notable increase of the photocurrent could be observed below 140-160 K by cooling the samples. Meanwhile by heating the photosensitivity remained increased up to 230-240 K. Most probably such phenomenon could be attributed to the light-induced morphology changes of the samples.

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STUDYING THE DIFFRACTION EFFICIENCY VARIATIONS OF HOLOGRAPHIC GRATINGS DUE TO SUCCESSIVE WRITE-ERASE PROCESSES IN AZO-DYE-DOPED POLYMER FILMS.

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Interference pattern of two pump beams on the surface of a sample of azo-dye-doped polymer film led to formation of a transient grating. An incident probe beam was diffracted and the intensity of the first order diffracted beam was measured for the sake of obtaining the diffraction efficiency of the grating. By turning one the pump beams off the grating was disappeared. Diffraction efficiency variations of the inscribed grating due to successive write-erase processes are studied. It is shown that time intervals for writing and erasing the grating were varying during the successive write-erase processes.

FABRICATION OF LOW-TEMPERATURE PASSIVATION OF Si WITH Al_2O_3 FILMS AND ITS APPLICATION TO MIS SOLAR CELLS

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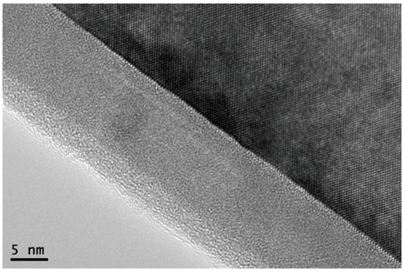
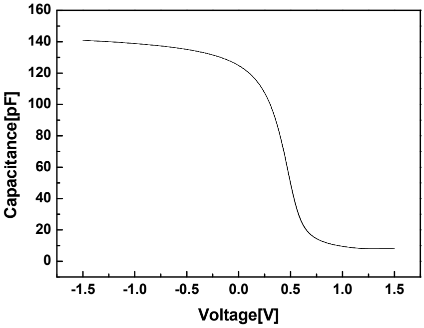
Low-temperature deposited aluminium oxide thin films were investigated at the silicon surface for MIS-IL solar cell applications. Aluminium oxides were deposited on Si substrate by remote plasma atomic layer deposition (RPALD) technique using alternative trimethylaluminum (TMA) precursor and oxygen plasmas in a temperature below 300 ℃.

In order to investigate the chemical state and structure of the deposited films, X-ray photoelectron spectroscopy (XPS) and high-resolution TEM (HR-TEM) were used.
Si MIS capacitors with ultra-thin Al_2O_3 (film thickness ranges from 1 nm to 12 nm) gate dielectric were fabricated in the ALD window temperature ranges and characterized the electrical properties such as capacitance-voltage (C-V), current-voltage (I-V). Interface trap density (D_{it}) was estimated using high frequency C-V and conductance method. The interface state density at around midgap was less than 5×10^{10} /$cm^2\cdot eV$.
In order to determine the bulk lifetime of silicon wafers, the microwave-detected photoconductance decay (MW-PCD) measurement system was used. The lifetime of the passivated Si increased twofold or more compared to the unpassivated sample.
The discussion about the other properties with aluminium oxide films on Si and the properties of the fabricated MIS-IL solar cells with passivated film thickness of 1 ~ 1.5 nm will be presented at the conference.





<HR-TEM image of Al_2O_3/Si interface>   <C-V curve of the Al_2O_3/Si MIS capacitor>

OPTICAL STUDY OF NANOCOMPOSITES BASED ON CHALCOGENIDE IMPREGNATED WITH ORGANIC DYE

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In recent years, organic-nonorganic nanocomposites have attracted considerable attention due to their enormous potential applications. There is a growing interest in incorporation of organic dyes within inorganic matrices, mainly for applications as nonlinear optical materials, in memory and recording devices, organic light-emitting devices, etc. Amorphous chalcogenide semiconductors are known as very useful materials for optical recording and switching, holography, because of the changes in physical and chemical properties, which take place in samples after illumination.

The aim of the present work was to investigate the changes in the structure and optical properties of thin films obtained from amorphous arsenic sulphide impregnated with highly luminescent organic dye (benzanthrone derivative). The composite films were prepared from solution of arsenic sulphide, organic luminophore and polymer Disperbyk-161 in diethyltriamine.

In order to evaluate the effect of the presence of the dye and to characterize the optical properties of the films, reflectance, photoluminescence and transmission spectra were measured using different concentration of the dye. The emission spectra of all samples consist of one broad peak centered at 610 nm and cannot vary with changing excitation wavelength. The absorption and emission spectra of the dye in solution, in polymer, and in presence of As_2S_3 are similar. It was found that films with dye concentration of 0.0009% display 5-fold increase of luminescence intensity after the film irradiation with laser.

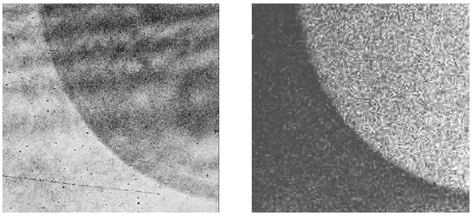

Fig.1. Reflection (left) and emission (right) of exposed (ring) and unexposed area of the films inside and outside of irradiated area of the film (with dye concentration of 0.0009%).

A dramatic decrease in the luminescence intensity has been observed from the composites with 10 times higher concentration of dye due to luminescence quenching during possible formation of nonemissive dimer, trimers, and aggregates.

The obtained luminescent nanocomposites can be promising for the development of multifunctional optoelectronics devices, waveguides, and applications in nanophotonics.

LOCALIZED VIBRATIONS OF SILICON DEFECTS IN QUARTZ

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Silicon vacancies and interstitials are native defects in α-quartz. We have studied local configurations and vibration states of these defects. The vibration states determine many applied properties of silicon dioxide, including optical and luminescence responses.

The shell model was used for simulation of the local atomic structure and the lattice dynamics of the crystalline quartz with silicon vacancies and interstitials. The calculations are performed by using two first-principles short-ranged pairwise potentials of the Buckingham type (Tsuneyuki, Tsukada, Aoki, Matui and van Beest, Kramer, van Santen) and empirical short-ranged pairwise potentials with a three-body harmonic-angle potential (Sanders, Leslie, Catlow). At the present time, interatomic-potential approaches are the efficient choice for probing the atomic structure and the dynamics for large numbers of atoms. The parameters of the potentials of the ion-ion interactions in α-quartz were adopted from the available literature.

A lattice relaxation around silicon vacancies and interstitials was calculated in the harmonic limit on the basis of a molecular static method by minimization of the total energy. The vacancy induces very strong and anisotropic lattice distortion.

The effect of defects on the vibration spectrum of α-SiO_2 crystals was studied by calculating the local densities of vibrational states in perfect and defective crystals taking a cluster of 2000 atoms. The local density of vibrations in independent directions of atoms in the 1st and 2nd coordination spheres was calculated by the recursive technique. The resonance vibration states in ideal and defective crystals were compared. The total density of states in all the directions was calculated separately for the atoms in the cation and anion sublattices.

For the calculation of the diagonal elements of the force constant matrixes of the long-range Coulomb interactions by the Ewald's method a region containing about 4000 atoms was considered.

Predictions for the structure and localized vibrations are discussed. The calculation results performed by using different potentials were compared with each other.

This study was supported by the Russian Foundation for Basic Research, project nos. 08-02-01072-a.

SPECTROSCOPIC INVESTIGATION OF Er-Yb CODOPED MATERIALS FOR 1.6 MICRONS LASER APPLICATIONS

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Solid-state lasers emitting around 1.5 μm are of great interest for optical telecommunications (wavelength corresponding to a minimum of absorption for silica fibres) and telemetry (wavelength around 1.5 μm are said to be eye-safe). The best device until now is based on Er,Yb-codoped phosphate glasses. But their performances are limited due to the poor thermomechanical properties of glasses. An Er,Yb-codoped crystalline host with enhanced properties is the way to improve these 1.5 μm solid-state lasers. Phonon cut-off frequency $h\omega_{max}$ is one the keys to get interesting optical properties when it is between 900 and 1400 cm^{-1}. Our investigations led us to consider two Er,Yb-codoped laser hosts of high thermal conductivity: $GdVO_4$ single crystals, and Er,Yb-codoped Y_2O_3 transparent ceramics. Lifetime of the $^4I_{11/2}$ and $^4I_{13/2}$ levels of Er^{3+} ions were measured to optimize the Er^{3+} and Yb^{3+} ions concentrations, with the attempt to decrease the $^4I_{11/2}$ lifetime and to increase the $^4I_{13/2}$ lifetime. Moreover, detailed optical absorption spectroscopy was carried out to determine the energy level diagrams of Er^{3+} ions and to identify the different environments they experience.

In Er-Yb: $GdVO_4$ single crystals, rare earth ions are expected to occupy only one crystallographic site of D_{2d} symmetry. The high quality of the obtained absorption spectra allowed determining the energy level diagrams of Er. Moreover, for some particular lines, a multisite character for Er environment is clearly detected. Different compositions in Yb (10% and 37.5%) were investigated (keeping 0.75% Er) to confront these observations with the statistical environments which can be drawn from the structure of $GdVO_4$.

Transparent Y_2O_3 ceramics of different compositions in Er and Yb were prepared for further optical fluorescence and laser tests. The energy levels diagrams were determined for Er and Yb and compared to the data published in the literature for equivalent single-crystals or powders. Er ions occupy two different crystallographic sites in the structure (point symmetry C_2 and C_{3i}). The centric C_{3i} site can only be detected for the allowed magnetic dipolar transition from $^4I_{15/2}$ to $^4I_{13/2}$, and this transition was used to estimate if the partitioning of Er^{3+} ions between C_2 and C_{3i} sites remained the same whatever the composition. This characterization will help to understand the differences observed in fluorescence (notably about up-conversion) among all the samples.

OPTICAL PROPERTIES OF LANGASITE FAMILY CRYSTALS AND THEIR CONNECTION WITH GROWTH CONDITIONS

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Langasite ($La_3Ga_5SiO_{14}$, LGS) and its isomorphs – langasite family crystals – are piezoelectric crystals with unique combination of physical properties, particularly for high-temperature application. They possess high piezoelectric coefficient, high electrical resistance and absence of phase transitions up to the melting point (~1500 °C), pyroelectric effect and twinning.
The structure of langasite family crystals is represented by chemical formula $A_3BC_3D_2O_{12}$, point group of symmetry 32, space group P321. Complex structure of langasite crystals allows large substitution of cations in 4 positions. In case of LGS dodecahedral A-sites are occupied by La^{3+}, octahedral B-sites, large tetrahedral C-sites and half of small tetrahedral D-sites are occupied by Ga^{3+}, another half of D-sites is occupied by Si^{4+}. This complex structure makes it possible to obtain crystals with special composition and demanded properties for specific applications. However, their structures may be disordered and may have destructive influence on important physical properties. The presence of structural defects and inhomogeneity of the crystal composition significantly affect the optical properties and may be investigated by optical methods.
Langasite family crystals were grown at Fomos-Materials by the Czochralski method on Crystal-3M systems. Crystal growth atmosphere – Ar, Ar with oxygen or air. We obtained crystals with compositions: $La_3Ga_5SiO_{14}$, $La_3Ga_{5,5}Ta_{0,5}O_{14}$ (langatate, LGT), and LGT crystals doped with Ga and Al.
The optical homogeneity was investigated by Fizeau interferometer on the wave-length 630 nm. This method alloys to observe the heterogeneity of refractive indices and calculate it. We used the method of optical polarization to define the coefficient of gyration and its homogeneity in the different areas of the samples.
Transmission spectra of these crystals were measured between 250 and 3300 nm using UV-VIS-NIR spectrophotometer Cary 5000. We observed absorption bands: in the visible region 3 absorption bands in the wave-rages ~290, ~360, ~480 nm and the near infra-red region ~1845 and ~2915 nm. The presence and intensity of these bands depend on the composition of the crystals and growth atmosphere.

TEMPERATURE DEPENDENCE OF SPECTRAL POSITIONS AND WIDTHS OF $^5D_J \rightarrow {}^7F_J$ FLUORESCENCE LINES ORIGINATING FROM Sm^{2+} IONS IN SrFCl CRYSTAL

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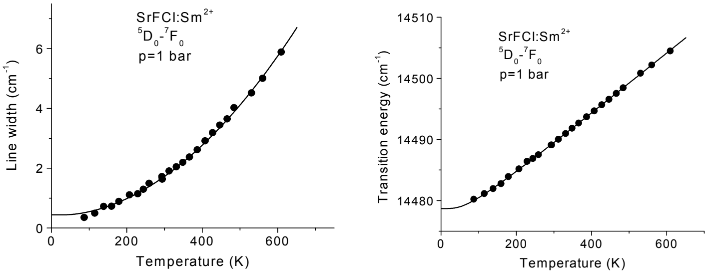
SrFCl crystals doped with Sm^{2+} ions showing bright and sharp emission lines are interesting objects for studying various aspects of the electron-phonon interaction and also a promising material for use as an optical pressure sensor, especially in diamond anvil cells [1].

In this work we have measured the temperature dependence of the spectral positions and widths of the emission lines corresponding to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_1 \rightarrow {}^7F_0$ transitions in Sm^{2+}-doped SrFCl crystal at $T = 87 - 625$ K and $P = 1$ bar.

The increase in the homogeneous width of all three lines studied (for the $^5D_0 \rightarrow {}^7F_0$ line see the left figure) can be described in the whole temperature interval by two-phonon Raman interaction with acoustic phonons in the Debye approximation with practically the same Debye temperature $T_D \approx 230$ K for all the lines.

The temperature-induced shifts of these lines (see the right figure for the $^5D_0 \rightarrow {}^7F_0$ line) can also be qualitatively described in the framework of the same model by Raman phonon scattering, bearing in mind that a part of the line shift is caused by the thermal expansion of a crystal [2].

Moreover, the effect of pressure-induced line narrowing, observed for the above electronic transitions in $SrFCl:Sm^{2+}$ crystal at 300 K [3], has been analysed, using the same theoretical model and in addition taking account of the pressure dependence of T_D.



Temperature dependence of the spectral line width and position for the $^5D_0 \rightarrow {}^7F_0$ transition in $SrFCl:Sm^{2+}$ crystal (points show experimental data and lines represent theoretical curves).

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FIRST-PRINCIPLES STUDY OF THE ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF THE PURE BaY_2F_8

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The fluorides compounds constitute an important class of materials that show peculiar chemical and physical characteristics: low refraction index, low phonon energy and wide-in-wavelength transmission region. These features, together with the spectroscopic characteristics of rare earth and transition metal doping ions when implemented into their matrix, make these crystals particularly appealing for laser and frequency conversion applications [1]. Barium yttrium fluoride, BaY_2F_8 (BYF), crystallizes in a monoclinic crystalline structure with C_{2h}^{3} (C2/m) symmetry group [2]. It is a very attractive material thanks to its low phonon energy ($\hbar\omega \sim 350 - 380\ cm^{-1}$) [3], being widely investigated as an active material for solid-state laser host. Recently, the BaY_2F_8 doped with rare earth ions provoked much of interest due to its promising scintillation properties [ ]. This work has the objective to study theoretically the electronic structure and optical properties of the pure BYF crystal. The self-consistent band-structure calculations were performed by density-functional theory based, full potential linear augmented plane wave (FP-LAPW) method as embodied in WIEN2k computer code. The crystal structure was computationally optimized, i.e. the equilibrium has been achieved in which the forces between the atoms are negligible. The band gap was calculated to be 7.5 eV. The electronic structure calculations revealed that the top of the valence band is dominated by the fluoride *p*-states, while the very bottom of the conduction band has predominantly yttrium *d*-character. The optical response is determined by calculating the complex dielectric tensor. The optical properties of the BYF pure (absorption spectrum, refractive index, extinction coefficient, reflectivity and electron energy loss spectrum) were analyzed in the ultraviolet region (up to incident radiation energy of 40 eV). These properties were interpreted in terms of the calculated electronic structure and results discussed and compared with available experimental data.

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Ab-INITIO STUDY OF STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF THE BTO SILLENITE CRYSTAL

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Dodecabismuth titanium oxide, $Bi_{12}TiO_{20}$ (BTO), has cubic symmetry and belongs to a family of sillenites crystals described by the general formula $Bi_{12}MO_{20}$ (M = Ge, Si, or Ti) [1]. The BTO is one of the most frequently investigated sillenites due to its remarkable optical properties such as high electro-optical coefficients, low optical activity and high photosensitivity in the visible red region [2]. More recently, this material has been considered as a potential photocatalytic for the degradation of organic pollutants [3]. A large number of experimental studies have been carried on about optical properties of the BTO crystal, investigating its optical absorption, reflectivity spectrum, optical activity, etc. There are, however, just a few reported theoretical studies focused on its electronic structure that determines the optical properties in the visible and ultraviolet range. This work has the objective to investigate the structural, electronic and optical properties of the pure BTO crystal. As a computational tool we utilized the full-potential linear augmented plane wave (FP-LAPW) method, one of the most elaborated first-principal methods for electronic structure calculations, based on density functional theory (DFT) and implemented in the WIEN2k computer code. The crystal structure was computationally optimized by total energy minimization. The relaxation of the lattice parameter resulted in $a = 10.332$ Å, corresponding to the 4% larger volume of the unit cell in comparison with the experimental volume determined at ambient temperature [1]. All atomic positions inside this unit cell were also optimized. The band gap was calculated to be 2.5 eV, near to the values of 2.4 eV by Yao *et al.* [3] and 2.8 eV by Marquet *et al.* [4], both estimated from the measured absorption spectra. The electronic structure calculations revealed that the top of the valence band is dominated by the O p- and the Bi s-states while the bottom of the conduction band has predominantly Bi p- and Ti d-character. The previous band structure calculations of Zhou *et al* [5] identified only the Ti d-states at the conduction band bottom. The optical properties of the BTO (absorption spectrum, refractive index, extinction coefficient, reflectivity and electron energy loss spectrum) were determined by calculating the complex dielectric tensor in the ultraviolet region (up to 40 eV). These properties were interpreted in terms of the calculated electronic structure and results discussed and compared with available experimental data.

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RAMAN AND INFRARED SPECTROSCOPY INVESTIGATE OF La AND Sb DOPED $BaTiO_3$

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In this paper, $BaTiO_3$, doped with 0.5 mol% of La and Sb and sintered at different sintering times was investigated. Doped barium titanate nanopowder was prepared by doping pure barium titanate starting from citrate solutions of all components: barium, titanium, lanthanum and antimony. Obtained powders were pressed in to pellets and sintered at 1300 °C for 2 and 16 h in air atmosphere. The formation of phase and crystal structure of $BaTiO_3$ was carried out by XRD analysis and Raman and IR spectroscopy. Microstructural properties such as grain size distribution and morphology of sintered samples were determined using scanning electron microscope. Therefore it was analyzed relation between grain size, structure and properties of obtained ceramics. Influence of La and Sb doping on barium titanate properties was discussed.

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EFFECT OF TEMPERATURE ON OPTICAL SPECTRA AND EXCITED STATE RELAXATION DYNAMICS OF Er^{3+} IN YVO_4

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Laser operation of a diode-pumped Er:YVO_4 crystal has been reported for the first time in the recent paper [1]. For this preliminary study a microchip laser system consisting of YVO_4 crystal containing 0.5at% of Er^{3+} with dielectric mirrors deposited directly on the crystal faces was prepared. It has been observed that at low power of pumping radiation at 975 nm the output of the microchip laser consisted of a single line at 1593.7 nm. With increasing pump power a second line at 1604.1 nm appeared ant its intensity increased with the expense of the shorter wavelength line. Optical pumping generates appreciable quantity of heat in a laser active medium resulting in temperature rise in the pumped region and mechanical stress induced by thermal gradients. It has been shown recently [2] that the temperature at the pumped facet of Nd:YVO_4 increased to 585.8K at pump power of 25W. Thermal effects in Er:YVO_4 are expected to be even stronger since the quantum defect of 0.39 for Er:YVO_4 is remarkably higher than 0.24 for Nd:YVO_4.

To examine the effect of temperature on spectroscopic features of Er:YVO_4 the optical absorption spectra related to the transitions from the ground $^4I_{15/2}$ level to the $^4I_{13/2,}$ $^4I_{11/2}$ and $^4I_{9/2}$ levels were recorded at temperatures ranging from 300K to 500K. Emission spectra and decay curves of luminescence related to transitions originating in the $^4I_{13/2}$, $^4I_{11/2}$ and $^4S_{3/2}$ levels were recorded at temperatures between 300K and 650K It has been observed that the evolution of optical spectra are consistent with combined effect of temperature dependent occupation of the crystal field levels of multiplets involved and temperature broadening of transitions. Influence of temperature on absorption coefficient at 975 nm is found to be negligible. The structure of the $^4I_{13/2}$ - $^4I_{15/2}$ emission band tends to disappear with increasing temperature especially at long wavelength wing. Spectral features of the laser emission reported are discussed based on energy level structure for Er:YVO_4 reported in [3]. Analysis of luminescence decay curves indicates that with the growing temperature the contribution of nonradiative decay to the relaxation of excited levels increases thereby enhancing the heat generation. This is especially significant for the $^4I_{11/2}$ pump level whose lifetime reduces by a factor of two roughly when the sample temperature rises from 300K to 650K.

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THULIUM DOPED SILICON LIGHT EMITTING DIODES

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Dislocation engineered silicon light emitting diodes, operating over the 1.2-1.35 μm range, have been fabricated. This was achieved by thulium implantation, incorporated in the trivalent Tm^{3+} state, into standard dislocation engineered silicon light emitting devices. Seven sharp lines were observed at 1211.5, 1231.0, 1250.8, 1269.3, 1288.8, 1311.3 and 1326.0 nm, corresponding to known internal Tm^{3+} transitions in the manifold from the $^3H_5$ to the $^3H_6$ ground states. The devices operated under forward bias, with a turn-on voltage of less than 1 V. Photoluminescence and electroluminescence measurements were used to characterize the materials and devices. The results showed that the luminescence is strong dependent on the sample fabrication processes. In this paper we will discuss the influence of Tm implantation and post-implant annealing conditions on the luminescence of Tm doped dislocation engineered silicon light emitting devices.

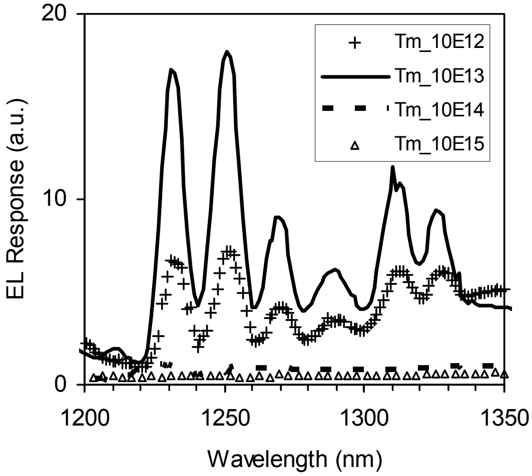

Figure 1: Electroluminescence response, measured at 80 K, for devices implanted at different Tm doses and annealed at 850 °C for 15 minutes.

SHIFT AND BROADENING OF SAPPHIRE SURFACE POLARITON BY QUASICRYSTALLINE FILM

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Quasicrystalline films is the new interesting materials for their practical application, specifically there was an attempt to use a quasicrystal as one of the layers of a multilayer coating for selective absorbers of solar radiation. Optical properties of quasicrystalline Al-Pd-Re films have just been studied in the infrared region using external reflection spectroscopy [1]. Now we have combined this technique with more sensitive one - surface polariton spectroscopy [2, 3].

Surface polariton (SP) is the non-radiative interface electromagnetic mode, propagating along the interface between 2 media, if one of them is absorbing (metal, semiconductor or dielectric with the strong absorption bands) and exponentially decaying out of the interface. The introduction of a transition layer at this interface results in the shift and broadening of SP. This effect can be used to obtain film parameters (thickness and optical constants) in the region of SP existence.

Quasicrystalline Al-Pd-Re films have been deposited on sapphire substrates using layer-by-layer ion-plasma sputtering with subsequent vacuum annealing. The attenuated total reflection (ATR) measurements in Otto configuration [2] and the measurements of external reflectivity have been done using IFS66v (BRUKER) infrared Fourier-transform spectrometer. The main attention was paid on the high frequency "reststrahlen region" of sapphire (600-900cm^{-1}). In this region the sapphire SP in the presence of the film is shifting down (due to the real part of the film dielectric function) and broadening (due to the film conductivity). The broadening is stronger if some metallic phase (increasing conductivity) is present in the film. These effects allow estimate film complex dielectric function in the region under consideration.

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HIGH-RESOLUTION SPECTROSCOPY OF $LiLuF_4:Pr^{3+}$ CRYSTALS

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$LiYF_4$ or $LiLuF_4$ scheelite type single crystals doped with rare-earth (RE) ions are well-known optical materials for laser applications and fundamental research. At present, a revived interest to these materials is connected with quantum information processing and storage [1]. As a rule, such applications involve optical transitions between hyperfine sublevels of the crystal-field (CF) energy levels of RE ion. Therefore, an accurate scheme of the CF levels and information on the hyperfine structure are of great interest. It is also useful to make a detailed investigation of interactions the RE ion is subjected to in a crystal.

In this paper, we present the results of high-resolution study of $LiLuF_4:Pr^{3+}$ crystals. Weakly doped $LiLuF_4:Pr^{3+}$ single crystals were investigated. The praseodymium concentration was 0.1 or 1%. High-resolution (up to 0.005 cm^{-1}) polarized absorption spectra were registered in the wide temperature range (4.3-300 K) for the $^3H_4 \rightarrow ^3H_{5,6}$, $^3F_{2,3,4}$, $^1G_4$, $^1D_2$, $^3P_{0,1,2}$ and $^1I_6$ optical transitions of the Pr^{3+} ion.

As a result of our investigation, crystal field levels of Pr^{3+} in $LiLuF_4$ were obtained. Experimental data on isotopic effects, hyperfine and interionic interactions in the crystals are discussed. A comparison of these results with our previous data [2-3] on Ho^{3+} and Tm^{3+} in $LiYF_4$ and $LiLuF_4$ is given.

This study was supported by the Russian Academy of Sciences (project 8.1 of the Program “Quantum macrophysics”) and by the RFBR (grant № 09-02-01067).

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MICRO-RAMAN CHARACTERIZATION OF Zn-DIFFUSED $LiNbO_3$ CHANNEL WAVEGUIDES

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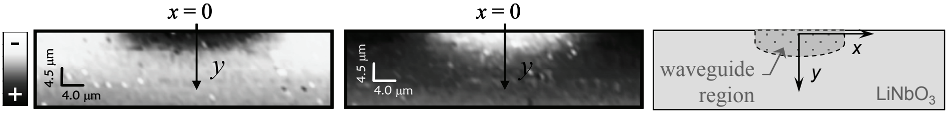
Nowadays, there is a great interest in the design of locally modified materials to create channel waveguides to be used in integrated optical devices, such as lasers or amplifiers. For that purpose, $LiNbO_3$ is a widely studied material, especially attractive due to its electro-optic, acousto-optic and non-linear properties [1]. There are several techniques developed to fabricate low-loss waveguides in the material. Unfortunately, the complete characterization of the obtained waveguides can not be easily achieved. Particularly, how the properties of $LiNbO_3$ are altered by the introduction of the refractive index modifier element is still a subject of great efforts.

In that sense, confocal microscopy has emerged as an adequate tool to perform the characterization of channel waveguides since it allows obtaining direct measurements of the luminescence and Raman modes produced in small regions of the material [2].

In this work, micro-Raman measurements have been carried out in $LiNbO_3{:}Tm^{3+}$ with channel waveguides fabricated by Zn^{2+} in-diffusion. By means of that technique, maps of the properties (half-width and relative position) of several Raman modes on the edge of the waveguide have been performed. In Fig. 1 it can be seen, as an example, the maps obtained for $A_1(TO_4)$ mode. The position described as $x = 0$ is the middle of the waveguide on the surface of the sample, and the arrow (y-axis) points to the inner region of the sample. Through the analysis of the changes in energy peak position and half-width of the Raman modes, it is possible to extract precise information of the modifications created in the material by the introduction of Zn^{2+} ions.



Half-width (cm^{-1})　Mode Position (cm^{-1})　Detail of the sample

Figure 1. Half.width and mode relative position measured on the edge of the sample.

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SPECTRAL AND LUMINESCENCE PROPERTIES OF Pr^{3+}, Er^{3+} AND Eu^{3+} IONS IN OXYFLUORIDE GLASS CERAMICS CONTAINING LaF_3 NANOCRYSTALS

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Transparent oxyfluoride glasses and glass ceramics containing LaF_3 nanocrystals are a subject of insensitive research for last few years because of their promising advantages – combining the attractive optical properties: highly efficient fluorescence of fluoride crystals with high durability and easiness of fabrication of oxide glasses. These properties address a wide area of applications like optical fibers, amplifiers and solid-state lasers [1].

In this work we present the results of research on the changes in luminescence properties of Pr^{3+} (^3P_J and $^1D_2$ states), Er^{3+} ($^4S_{3/2}$ state) and Eu^{3+} ($^5D_3$ – $^5D_0$ states) ions due to thermal treatment oxyfluoride borosilicate SiO_2-B_2O_3-Na_2O-LaF_3 glass at 600 – 640 ˚C and production glass ceramics. The annealing process of based glass leading to the LaF_3 crystalline phase formation [2], influenced on the spectroscopy properties of the rare earth ions mentioned above. The detailed analysis of luminescence spectra and the result of measurements with application of time resolved spectroscopy allowed as to combine the observed changes in intensity of luminescence and also the live time of the regarding state with appearing low-phonon crystalline phase of LaF_3 as a result of heat-treatments. The comparison of the calculated fraction of the studied ions in the LaF_3 crystallites points dramatically to strong vary ability of the incorporation with rare earth ion used [3]. We have considered the possibility of influence on this issue by changing the composition of the base glass.

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COPRECIPITATION STUDY OF GOLD AND HYDROXYAPATITE NANOPARTICLES

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Remarkable efforts are assisting the development of new bio-functional materials aiming at the fabrication of immunosensor and biosensor devices for applications in biology, electronics and electro-chemistry [1]. Metal nanoparticles such gold, silver or iron nanoparticles can be used as functional materials but do not have biological properties. The combination of the metal with a bioactive and biocompatible material may be a useful strategy for enabling bio-applications. Hydroxyapatite (Hap- $Ca_5(PO_4)_3(OH)$) can be the selected biomaterial because of its chemical similarity to the bone mineral component. Moreover it can be synthesized by different methods depending of the final application.

In the present work an hydrothermal synthesis method was used to precipitate Hap and gold. Solutions containing adequate amounts of calcium and phosphate ions at pH=8.12 were added with different concentrations of gold ion and autoclaved at 180ºC for 24 hours. After that period the obtained red colored precipitated particles were fully characterized. The particles X-ray diffraction patterns revealed the presence of metallic gold and Hap as crystalline phases. Transmission and scanning electron microscopy were used to access the particle morphology: plate-shaped or assembled nanorods Hap particles were observed, depending on the used gold concentration; gold rounded shaped particles were also detected, with average sizes ranging from 0.3 µm down to 50nm (see the dark spots on the bottom figure of the right). The UV-vis spectra of the particles display differently shaped absorption bands depending on the gold concentration. Nevertheless an absorption band at ~520 nm, which is normally attributed to the plasmon resonance effect of nanometric gold particles, is always observed. It is also remarked that the shapes of Hap precipitated particles are different from those obtained from equivalent calcium phosphate precursor solutions free of the gold ion (Au^{4+}). It is thereby concluded that the presence of gold ion and/or its corresponding reduction reaction to metallic gold plays an effective role on the growth mechanism of Hap particles. The obtained results are thus comparatively discussed with literature data attempting to clarify the effects of gold precipitation on the characteristics of the coprecipitated Hap particles.

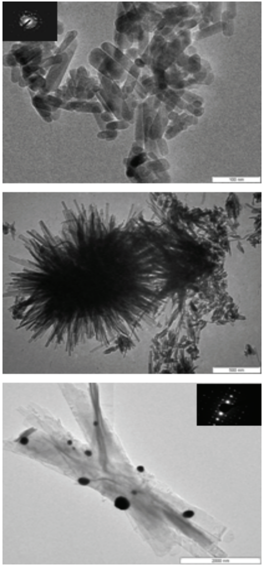

Figure1-Electron microscopy pictures of precipitated particles: [Au] in b) is 5 x [Au] in a).
c) amplified detail showing gold nanoparticles on Hap particles

As a conclusion the present work demonstrates the possibility of precipitating gold and Hap particles with nanometric size from the same precursor solution. The presence of gold ion seems to play an effective role on the Hap growth mechanisms which is here tentatively discussed.

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TOWARDS THE MANIPULATION OF HYDROXYAPATITE PARTICLE MORPHOLOGY

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The ability to predict the necessary experimental conditions for synthesizing a particle having a desired schedule of properties is being pursued from a long time ago. Recently many efforts have been particularly directed towards the geometrical characteristics (size and shape) of synthesized particles as it is known that they may dramatically change the material properties. Hydroxyapatite [Hap-$Ca_5(PO_4)_3OH$] has been the focus of intensive research due to its bioactive and biocompatible properties which make it a potential material for several biomedical applications. In addition to chemical and crystal phase composition issues, geometrical factors are also important requirements to be met when searching synthetic Hap particles to a specific biological role. For instance biological Hap is non-stoichiometric, but nanometric-sized in bone and dentin while micrometric-sized in enamel [1].

In the present work Hap particles are synthesized by two different methods starting from the same precursor solution prepared as follows: adequate amounts of citric acid, calcium nitrate, ammonium hydrogen phosphate and ammonia for adjusting pH to the desired value were mixed. The selected synthesis methods were chemical precipitation (CP) at 37ºC and hydrothermal synthesis (HS) at 180ºC. The manipulation of the pH value (pH=8.12 and 8.53) and of the (citrate/calcium) ratio (Cit/Ca=3:1 and 5:1, respectively) allowed to control the crystallite size, the morphology and the shape of the precipitated particle. The obtained results showed that all the precipitated particles are hydroxyapatite, though with higher crystallinity when prepared by HS as compared to CP. The particle sizes and shapes revealed to be highly conditioned by the selected combination of pH value and Cit/Ca ratio. As shown in fig.1 individual nanosized particles, needles and nanorods, were produced at pH= 8.12 and Cit/Ca =3:1 by both methods. However, increasing Cit/Ca to 5:1 and pH to 8.53 the precipitated particles exhibit a micrometric sized spherical shape (balls and hedgehogs) which seem built up by assembled smaller elementary units (fig.1). The specific surface area of the particles reflect the observed differences on particle sizes, ranging from170 m^2/g for Hap obtained by CP under Cit/Ca=3:1, to 26 m^2/g for Hap obtained by CP under Cit/Ca=5:1. The particle properties evaluated by X-ray diffraction, X-ray photoelectron spectroscopy, high-resolution transmission and scanning electron microscopy , Fourier transform infrared spectroscopy, N_2-gas adsorption (BET) and Zeta potential measurements will be used to discuss the interplay of pH and (Cit/Ca) conditions during the particle growth attempting to clarify their role as shape tailoring variables.

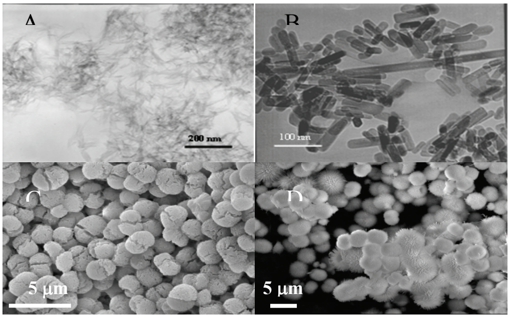

Figure 2-nano Hap with Cit/Ca ratio 3:1 obtained by CP (A), HS (B). Micro Hap with Cit/Ca ratio 5:1 obtained by CP(C) and HS(D).

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OPTICAL PROPERTIES OF ONE-DIMENSIONAL PHOTONIC CRYSTALS IN DICHROMATED PULLULAN

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In our laboratory the fabrication of one-dimensional photonic crystals by holographic method is investigated. The interference pattern is recorded as a volume hologram. The hologram was obtained by interference of two oppositely directed beams inside the emulsion [1,2]. The interference pattern consists of planes parallel to the substrate surface with spacing $d = \lambda/2n$, where λ is the wavelength of the laser source and n is the refractive index of the recording material. Pullulan, linear polysaccharide, sensitized with ammonium dichromate, is used as a recording medium. A single-frequency, diode pumped Nd-YAG laser, at 532 nm, is used for exposure. The exposed part is hardened and becomes relatively insoluble in water. During the exposure hexavalent chromium ion Cr^{+6} is reduced to trivalent Cr^{+3}, which then forms a covalent cross-link with pullulan molecules, and reduces the solubility of the exposed regions. The unexposed portion of the DCP is dissolved in the water wash. After exposure the holographic plate is developed in the mixture of water and isopropyl alcohol. The optical properties of photonic structures fabricated by holography are studied by means of both transmission and reflection experiments. Wide band gaps more then 100 nm in the visible range are observed.

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MANUFACTURING OF SOLID-STATE WHITE LIGHT EMISSION MATRIX USING YAG:Ce PHOSPHOR

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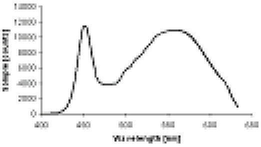
Since the first demonstration of the brightness blue light emitting diodes and subsequently the white LED, the interest in using solid-state light sources for general illumination has been rapidly growing. But only one LED it isn't enough to manufacture a light sources comparable with classical light sources. In this paper we present the manufacturing steps of solid-state matrix with white light emission for application in illuminate systems. Development of matrix, chips on substrate and packaging in the same material, leads to uniformity of the emission parameters, but technology generates new problems. Using blue-emitting GaN chips as primary light sources and YAG:Ce nanopowder, we have fabricated white emitting matrix. The optimizations of technology for sintering of YAG:Ce phosphor is the first step in obtaining the white lighting matrix with high performances. A sol–gel method, simple reproducible and with superior potential, has been developed for the preparation of nanoparticles of phosphor luminescent powders having potential for application in luminescent lighting devices. The main advantage of this process is the sintering temperature. We design the layout for the matrix and then it is printed on cooper substrate and finalized the engrave circuit by chemical etching. The blue GaN chips were mounted on engrave circuit and gold wires were solder. Finally the garnet is mixed with epoxy resin and deposition like a film on the blue chips. The chemical structure and morphology of YAG: Ce was studied. The matrix was tested from optical and electrically point of view.

YAG:Ce nanophosphor

Solid-state matrix with white light emission



Emission spectra of white matrix

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PE-MOCVD GROWTH AND CHARACTERIZATION OF ZnO AND ZnO:Al THIN FILMS

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Transparent conducting oxide (TCO) thin films are important for the electrode materials in solar cell applications. Among TCOs, Al-doped Zinc oxide (AZO) is promising candidate for a substitution of indium tin oxide (ITO) because of its low cost and wide availability. In this study, undoped ZnO and AZO thin films were deposited by plasma enhanced-metal organic chemical vapor deposition (PE-MOCVD) using diethylzinc (DEZn) and N-methyl pyrrolidine alane (MPA) precursors and oxygen on Si(100) and glass substrates. Effects of substrate temperature, reaction pressure, feed ratio of Zn/O and Zn/Al on the growth rate, preferred orientation, resistivity and transparency were investigated. Especially, effect of plasma enhancement on the properties of film such as optimum substrate temperature, film quality were investigated. The use of PE-MOCVD method allows for a deposition of good quality even at low substrate temperature below 300°C, and gives quite a high deposition rate of up to 5 nm/s. The structure and morphology of deposited film were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscope (AFM). XRD analyses showed a great preferred orientation of ZnO(0002) plane below 500°C. In order to analyze the composition and chemical state of the film and interfacial layer, X-ray photoelectron spectroscope (XPS) depth profile technique was used. Resistivity and optical transparency of films which is important for its application as a TCO material were measured with 4-point probe and UV-Vis spectrophotometer respectively. More detailed results and discussion will be presented at the conference.

APPLICATION OF FOURIER-PADE APPROXIMATION IN ANALYSIS OF MATERIALS FOR OPTICAL APPLICATIONS

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Fast Fourier transform (FFT) is the most popular tool in spectral analysis, primarily because of its computational efficiency and a steady convergence as a function of increasing the sequence length. In this paper a method based on Fourier transform and Pade approximants is investigated for analysis of materials used in holography. Pade approximants are numerical tool that can be used to accelerate the convergence of a slowly converging sequence. Namely, for a power series

$$F_n(z) = \sum_{n=0}^{N} c_k z^k \qquad (1)$$

of order N in the variable z (real or complex) with coefficients c_k, Pade approximant is a rational fraction $P_m(z)/Q_n(z)$, which approximates the fully converged values of the function F_n (z). If we let $z=e^{-jkn}$, then equation (1) corresponds to DFT, so Pade method is used to improve spectral resolution of FFT. This method is usually called Fourier-Pade (FP) approximation.

We applied Fourier-Pade approximation on data acquired by AFM scans of diffraction grating investigated in [1,2], proving advantages of using FP for spectral analysis instead of FFT.

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MEASUREMENT OF LASER-INDUCED FLUORESCENCE OF OPTICAL MATERIALS USING A TIME-RESOLVED SPECTROMETAR

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Depending on the specific application, fluorescence measuring systems strongly differ in instrumental design, i.e. use of optical components, detection systems as well as in measurement geometries including the sample cell. Therefore, it is necessary to calibrate almost every system individually in order to ensure accurate signal interpretation.

We report here various approaches for the calibration of the time-resolved laser-induced fluorescence (TR-LIF) detection system. This system is based on the tunable Nd:YAG laser (320-475 nm) to excite samples and on the detection part with high spatial and temporal resolution [1]. In this paper we shall describe different methods for calibration [2-4] and the possibility of their application to our TR-LIF system, having in mind the most important experimental parameters of calibration procedures. Feasibility of some methods will be tested with standard fluorescent dyes, such as fluorescein which is intended for use in establishing a reference scale for fluorescence intensity [5]. The data will be compared with values reported in literature for these dyes. The sources of errors due to an inadequate calibration system will be also discused.

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INVESTIGATING THE INSERTION LOSS DUE TO FRESNEL REFLECTION AT THE LITHIUM NIOBATE–AIR INTERFACES

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Recent progresses in fiber optics communications are strictly indebted to utilization of electro-optic crystal of $LiNbO_3$ which has shown fair electro-optic characteristics while utilizing in fiber optics devices [1]. In spite of this, they have been observed some undesired properties of it[2-4]; one of these properties is known as **insertion loss due to Fresnel reflection at the lithium niobate–air interfaces** which is a result of light beam reflection at $LiNbO_3$-air interfaces; this effect causes undesired changes in the output intensity of $LiNbO_3$ electro-optic modulator; designers try to minimize the effect of this property[2,5,6]. In recent experiment, the electro-optic behavior of $LiNbO_3$ is investigated experimentally via applying a DC bias voltage on it and the effect of insertion loss due to Fresnel reflection at the lithium niobate–air interfaces is observed. Afterward the effect is justified via obtaining **Output Characteristic Curve**[7] of electro-optic modulation and related equations [2,6-9]. Theoretical model is also provided to describe the effect; The experimental setup contains a 17 mW He-Ne laser as a light source, two polarizers as the analyzer and polarizer, a $LiNbO_3$ Z-cut crystal uncoated with any antireflection layer, a DC voltage generator in order to applying DC bias voltage on LiNbO3 crystal -in the form of transverse modulation- and a photodetector in order to detecting, monitoring and recording the Output Characteristic Curve of the electro-optic modulation. In order to remove this effect, antireflection coatings or index matching can be helpful [5, 6, 8, 10-13]. Description in details is given in complete version of the paper containing the experimental data, diagrams, equations and more references.

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INTRINSIC LUMINESCENCE OF ZrO_2 NANOPOWDER AND ITS POSSIBLE APPLICATIONS

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Zirconia (ZrO_2) as high-k material is a promising material primarily for the future semiconductor industry. One of the most important properties relevant to electrical and optical properties of zirconia is the purity of the material as well as its intrinsic defect structure within the band-gap. In addition, the defects and nanocrystalline phase structure may have pronounced impact on gas sensing response.

For investigating the defect structure a set of ZrO_2 nanopowders were prepared by using a sol-gel route. Subsequent thermal treatment at 500, 750 and 1000°C in air allowed to obtain powders with a variable amount of tetragonal phase within monoclinic zirconia. Luminescent properties of the powders were carefully investigated in the temperature interval of 10–300 K by using for excitation a pulsed OPO light source with tunable wavelength in the UV spectral range. Band-to-band transitions as well as deep levels within the forbidden gap of zirconia were probed. Three broad emission bands at 2.5, 3.0 and 4.3 eV were recorded under 5.3 eV excitation (Fig. 1). Under 4.3 eV excitation only the 2.5 eV luminescence band was observed and interpreted as a transition of an electron from the valence band to an F-center. An unusual blue shift of the 2.5 eV emission band with a jump of the whole emission band at about 140 K was noticed (Fig. 2) and attributed to a rearrangement of the emitting F-center surrounding. Such a behavior seems to be a common feature to ZrO_2 and HfO_2. Decay kinetics of 2.5 eV emission in dependence on temperature indicates afterglow up to 50 ms determined by a thermally induced migration of the mobile charge carrier. Ab initio modeling of the optical properties of pure ZrO_2 and ZrO_2 with defects is being performed to understand better the above-described properties.

At RT the influence of the ambient gas to the luminescent properties of differently treated powders were investigated. It indicates the possibility to use specially treated zirconia powders for optical oxygen gas sensing.

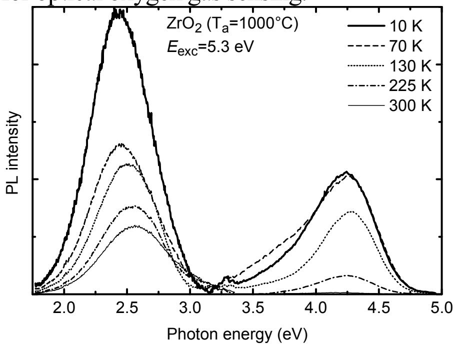

Figure 1. Temperature dependence of PL spectrum under 5.3 eV excitation.

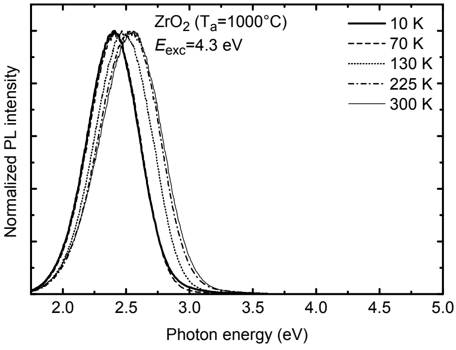

Figure 2. Temperature dependence of PL spectrum under 4.3 eV excitation.

SELECTIVE IC ABSORPTION IN MOLECULAR NANOFILMS

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We have formulated a microscopic theory of optical properties of ultrathin molecular films (nano-films), i.e. quasi 2D systems bounded by two surfaces parallel to XY planes (number of these planes is maximum ~10). Exposing nano-films to the external electromagnetic fields has result in creation of excitons – quasi particle composed of electron and hole bounded with Coulomb's interaction, but different to bulk ones. Harmonic exciton states were calculated using the method of two-time, retarded, temperature dependent Green's functions. It has been shown that two types of optical excitations can occur: bulk and surface exciton states. Exciton energies, i.e. energy dispersion laws show very discrete behavior with non-zero values. Analysis of the optical properties (i.e. dielectrical permittivity) of these crystalline systems for low exciton concentration shows that the permittivity strongly depends on boundary parameters and the thickness of the film. Also, permittivity shows very narrow and discrete dependence of external electromagnetic field frequency, which is a consequence of very thin thickness of the film, i.e. of the quantum effects. Influences of boundary conditions on optical characteristics (absorption coefficient) of these nanostructures have been especially analyzed.

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HYBRID MATRICES FOR EMBEDDING OF OXIDE NANOPARTICLES WITH MAGNETO-OPTICAL PROPERTIES

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This paper presents a study regarding the synthesis of some hybrid matrices tetraethyl orthosilicate (TEOS) / polyvinyl alcohol (PVA) / 1,3 propane diol (1,3PG) with appropriate characteristics for embedding magnetic γ-Fe_2O_3 nanoparticles.

PVA/TEOS hybrid gels have been intensively studied for the obtaining of hybrid organic-inorganic matrices [1]. Our previous studies on the influences of small molecule diols on the formation of TEOS and PVA gels, have evidenced that these diols can act as cross-linking agents [2]. The properties of these hybrid gels recommend them for the obtaining of thin films.

The formation of the hybrid gels TEOS/PVA/1,3PG with different compositions was studied by FT-IR spectrometry and thermal analysis, in order to correlate their properties with the interaction between the organic and the inorganic polymers. The gels with optimal composition have been further used for embedding γ-Fe_2O_3 nanoparticles by ultrasonation. The obtained gels were deposed as thin films and further studied from magneto-optical point of view. We have investigated the effects of magnetic induced polarization and the photo-elastic properties measured in monochromatic polarized light.

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SOLITON BREATHERS IN NEMATIC LIQUID CRYSTALS

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Dynamical behavior of beams propagating in nematic liquid crystals (NLC) is investigated. A well-known model for the beam propagation and the director reorientation angle in a NLC is treated numerically in space and time. The formation of soliton breathers in a threshold region of beam intensities is displayed. Below the threshold region the beams diffract, above the region spatio-temporal instabilities develop, as the input intensity and the optical and static permittivity anisotropies of NLC are increased. We analysed breathing soliton transverse profiles of the optical field intensity and optical induced molecular reorientation. Using transverse profiles along the propagation axis, we calculated the period of breathing solitons.

VACUUM ULTRAVIOLET SPECTRA OF LANTHANIDE BORATES

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Several phosphor compositions based on rare earth orthoborates, $LnBO_3$, with Ln=[$Y_{0.95-y}Gd_yEu_{0.05}$] or [$Y_{0.95-y}Gd_yTb_{0.05}$], have been synthesized by spray-pyrolysis and additional thermal treatments. Samples with the unique hexagonal YBO_3 type phase have been obtained. The cubic oxide $(Y_{0.96}Eu_{0.04})_2O_3$ has also been obtained by same synthesis method and analysed for comparison. The response of these phosphors to VUV excitation has been investigated by two complementary experiments: i) the luminescence excitation spectra have been recorded in the 130 – 300 nm wavelength range, and ii) the relative intensities in the emission spectra of these phosphors excited by rare gas discharges have been measured in a specially developed experimental set-up. This specific set-up consists of a stainless steel chamber filled with a mixture of Ne-Xe at variable composition and pressure (50-200 torr). The objective is to mimic the working conditions of the phosphors in plasma display panels or in Hg-free lighting.

The excitation spectra of Eu^{3+} in the VUV-UV range are interpreted considering the absorption into the ligand to metal charge transfer state, and the host absorption, besides the intra-$4f^7$ absorption of Gd^{3+} for the mixed yttrium-gadolinium borates. Compared to the excitation spectra of Eu^{3+} in the oxide (Y_2O_3), borates may be much more efficiently excited at wavelengths shorter than 175 nm (down to 140 nm). This effect is well reproduced by comparing the luminescence efficiencies of europium-doped borates and oxides in the plasma chamber. In pure Xe at low pressure, the VUV photons are emitted by the resonance states of xenon (147 nm), and the borates are more efficient than the oxide. With increasing pressure of the Ne-Xe mixture, the first continuum (150 nm) and second continuum (173 nm) become more prominent, and it is observed that emission from Eu^{3+} in the oxide is more intense than in borates. Also it is observed that the borates with higher Gd/Y ratio are more efficient, specifically at high pressure.

Terbium excitation spectra in the VUV-UV range are interpreted considering the $4f^85d^0$ to $4f^75d^1$ transitions of Tb^{3+} and the host absorption, besides weak intra-$4f^n$ absorptions of Tb^{3+}, or of Gd^{3+}. Under plasma excitation, it is observed that the phosphor with higher Gd/Y ratio is more efficient, specifically at high pressure.

These results will be discussed with consideration of experimental specific conditions in each set of experiments (i.e. synchrotron or plasma).

Acknowledgements: Financial support for this work is acknowledged under the CityU Strategic Research Grant 7002292. Travel expenses under the HK-France Research Grant 9050206 are also acknowledged.

CRYSTAL STRUCTURE AND LUMINESCENT PROPERTIES OF MANGANESE RARE-EARTH TETRAMETAGERMANATES

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The manganese rare-earth tetrametagermanates $Ln_2M^{2+}Ge_4O_{12}$, Ln = Eu – Lu, Y, were synthesized from oxides by annealing at 1050°C with conventional heating and microwave heating. The application of a microwave field allowed reducing the time of synthesis by a factor of twenty. An analysis of XRD and ED patterns indicates the space group *P4/nbm* (No. 125, Z=2) for all compounds. The crystal structure of the manganese rare-earth tetrametagermanates consists of two alternating layers: one formed by Ln and Mn atoms and another by cyclic anions $[Ge_4O_{12}]^{8-}$ in boat-type conformation. Between these layers octahedral and square antiprismatic cavities are formed. The Ln and Mn atoms are positioned inside elongated oxygen octahedrons with ratio 0.5/0.5. The rare earth cations have oxygen square antiprism configuration. The decreasing atomic radius of the rare earth elements leads to a change of the island structure motive to the 2D layered type. The factor of atomic radius also makes impossible the obtaining of Pr- and Nd-members of the series. However, the partial substitution of Pr in the $Y_2MnGe_4O_{12}$ matrix leads to the formation of the solid solution $Pr_xY_{2-x}MnGe_4O_{12}$, $0 \leq x \leq 0.5$.

The NIR absorption spectra at T = 95 K of the $Ln_2MnGe_4O_{12}$, Ln=Dy, Ho, Er, Tm, Yb and the solid solution $Pr_xY_{2-x}MnGe_4O_{12}$ ($0 \leq x \leq 0.5$) have been measured. The data show the entire set of lines due to *f-f* transitions from the Ln^{3+} ground state to a series of excited states. The optical absorption spectra were measured in the range $\Delta\lambda = 190 – 1050$ nm. According to the value of the fundamental absorption edge for each of the compounds the optical band value has been estimated to be ~ 4.96 eV for all tetrametagermanates.

Under the excitation of a 1064 nm Nd:YAG laser significant emission was revealed for $Ln_2MnGe_4O_{12}$, Ln= Dy, Er, Tm, in the range around 1480 – 1750 nm, due to corresponding transitions in the rare-earth ions: $^6H_{11/2} \rightarrow {}^6H_{15/2}$, $^4I_{13/2} \rightarrow {}^4I_{15/2}$, $^3F_4 \rightarrow {}^3H_6$, respectively.

The optical properties and structural features of the manganese rare-earth tetrametagermanates make them promising materials for optical elements, such as converters of laser emission in the IR range.

This work was supported by the Russian Foundation for Basic Research under Grant No. 07-03-00143, the Program of the Presidium RAS for Basis Research No.18.

DESIGN A HOLLOW AgI SPHERES BY ULTRASONIC SPRAY PYROLYSIS

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Theoretical models describing the mechanism of droplet formation and structure of AgI particles prepared by the process of ultrasonic spray pyrolysis (USP) were investigated. Theoretical approaches describe very well the properties of silver iodide particles, collected and aged in 2-propanol after the USP process. The morphology of hollow silver iodide particles aged in 2-propanol was found to be connected with mechanism of surface precipitation caused by low precursor density. Beyond that, the structures of small complexes used are directly connected with structural changes of AgI particles. The proposed model and experimental results imply that the structure of the starting thermodynamically stable AgI complexes used as a precursor solution influences a final particle structure.

PHOTOLUMINESCENCE FEATURES OF Eu^{3+}-MODIFIED DI-UREASIL-ZIRCONIUM OXOCLUSTER HYBRIDS

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The potential applications of the so-called organic-inorganic hybrids (OIH) in integrated optics (IO) have been extensively explored [1]. The simplicity and low cost of the sol-gel process make this method very suitable for the development of OIH materials for the production of functional IO devices at low cost. Among the various OIH, those containing amine functionalities, classed as di-ureasils, present acceptable transparency, mechanical flexibility and thermal stability to be processed as thin films and tailored monoliths [2-3]. The refractive index control is recursively made through the addition of metal oxide precursors, specifically methacrylic acid modified zirconium tetrapropoxide (ZrMcOH). In particular, monomode planar waveguides based on the di-ureasils with low losses both in the visible and infrared (0.4-1.5 dB/cm) regions and channel monomode waveguides, diffraction gratings, and Fabry-Perot cavities were obtained by UV writing [3]. Moreover, di-ureasils are good Ln^{3+} cages leading to enhanced quantum yield and improved UV photostability of Ln^{3+} complexes enabling high luminescence efficiency (desirable for optical amplifiers and lasers)[4]. In this work, a series of di-ureasils hybrids containing different amounts of ZrMcOH nanoclusters (20-80 % w/w) and incorporating $EuCl_3$ and $[Eu(tta)_3(H_2O_2)_2]$ (tta=thenoyltrifluoroacetonate) complex will be prepared. The influence of the ZrMcOH nanoparticles in the photoluminescent features of the OIH will be studied in steady-state and time resolved modes. Preliminary results point out that the ZrMcOH incorporation deviate the maximum excitation wavelength of the OIH intrinsic emission from the UV (365 nm) to the blue (420 nm) and enhances the emission quantum yield from 0.06 to 0.10. The Eu^{3+}-doped hybrids show an enlargement of the excitation spectra and the $^5D_0$ decay curves displays a non-exponential behaviour with average lifetime values higher than those estimated for the isolated complex, suggesting changes in the ligands-to-Eu^{3+} energy transfer processed due to the presence of the ZrOMc nanoclusters.

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ACOUSTOOPTIC INTERACTION IN α-BaB_2O_4, SrB_4O_7, PbB_4O_7 AND $LI_2B_4O_7$ CRYSTALS

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The present report is devoted to experimental studies and analysis of acoustooptic (AO) diffraction in α-BaB_2O_4, SrB_4O_7, PbB_4O_7 and $Li_2B_4O_7$ crystals. Ultrasonic wave velocity, elastic compliance and stiffness coefficients, piezooptic and photoelastic coefficients of α-BaB_2O_4 and $Li_2B_4O_7$ crystals are determined. The AO figure of merit has been estimated for different possible geometries of AO interaction. It is shown that the AO figures of merit for α-BaB_2O_4 crystals reach the value $M_2 = (230 \pm 50) \times 10^{-15}$ s^3/kg for the case of interaction with the slowest ultrasonic wave. The directions of propagation and polarization of those acoustic waves are obtained on the basis of construction of acoustic slowness surfaces. The AO diffraction is experimentally studied for α-BaB_2O_4 and $Li_2B_4O_7$ crystals.

The acoustic, elastic, piezooptic, photoelastic and AO properties of SrB_4O_7 and PbB_4O_7 crystals have been studied. The complete matrices describing the corresponding properties have been obtained. The AO diffraction in PbB_4O_7 crystals has been observed. It is shown that the highest value of AO figure of merit ($M_2 = (10.4 \pm 6.6) \times 10^{-15}$ s^3/kg) for SrB_4O_7 crystals can be reached for AO interaction with the slowest acoustic wave ($V_5 = 5470 \pm 80$ m/s). Since the SrB_4O_7 crystals are transparent down to 130 nm and all their optical parameters should increase there due to dispersion, one can expect that these crystals could be efficient materials for AO devices operating in a deep ultraviolet spectral range. We have found out that the velocities of acoustic waves reveal small anisotropy for the both crystals and the latter manifest high velocities for the longitudinal waves and lower ones for the transverse waves. Then just the values of photoelastic coefficients and their anisotropy could have a principal influence on the magnitude of AO figure of merit. Those coefficients are high enough for providing a notable AO efficiency (in particular, in SrB_4O_7 crystals) as well as observable diffraction in PbB_4O_7 crystals. On the other hand, small anisotropy of the acoustic velocities in SrB_4O_7 and PbB_4O_7 crystals can be useful when elaborating acousto-electronic devices, since it would not be necessary to associate the velocity components with certain crystallographic directions. Moreover, since the rise time of AO modulators is proportional to the time taken by the acoustic wave for travelling through the laser beam, AO devices based on SrB_4O_7 and PbB_4O_7 crystals should be quite fast. Besides, these crystals can be used in Q-switching AO devices, owing to a high optical damage threshold and transparency in the ultraviolet range.

ON THE CRYSTALLIZATION KINETICS OF THE $Fe_{70}Cr_{10}B_{20}$ AMORPHOUS ALLOYS

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The physical properties of the amorphous alloys depend on the production technique and their state can be changed by annealing or by irradiation. If the annealing temperature is below the crystallization temperature, stuctural relaxation processes are initiated inside the amorphous alloy. If the annealing temperature is near the crystallization temperature then crystallization processes are initiated.

In this paper we examine some aspects of the crystallization kinetics of $Fe_{70}Cr_{10}B_{20}$ amorphous alloys. The analysis is based on isothermal annealing, non-isothermal annealing, Mossbauer spectroscopy (MS) and X-ray diffraction (XRD).

In the isothermal annealing some samples (80 mm x 30μm x 2.5 mm) have been introduced in thin vacuumed glass tubes and subjected to isothermal flash at annealing temperatures T_a = 701K, 708K, 715K. The isothermal crystallization kinetics has been examined by measuring the changes in the coercitive force, H_c.

Using the Johnson-Mehl-Avrami (JMA) equation to describe the kinetic reaction under isothermal conditions, two processes have been identified : one characterized by an activation energy of crystallization $\varepsilon_{k1} = 2.31 \pm 0.04$ eV and by an order of reaction $n_1 = 2.41 \pm 0.07$ and another one characterized by an activation energy of crystallization $\varepsilon_{k2} = 3.00 \pm 0.02$ eV and by an order of reaction $n_2 = 1.13 \pm 0.02$. These results suggest that the dominant mechanism is the grain growth at a constant or increasing nucleation rate for the first process and a diffusion controlled growth of grains for the second one.

Non-isothermal crystallization kinetics were performed on a C-Derivatograph at constant heating rates 9 K/min, 12 K/min, respectively 15 K/min. By DTA analysis only one exothermal process has been identified, characterized by an activation energy $\varepsilon_k = 2.60 \pm 0.20$ eV. This value of energy in non-isothermal annealing is similar with the averaged activation energy, 2.66 eV, corresponding to the isothermal annealing.

For the sample annealed at 701K/14400s the Mossbauer spectrum have been recorded by using a constant acceleration spectrometer in transmission geometry which uses a ^{57}Co source in Rh matrix. For the sample annealed at 715K/144000s a XRD pattern has been recorded on a DRON using $Mo - K\alpha$ line (λ = 0.71 Å).

Using both methods the following crystalline phases have been identified: $Fe - \alpha$, $(Fe,Cr)B$, $(Fe,Cr)_2B$, $(Fe,Cr)_3B$.

A COMPARATIVE STUDY OF THE PARABOLIC CONCENTRATOR INSTALLED ON ORIENTED ROOFS

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The solar radiation represents an important alternative source for generating electrical energy but because of the high price of photovoltaic cells, the cost of converting solar energy in electrical energy can be prohibitive. In order to make thr solar radiation an efficient source of energy, a solution is to concentrate it by using static concentrators which are easy to be constructed based on rather cheap materials. In this way one can achieve an increase of the efficiency from 12-14% to 28-30%. In order to design such concentrators it is useful to simulate the trajectory of the solar rays. The simulation can be achieved by using the Ray-Tracing technique.

Based on this technique we implemented a software application, Ray-Tracer [1], [2], which allows us to compute several physical quantities which characterize the solar energy. More specifically, these quantities are: the solar irradiance; the incidence angle of the radiation on the input aperture; the irradiance in the point which contains the input aperture; the density of the radiant flow in the plane which contains the receiver; the optical concentration factor; the quantity of energy which passes through the input aperture during the measurements; the quantity of energy received by the cell; the average optical efficiency of the concentrator. These quantities are computed starting from several input values provided by the user: the input aperture radius; the output aperture radius; the receiving cell position; the incrementation step of the distance between the cell and the parable; the final position of the cell; the initial moment of the measurements; the final moment of the measurements; the incrementation of time; the roof's inclination angle; the azimuthal angle of the roof; the month; the day.

In this paper we present a comparative study for a paraboloidal concentrator placed on roofs oriented toward south, south-east and south-west and corresponding to the equinoxes and solstices. For each case we identified the time intervals for which the concentrators corresponding to different orientations generate the highest values of the efficiency.

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THE EFFECT OF TEMPERATURE AND Fe^{3+} CONCENTRATION ON THE FORMATION OF γ-Fe_2O_3 NANOPARTICLES EMBEDDED IN SILICA MATRIX

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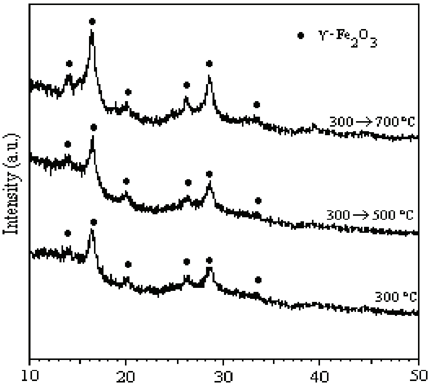
The paper presents a study on the formation and thermal stability of γ-Fe_2O_3 nanoparticles within the silica matrix depending on the Fe(III) carboxylate type precursor and their annealing temperature. The obtaining of the precursors, within the gels pores, bases on the redox reaction between $Fe(NO_3)_3$ and the diols: ethylene glycol (EG) and 1,4 buthane diol (1,4 BG), respectively.Thus, we have prepared gels for different Fe_2O_3/SiO_2 ratios (20, 30, 50, 70 wt% Fe_2O_3) which were annealed in the temperature range 300÷1000°C. The presented figure shows the XRD patterns of the nancomposite with 50 wt% Fe_2O_3/SiO_2 obtained in the synthesis with 1,4 buthane diol. All patterns evidence the formation of the sole phase γ-Fe_2O_3 as nanoparticles with diameter in nanometer scale calculated with the Scherrer formula.



XRD patterns of the samples with 1,4 BG annealed at different temperatures

γ-Fe_2O_3 nanocrystallites diameters annealed at different temperatures

Temperature (°C)	Mean diameter (nm)
300	6.1
500	5.8
700	6.8

The nanocomposites resulted in the synthesis with ethylene glycol, thermally treated in the same conditions, also lead to the formation of γ-Fe_2O_3, but less crystallized.
The composites synthesized with different ratios Fe_2O_3/SiO_2 and different diols, form at 1000°C a mixture of crystalline phases: γ-Fe_2O_3, α-Fe_2O_3 and Fe_2SiO_4 evidenced by XRD.

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AFM STUDY OF ADSORPTION KINETICS OF FERRITIN NA GOLD SURFACE

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The interaction of proteins with solid surface is a fundamental phenomenon with implication for biomaterials, biotechnological processes and nanotechnology. Quantification of adsorption and microstructural parameters of thin organic layers on planar surfaces is of high interest, especially in areas like biomaterials and surface-based biointeractions.

The kinetics of adsorption of horse spleen ferritin on gold (Au) surface was studied. The thickness resolution and *in situ* advantage of atomic force microscopy (AFM) make this technique particularly suitable for studies of thin layers of biological interest. Received was also the relation between parameters of adsorbed layer and pH, and protein concentration. The results suggest that the ferritin adsorption can be described as a multistage process.

The data enable modeling of the protein adsorption on blood vessels and tissues in pathological processes.

OPTICAL PROPERTIES AND PHOTOCATALYTIC ACTIVITY OF RUTILE NANOPOWDERS DOPED WITH Fe IONS

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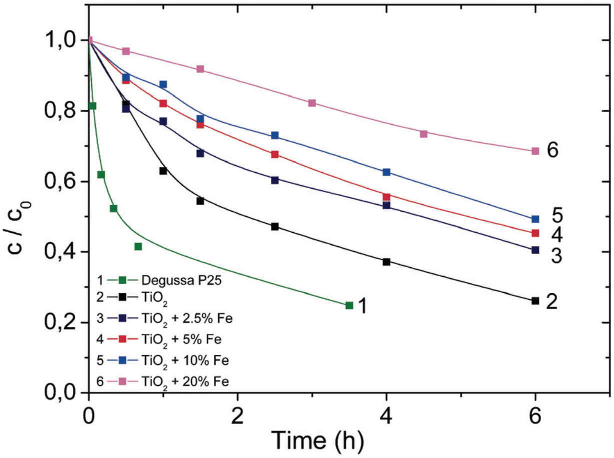
TiO_2 nanopowders doped with different concentration of Fe ions were synthesized by coprecipitation method. Applied synthetic procedure induced formation of pure rutile crystalline structure. TEM measurements revealed formation o flower like agglomerates with diameters in the size range from 100-150 nm. XPS measurements showed that Fe ions are mainly in Fe^{3+} oxidation state and that concentrations of incorporated iron ions are much lower than stoichiometric. Doping with Fe ions has great influence on optical characteristics of the host material. Reflection measurements showed that doping of TiO_2 with Fe^{3+} causes shift of the absorption threshold towards visible spectral region. No increase of TiO_2 photocatalytic activity after doping was observed (Figure). The induced photoluminescence as well as the decrease of photocatalytic activity is probably the consequence of the introduction of oxygen vacancies through doping procedure. For higher dopant concentrations (> 5%, stoichometric concentration) also recombination of photogenerated charge carriers occurs with higher probability.



Kinetics of mecoprop degradation (2.7 mmol dm^{-3}) under UV irradiation monitored by spectrophotometry, in the presence of Fe-TiO_2 with various amounts of Fe ions, pure TiO_2 and Degussa P25 Catalyst amounts: 2 mg cm^{-3}.

SYNTHESIS OF COLLOIDAL TERNARY CHALCOGENIDE NANOCRYSTALS IN NON-COORDINATING SOLVENT

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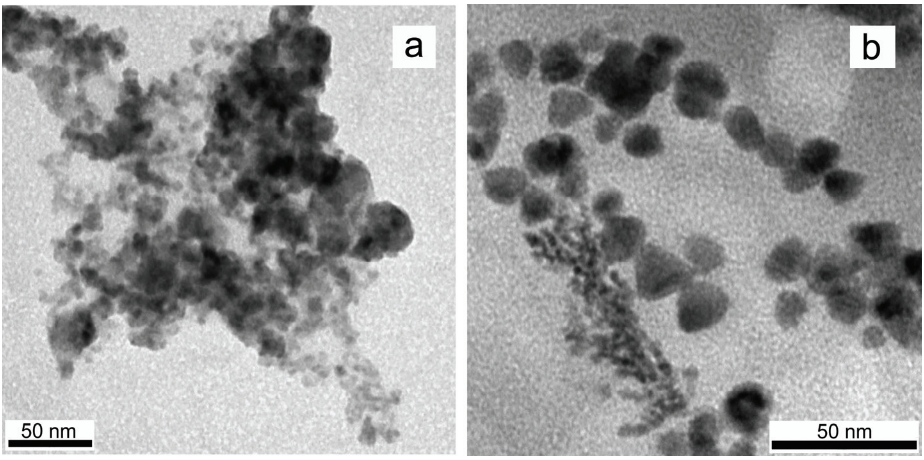
I-III-VI$_2$ compounds, like CuInS$_2$ and CuInSe$_2$ are effective light-absorbing materials which can be used in thin-film solar cells, in printed and flexible photovoltaic devices.We synthesized CuIn-chalchogenide nanoparticles by solvothermal method. Myristic acid complexes of Cu and In (1:1 stoichiometry) were allowed to react with S or Se ions at 300°C. Colloidal dispersions were cooled after nanoparticles were formed and obtained materials were washed and redispersed in appropriate solvents for characterization. XRD showed that chalchopyrite crystalline structure was dominant in both materials, with a traces of metallic copper and indication of In-rich ternary compounds. Stoichiometry was confirmed by ICP-OES technique, Cu/In = 0.546 in CuInS$_2$ and Cu/In = 0.627 in CuInSe$_2$. According to Cu/In ratio we can expect n-type conductivity. Typical TEM images of obtained materials are presented which reveal that both materials have at least two main sizes of particles, CuInS$_2$ has diameters about 8 and 20 nm and CuInSe$_2$ has diameters about 5 and 15 nm.



TEM images of CuInS$_2$ (a) and CuInSe$_2$ (b) nanoparticles.

EFFECTIVE CHARGE APPROXIMATION FOR TWO-ELECTRON QUANTUM DOTS

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Using an adiabatic approximation based on action-angle variables, we develop a consistent approach which enables us to include effect of quantum dot thickness upon its electronic spectrum. We show that a difference in time scales of vertical and lateral dynamics in the dot permits one to analyze three-dimensional problem of interacting electrons by means of the effective Hamiltonian with a screened two-dimensional Coulomb interaction. Analytical expressions for effective charge of the Coulomb interaction (screening) are obtained for a vertical confinement potential simulated by parabolic, square and triangular wells. A remarkable agreement between experimental data and calculations for the additional energy exhibits important role of the dynamical screening for analysis of ground state transitions of the dot in a perpendicular magnetic field.

SURFACE MODIFICATION OF COLLOIDAL TiO_2 NANOPARTICLES WITH BIDENTATE BENZENE DERIVATIVES

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Surface modification of nanocrystalline TiO_2 particles (45 Å) with bidentate benzene derivatives, i.e., 2-hydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,3-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid and catechol was found to alter optical properties of nanoparticles. The formation of the inner-sphere charge transfer (CT) complexes results in a significant change in the onset of absorption and the effective band gap compared to unmodified nanocrystallites. From the Benesi-Hildebrand plot, the stability constants at pH 2 of the order of 10^3 M^{-1} have been determined. The binding structures were investigated by using FTIR spectroscopy. For chosen endiol modifiers binding was found to be through bidentate binuclear (bridging) complexes leading to restoration of six-coordinated octahedral geometry of surface Ti atoms. Salicylate type (OH, COOH) of binding is characteristic for 2-HBA and 2,5-DHBA, catecholate type (OH, OH) is obvious in CAT and 3,4-DHBA, while both salicylate and/or catecholate type may participate in the binding of 2,3-DHBA. It is evident that choosing the proper ligand can result in fine-tuning of the electronic properties of TiO_2. Stabilized charge separation, being important feature of these systems, opens-up possibility for using modifier molecules as conductive leads that allow electronic linking of the nanoparticle into molecular circuits providing further extension of photoinduced electron transfer

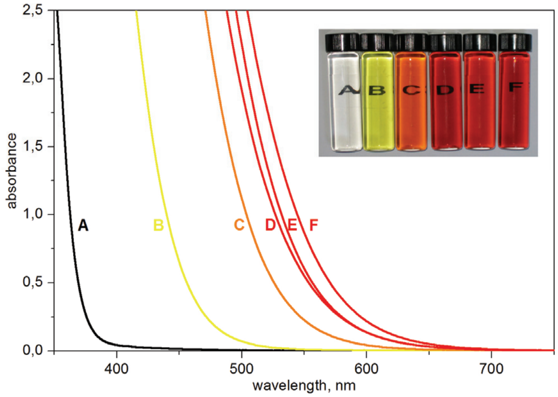

Figure 1 Absorption spectra of surface modified TiO_2 nanoparticles (0.09 M, pH 2) with different ligands (2.5 mM): A) bare TiO_2; B) 2-hydroxybenzoic acid; C) 2,5-dihydroxybenzoic acid; D) 2,3-dihydroxybenzoic acid; E) 3,4-dihydroxybenzoic acid; F) catechol.

EFFECTS OF DEPOSITION PARAMETERS AND Ar ION IRRADIATION ON COMPOSITION AND MICROSTRUCTURE OF Cr-N THIN FILMS

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This paper presents a study of Cr-N thin films deposited by reactive ion sputtering on (100) Si substrates. The layers with various compositions and structures were deposited under different values of nitrogen partial pressures and different substrate temperatures. After deposition the samples were irradiated with 120 keV argon ions, to the fluences of $1x10^{15}$ ions/cm^2 and $1x10^{16}$ ions/cm^2. Rutherford backscattering spectroscopy, x-ray diffraction and transmission electron microscopy were used to characterize chemical composition, phases and microstructure of the samples. It has been found that the nitrogen partial pressure determines the phase composition and the morphology of the layers, while the substrate temperature have effect on grain size and the texture of the films. Thin films with lower nitrogen contents exhibit mixture of Cr and Cr_2N phases, whereas the pure CrN phase is observed in films with ~48 at.% of nitrogen. After ion irradiation the crystalline grains decrease in size, while both micro-strain and dislocation density increase with argon ion fluence.

EFFECT OF ARGON IONS IMPLANTATION ON THE REACTIVELY SPUTTERED TiN LAYERS

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Thin films of titanium nitride (TiN) were deposited by d.c. reactive sputtering on (100)Si. The layers were deposited to a total thickness of ~240 nm at room temperature (RT) and 150°C. After deposition the samples were irradiated with 120 keV argon ions to the fluences of $1x10^{15}$ and $1x10^{16}$ ions/cm^2. The TiN phase has been identified with low angle X-ray diffraction analysis. The characteristic lines in the diffraction spectra correspond to the (111), (200), (220) and (311) planes of TiN. From a broadening of the characteristic peaks it was found that ion irradiation induced changes in grain size, lattice constant and micro-strain. Rutherford backscattering spectrometry (RBS) shows that the TiN layers stoichiometry is Ti:N=1:1, corresponding to a pure TiN phase. Cross-sectional TEM analysis indicated the presence of dense columnar and polycrystalline structure. The results showed that ion irradiation induced microstructural changes due to the formation of the high density damage region in the TiN film structure.

THERMAL PROPERTIES OF TiO_2/PVA NANOCOMPOSITES

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The TiO_2 nanoparticles of different shapes (spheres, tubes and rods) were used separately as precursors for the synthesis of TiO_2/PVA nanocomposites. The concentration of TiO_2 nanoparticles for each sample was kept constant, 0.25 mass % in respect with pure PVA. Thermal properties of pure PVA and TiO_2/PVA nanocomposites were investigated by non-isothermal thermogravimetry analysis (TGA) in argon and air atmosphere and differential scanning calorimetry (DSC), while the shapes of TiO_2 nanoparticles were confirmed by transmission electron microscopy (TEM). Thermal stability has been compared at 50% of their weight loss in each sample. The presence of different shapes of TiO_2 nanoparticles within polymer matrix does not change the mechanism of degradation in both atmospheres, but has considerable influence on its thermal stability. The thermal stability of TiO_2/PVA nanocomposites in the presence of spherical TiO_2 nanoparticles was increased. On the other hand, the presence of titania nanotubes or nanorods in TiO_2/PVA nanocomposites induced decrease of its thermal stability. The melting temperatures and crystallization temperatures of TiO_2/PVA nanocomposites were followed by a DSC curves analysis. The melting temperature of PVA polymer matrix decreases by adding spherical TiO_2 nanoparticles and increases by adding TiO_2 nanotubes and TiO_2 nanorods, while crystallization temperature has the completely opposite behavior.

SYNTHESIS AND CHARACTERIZATION OF POLYANILINE/TiO_2 NANOCOMPOSITE

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Novel semiconducting polyaniline/titanium dioxide (PANI/TiO_2) nanocomposite was synthesized in water via oxidative polymerization of aniline with ammonium peroxydisulfate in the presence of colloidal TiO_2 nanoparticles of an average diameter ~4.5 nm, without added acid. The initial aniline/TiO_2 mole ratio was 80:1. The presence of colloidal TiO_2 causes the shorter athermal period between two exothermic phases during the synthesis of PANI/TiO_2 nanocomposite, in comparison with corresponding synthesis of pure PANI. The electrical conductivity of synthesized nanocomposite was 1.9×10^{-3} S cm^{-1}, slightly higher than that obtained for pure PANI prepared under the same conditions, without TiO_2. The network of nanorods (an average outer diameter 60–90 nm) predominates in the morphology of PANI/TiO_2 nanocomposite, as revealed by scanning electron microscopy. The molecular structure of nanocomposite was studied by FTIR spectroscopy.

AN AFM AND ELLIPSOMETRICAL STUDY OF FERRITIN ADSORPTION KINETICS ON A GOLD SURFACE

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The kinetics of ferritin adsorption on gold (Au) surface is studied with atomic force microscopy (AFM) and ellipsometry.

The thickness and the refraction index of the adsorbed layer were determined using a four-layer theoretical model of the "prism-gold surface-adsorbed layer-solution" system. The relations between parameters of adsorbed layer and pH and protein concentration are obtained. It seems that the ferritin adsorption is a relatively slow multi-stage process.

The obtained results enable modelling of the protein adsorption on blood vessels and tissues in pathological processes. The kinetics of protein adsorption could be implemented in medical applications and in development of new biosensor systems.

THERMAL PROPERTIES OF NANOCOMPOSITE FILM CONSISTING OF PVA AND SHAPED Ag NANOPARTICLES

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Manipulation of the size and shape of metal nanoparticles has attracted a great deal of attention recently and opened-up possibility for their usage in various fields such as microelectronics and optics. Prismatic and plate-like silver nanoparticles synthesized in water by colloidal chemistry methods, were used as a precursor for preparation of transparent and colored Ag/PVA nanocomposite films. Due to structural anisotropy of prismatic and plate-like silver nanoparticles, confirmed by TEM measurements, in absorption spectrum were observed three surface plasmon resonance bands. In absorption spectrum of Ag/PVA nanocomposite film appears only one absorption band. Interaction between Ag nanoparticles and PVA matrix was followed using FTIR spectroscopy. The thermal properties of Ag/PVA nanocomposite film has been examined using TGA and DSC techniques. The thermal decomposition of the PVA matrix in the presence of shaped Ag nanoparticles is shifted towards higher temperatures for about 14°C in argon atmosphere. Slightly higher thermal stability was obtained during thermo-oxidative degradation process. DSC measurements revealed that shaped Ag nanoparticles incorporated in PVA matrix do not have significant influence on the crystallization temperature changes.

OPTICAL PROPERTIES OF Au NANORODS/PVA NANOCOMPOSITE FILMS

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Polymer based nanocomposites have emerged as a new class of materials and attracted considerable interest due to their new or much improved optical, electrical and thermal properties. Au nanorods are synthesized in water using seed-mediated growth method in the present of surfactant CTAB and silver ions. The size and shape of Au nanorods (length-width aspect ratio 4) were examined by TEM technique. Colloidal solution of Au nanorods was used as a precursor for synthesis of Au/PVA nanocomposite films. The optical properties of transparent and colored nanocomposite films were evaluated by UV/ViS absorption spectroscopy. The appearance of two surface plasmon resonance bands in absorption spectrum of Au nanorods colloidal solution is consequence of structural anisotropy. Different dielectric properties of PVA polymer compared to water environment induced position changing of the longitudinal and transversal plasmon resonance bands in absorption spectrum of Au nanorods/PVA nanocomposite films.

SYNTHESIS AND CHARACTERIZATION OF THE Pr-DOPED CERIA

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In this paper nanometric powders of solid solution of the host compound ceria (CeO_2) with Pr dopant in the lattice were synthesized by self-propagating room temperature synthesis (SPRT) with very precise stoichiometry according to tailored composition. Powder properties such as specific surface area crystallite and particle size, dopant content and lattice parameters have been studied. BET, TEM, X-ray diffraction analysis (XRD) and Raman scattering measurements were used to characterize the samples at room temperature. All obtained solid solutions exhibit a fluorite-type crystal structure with composition dependent lattice parameters. The average crystallite size is about 5 nm. Williamson-Hall plots were used to separate the effect of the size and strain in the nanocrystals. Defect model introducing anion vacancy's radius can be applied to calculate lattice parameters of doped ceria nanosized solid solutions and their theoretical densities. The Rietveld refinement was employed for some samples to get the structural information of the synthesized powder. Different factors like phonon confinement; strain, size distribution, defects and variations in phonon relaxation with particle size can contribute to the changes in the Raman peak position and linewidth. To explain properly the changes in the Raman spectra of doped ceria nanosamples (large shift and assymetrical broadening of the Raman line), the phonon confinement model (PCM) is used to compare experimental data with theoretical predictions in nanomaterials. It is noticed the redshift and asymmetric broadening of the Raman F_{2g} mode which is explained with combined confinement and strain effects due to nanocrystalline powders nature. The appearance of the additional peaks at ~ 560 cm^{-1} and at ~ 600 cm^{-1} is attributed to extrinsic and intrinsic oxygen (O^{2-}) vacancies in the ceria lattice. Colour characters of solid solutions and their position in the chromaticity diagram were studied by UV-Visible spectrophotometry (diffuse reflectance).

CRYSTALLIZATION OF TRIPHENYLDIAMINE (TPD) THIN FILM

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TPD (N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'biphenyl 4,4'diamine) is a well known hole transport material, widely used in organic optoelectronic devices due to its higher carrier mobility and the ability to form amorphous thin films. On the other hand, different surface morphologies and morphological modifications induced by the crystallization in the amorphous layers have a significant effect on the performance and stability of these devices. In this paper, TPD thin films with different nominal thicknesses, obtained using physical vapor deposition, were stored up to one year and their crystallization ability was investigated. Differential scanning calorimetric (DSC) measurements confirmed the high crystallization potential of TPD molecules, while the structural differences between the amorphous and semicrystalline thin films were successfully determined using wide angle X-ray diffraction (WAXD). A comparison between the virgin (amorphous) and aged thin film morphologies was made by atomic force (AFM) and optical microscopy (OM). The crystallization-induced changes in the optical properties of thin films were also investigated by absorbance and photoluminescent (PL) measurements; the obtained spectra are strongly dependent on the changes in the microstructure of thin films.

CONFINED GROWTH OF METAL AND SEMICONDUCTOR NANOPARTICLES WITHIN BIOPOLYMER MATRICES

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As a result of the insatiable demand for new materials in emerging fields like nanotechnology, the preparation of metal- and semiconductor-polymer nanocomposites is a rapidly evolving area of research. It is well known that inorganic nanoparticles often show characteristic electronic, optical and other properties, different from those of the bulk phase. These properties can be successfully utilized by incorporation of the nanoparticles into polymer matrices, since a polymer can be easily designed into almost any shape required by a particular application. Recently, because of their possible applications in medical diagnostics, targeted therapeutics and molecular biology, there is an increasing number of studies on nanocomposites that employ biopolymers (particularly polysaccharides) as host materials. The macromolecular chains of these biopolymers possess a large number of hydroxyl groups and they can complex well with metal ions, which in turn enables a good control of size, shape and dispersion of the nanoparticles formed. Here we will present the results on the structure and the optical properties of metal- (Ag, Au), semiconductor (CdS, CdSe, PbS, Ag_2S) and core-shell (Ag@Ag2S) nanoparticles synthesized in various biopolymers (chitosan, alginate and starch).

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PHOTOLUMINESCENCE OF $Cd_{1-x}Mn_xS$ NANOCRYSTALS IN MAGNETIC FIELD

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The influence of applied magnetic field (up to 7T) on photoluminescence of $Cd_{1-x}Mn_xS$ (x = 0.01, 0.05, 0.30) was investigated. The shape of these spectra does not change significantly with a change of magnetic field intensity. However, it is clear that the emission band intensities at ~ 1.7 and ~ 2.1 eV are changing in different ways. Because the emission energies of 2 and 2.13 eV change in the same way, we conclude that they have the same origin and that they correspond to two different emissions from Mn^{2+} ions. This can be explained by the fact that Mn^{2+} ions are present in different local environments. The higher energy level of 2.13 eV is related to the Mn^{2+} in a tetrahedral site while the lower level of 2 eV is caused by a lattice disturbance and Mn^{2+} in an octahedral symmetry in MnS that is formed on some parts of the nanocrystal surfaces, when material is heavily doped. We propose the scheme of energy levels that explain the obtained experimental results.

SYNTHESIS AND OPTICAL PROPERTIES OF Mn DOPED ZnO THIN FILMS

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Technology aspects, and optical study of ZnO:Mn nanocrystalline thin films deposited on fused quartz substrates by atmospheric barrier torch discharge technique are presented here. This technique is based on the plasma stream, which is established by the stream of gas flowing through a hollow metallic needle-like electrode. Such technique is suitable for the fast and cheap deposition of transparent conductive oxides on the variety of the substrate materials. Structural XRD and AFM analysis of the ZnO:Mn films deposited in air confirmed well-formed, [001] preferably oriented, hexagonal structures. The optical measurements of the samples were realised by variable angle spectroscopic ellipsometry (VASE) and by spectroscopic reflectometry at near – normal incidence (NNR) within the spectral range of 1 – 5 eV. Both sets of experimental data were fitted simultaneously using the dielectric function model based on an excitonic structure. The model was developed by Tanguy [Phys. Rev. B 60 (1999) 10660] to provide an analytical expression for Wannier excitons, including bound and unbound states. The function depends on five parameters including band gap energy (E_g).The experimental data around the absorption edge were then fitted by "point- by- point" method and the result was compared with the parameter E_g obtained from dielectric function model. The surface roughness was modelled by the effective Bruggeman medium approximation (EMA) assuming 50% voids and 50% of the film material.

The optical study of the deposited layers was mainly focused to the grain size and Mn doping effect on its optical properties. It was shown that the absorption edge of the Mn doped ZnO is strongly dependent on both Mn concentration and grain size (mainly for the grains smaller than 40 nm). Such pronounced sensitivity of the near band edge and optical band edge absorption parameters to the grain size and Mn doping gives a possibility to produce films with controlled properties for band gap engineering.

GREEN SYNTHESIS OF SILVER-CHITOSAN NANOCOMPOSITES

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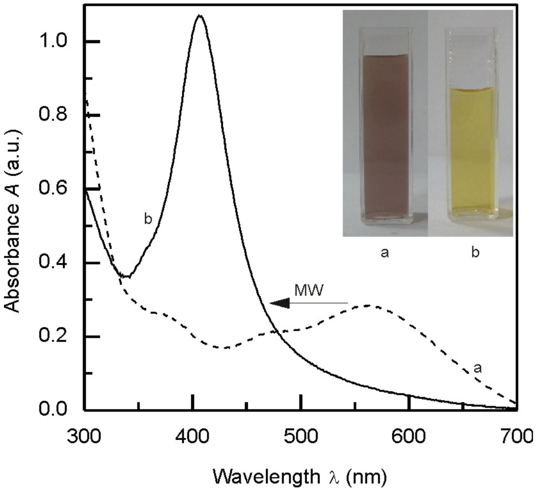
Silver nanoparticles were synthesized in a chitosan biopolymer using D-glucose as a reducing agent. The reduction procedure was carried out under microwave irradiation. The resulting nanocomposites were investigated using structural, optical and thermal methods. TEM micrographs showed that the nanoparticles are mostly spherical in shape with an average diameter of approximately 10 nm. The results of the optical properties of the silver-chitosan nanocomposites were analyzed using classical theories for absorption of light by small metallic particles.



TRYPTOPHAN-FUNCTIONALIZED GLOWING SILVER NANOPARTICLES EMBEDDED IN BIOPOLYMER MATRIX

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Silver nanoparticles were prepared by non-toxic synthesis procedure using luminescent amino acid tryprophan as a capping agent. Trypthophan-functionalized silver nanoparticles showed bright luminescence at 360 nm and surface plasmon resonance band around 400 nm owning it to tryptophan and silver nanoparticles, respectively. The obtained nanoparticles were embedded in water soluble biopolymer chitosan. The ensuing polymer nanocomposites were investigated using structural and spectroscopic methods. The differences between the emission spectra of pure tryptophan, functionalized silver nanoparticles, and nanocomposites are thoroughly discussed.

SEMICONDUCTOR NANOPARTICLES IN POLY(2-(DIMETHYLAMINO)ETHYL METHACRYLATE-CO-ACRYLIC ACID) COPOLYMER

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The lead sulfide (PbS) and cadmium selenid (CdSe) nanoparticles in poly((2-(dimethylamino)ethyl methacrylate-co-acrylic acid) copolymer were prepared and investigated. Co-polymers were synthesized by radical polymerization of the co-monomers in different molar ratios. Nanocomposites were characterized using optical and structural methods. TEM analysis showed spherical, well dispersed particles, with size distribution in nano range. X-ray diffraction analysis revealed that PbS and CdSe nanoparticles have a cubic crystal structure. Interaction between semiconductor nanoparticles and copolymer was studied by FTIR spectroscopy.

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TEMPLATING LUMINESCENT ZnO NANOPARTICLES USING ALGINATE BIOPOLYMER

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The affinity of the alginate for divalent metals was employed for templating semiconductor ZnO nanoparticles. The nanoparticlese were obtained by the crosslinking of poly(α -L-guluronic) residues in alginate using Zn^{2+} ions and later oxidation of zinc at elevated temperatures. The obtained materials were investigated using structural and spectroscopic investigations. Photoluminescence spectra showed strong emission of the material in the visible part of the EM spectrum.

MULTICOLOUR EMISSION PATTERNS BASED ON THE MICROMETRIC SPATIAL CONTROL OF RE^{3+} IONS IN LiNbO$_3$

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We show the possibility of preparing heterogeneous micro-structures out of rare earth based optically active materials. Two-dimensional multicolour emission arrangements have been obtained by embedding high refractive-index Er^{3+} doped CaTiO$_3$ nanoparticles into Nd^{3+} doped LiNbO$_3$ substrates pre-patterned with two dimensional arrays of micro-voids. The void structure on LiNbO$_3$ was obtained after selective chemical etching on the c face of a pattern of polarization inverted domains created by electron beam writing. The two dimensional pattern consist in circular shaped voids of 5 μm in diameter distributed in an hexagonal lattice with a total spatial extension of 2x2 mm^2.

To optically activate those micro-voids, Er^{3+} doped CaTiO$_3$ nanoparticles were mechanically incorporated inside them. The Er^{3+} doped CaTiO$_3$ nanocrystals were consolidated into the voids by means of a thermal treatment at 900 °C for 1 hour. After that, the appearance of ~ 1 μm-thick crown around the walls of the filled voids (surrounding the optically active CaTiO$_3$:Er^{3+} nanocrystals) was observed. X-ray diffraction at glazing incidence and spatially resolved confocal micro-Raman spectroscopy, allowed us to identify the compound forming this shell as CaNb$_2$O$_6$.

Figure 1 shows three scanning confocal micro-fluorescence maps obtained by selecting the different spectral emission regions associated with the different structures forming the pattern. The results reveal the possibility of a simultaneous spatial and spectral control of the RE^{3+} emission in a two dimensional array at the micrometer scale and can be useful for the development of new micro-composite rare earth based photonic devices, such as multicolour emission displays or pixelated colour structures.

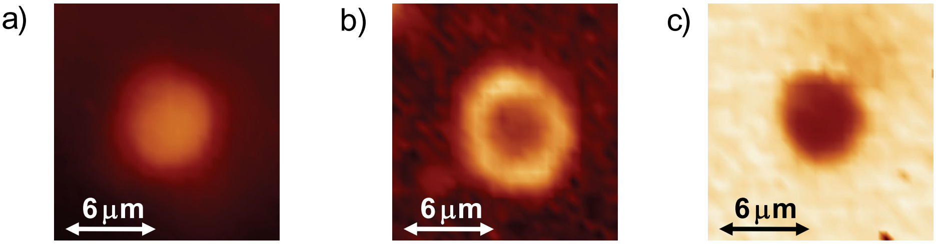

Figure 1. Fluorescence maps selecting a) the Er^{3+} emission from CaTiO$_3$ nanoparticles at the voids (846.8 nm); b) Nd^{3+} emission from the CaNb$_2$O$_6$ crown (878.8 nm); c) Nd^{3+} emission from the substrate (924.1 nm).

NANOPARTICLE FORMATION AND ENRGY TRANSFER IN CODOPED GLASS

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The formation of noble metal nanoparticles inside glass has been extensively investigated in the past decades because of their excellent properties such as an ultrafast optical response and large third-order non-linear susceptibility [1]. Recently, the precipitation of silver nanoparticles in glass by means of femtosecond-laser irradiation and following thermal annealing at high temperature in silicate glasses was reported [2]. However, the systematic study to understand the mechanism was not reported. In this presentation, we report the spectroscopic investigation on formation of silver clusters and nanoparticles in Ag-doped glasses, Ag,Ce-codoped glasses, and Ag,Mn-codoped glasses with various concentrations. We studied characteristics of absorption, photoluminescence, and excitation spectra as well as the temporal behavior of the emissions for the materials annealed at different temperatures up to 500C. Different kinds of defects were found and disappeared as temperature changed. The more Ce ions produced the less surface plasmon resonance bands of silver nanoparticles. In contrast, the more Mn ions enhanced the surface plasmon bands at high temperatures. Figure 1 shows the temoral profile of the emission from the irradiated Ag,Ce-codoped glass. In addition, we found the energy tranfer from Ce ions to Ag ions in the irradiated glass.

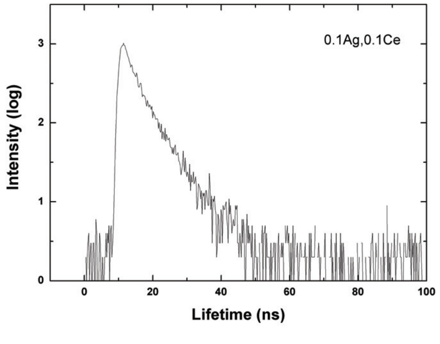

Fig. 1 Decay curve of the emission at 500 nm from Ag-clusters in the irradiated Ag,Ce-codoped borate glass.

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Cr^{3+} DOPED NANO-PHOSPHOR FOR SOLAR CELL CONCENTRATOR

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The idea to enhance efficiency of a photovoltaic cell (PV) by applying solar concentrator has been proposed already many years ago. While solar concentration by means of mirrors and lenses require mechanical system which tracks the Sun during the day, emission solar concentrator based on dyes will work efficiently even with dispersed light during cloudy day.

The letter system consists of transparent plate doped with a phosphor. On the edges of the plate PV cells are attached. A part of the emission excited by the Sun is guided within the plate toward the edges. Emission's wavelength matches the maximum sensitivity of the attached PV cell.

An ideal phosphor for such application should absorb whole Sun spectrum and than generate narrow emission line with energy below the absorption bands to avoid re-absorption. The phosphor should be resistant to UV and atmospheric conditions. Inorganic phosphors doped with transition metal ions could be attractive candidates for such purposes.

We decided to investigate $ZnAl_2O_4$ nanocrystallites doped with chromium ions. Small diameter of obtained crystallites (around 10 nm) permits to immerse them into glasses or polymers or deposit them on the PV surface. Nano size of the crystalline ensures low dispersion losses. Trivalent chromium ions located at high crystal field in $ZnAl_2O_4$ have broad intense spin allowed absorption bands and narrow emission at 686 nm. Therefore this phosphor seems to be an ideal candidate for manufacture a solar concentrator coupled to GaInP photovoltaic cell which have the band-gap of around 1.8 eV (688 nm).

$ZnAl_2O_4$: Cr^{3+} were synthesized by modified solvothermal method. The nanocrystallite size depends on annealing temperature and varies from 3 to 15 nm. Together with crystalline size specific surface area changes from 220 to 45 m^2/g, respectively. Since chromium is situated in strong ligand field the emission is narrow and assigned to the $^2E_g \rightarrow {}^4A_{2g}$ transition. The main emission line is associated with vibronic and N_i lines. Intensity of the emission increases strongly with increasing of the annealing temperature. In this work we will present spectroscopic properties of the nano powder samples, compare them with those of bulk and discuss how they depend on growing conditions.

AN APPROACH TO THE DEFECT STRUCTURE ANALYSIS OF DOPED LITHIUM TANTALATE CERAMICS: EFFECTS OF NONSTOICHIOMETRY AND DOPING ON CURIE TEMPERATURE

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New approach of the ferroelectric phase transition is proposed to study the Curie temperature in Nickel doped lithium tantalate ceramics. The optic modes of lattice vibration were used to derive the Ni incorporation mechanism in the $LiTaO_3$ lattice. To understand the mechanism responsible in this phenomenon, we have proposed a theoretical description of the defect structure in doped $LiTaO_3$ on the basis of the generalized vacancy models combined with a ferroelectric phase transition theory. A comparison between the calculated values from this approach and the experimental data of the Curie temperature is detailed.

MODELLING AND SIMULATION OF I-V CHARACTERISTICS FOR POLYMER SOLAR CELLS BASED ON CARRIER GENERATION RATE

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The behaviour of the polymer solar cells based on the diode model is analyzed. A dependence between the carriers generation rate, respectively the parallel resistance of the cell versus the power density of the incident flow is obtained using the statistical analysis of the experimental data. Based on these equations, the *J-V* characteristics curves are simulated and the influence of different parameters on the behaviour of polymer solar cells is analyzed. At the same time, the different quantities specific for solar cells are calculated.

In Fig. 1 we can see the variation of the total current with the cell voltage for different values of the active layer thickness. In Fig. 2, the dependence of J_L on the cell voltage for different densities of the incident illumination flux is presented.

Fig.1

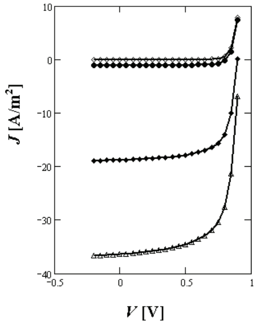

Fig.2

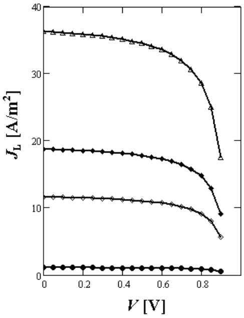

Fig. 1. *J* current density variation with cell voltage for different active layer thicknesses
Fig. 2 J current density variation with cell voltage for different incident illumination flux values.

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NEW MATERIALS FOR HYBRID DYE SENSITIZED SOLAR CELLS

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Starting with the nanocrystalline dye sensitized solar cell invented by Graetzel, research in photovoltaics experienced an increased interest by many research teams. [1,2].

This paper deals with the synthesis and characterization of new phthalocyanine based chromophores for the fabrication of dye sensitized solar cells and hybrid dye sensitized solar cells.

We have synthesized cromophores based on phthalocyanine with different number of pending carboxy groups and utilized them to fabricate solar cells, investigating their photovoltaic properties. Based on this, our team developed a hybrid design using polymers obtained by chemical means in the laboratory. As conductive polymers, polyaniline doped with different doping agents and polythiophenes were used. For the cell fabrication we have performed the deposition of TiO_2 followed by the dye absorption and the polymer film formation in the case of hybrid cells.

Using the solar cells based on the materials previously analyzed, a specific experimental circuit was developed and the I-V curves were plotted. The experimental I-V curves were statistically analyzed and using the model developed by Mitroi M. R. et. al [3], specific material parameters as the product between the mobility and carrier lifetime, as well as parameters characteristic for a solar cell (fill factor and conversion efficiency) were determined. The obtained results showed relative low efficiency similarly to those presented in the literature [4,5].

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LIGHT EMISSION FROM Er-DOPED Ta-OXIDE FILMS FABRICATED BY RF-SPUTTERING

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Er^{3+}-doped Ta-oxide films were fabricated by RF-sputtering. Visible light emission observed from films after annealing around 550 and 670 nm. Effects of Er^{3+} concentration, annealing temperature and time on light emission have been discussed.

Optical properties of rare-earth ions in solids have been investigated widely and are well understood [1]. Er^{3+}-doped materials are attracting much attention in recent years because of search for solid-state-laser devices operating in the green region, optical devices for 3D displays and for waveguides which can work in telecommunication window. Recently green light emitting materials are in demand because they are useful in applications such as skypointer, unmanned aerial system and mini projection system. Erdle et al have reported that 670 nm wavelength is useful in medical sciences in light therapy. It has been reported that it accelerates wound healing and increase cell growth in tissue cultures [2]. Beyond that 670 nm wavelength is useful in laser pumping, marking and printing applications.

In this paper we report visible light emission having two peaks around 550 and 670 nm from Er-doped Ta-oxide films prepared by radio-frequency (RF) magnetron sputtering for the first time to the best of our ken.

Er doped Ta-oxide films were fabricated by RF magnetron sputtering system, Ta_2O_5 disc was used as sputtering target. We placed Er_2O_3 tablets on the Ta_2O_5 disc. Ta_2O_5 and Er_2O_3 co-sputtered films were deposited by supplying RF power to the target.

PL of samples were measured with monochromator CCD camera setup. He-Cd laser 325-nm wavelength with 200 mW power was used for excitation of the samples.

Concentration of Er in the films after annealing were measured by using electron probe micro analyzer (EPMA).

Figure**1** shows the PL spectra of Er doped Ta-oxide films. As-deposited samples did not show any PL peaks. We annealed samples from 600 - 1100°C. Two clear peeks can be seen at 550 and 670 nm in post-annealed samples. Rigneault et al [3] reported fluorescence spectra centered at 532 and 1530 nm from Er^{3+}doped Ta_2O_5 samples, however no peek was seen at 670 nm in their work. Kojima et al [4] also observed only green fluorescence peak around 550 nm.

PL at the wavelength of 550 nm and 670 nm has been observed from the Er^{3+} doped Ta-oxide films annealed at 600 to 1100°C. We optimized the annealing temperature, annealing time and Er concentration, to obtain strongest intensity of PL peaks.

These results demonstrate that Er^{3+}-doped Ta-oxide films fabricated by RF sputtering are high quality luminescent layers. Microdevices useful for green and red light emission can be fabricated from Er^{3+}-doped Ta-oxide films.

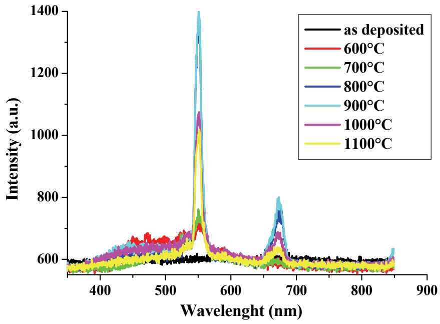

Figure 1. PL spectra of Er-doped Ta-oxide

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EFFECT OF TEMPERATURE ON THE KINETICS OF MECHANOLUMINESCENCE OF POLYMERS

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The effect of temperature on the mechanoluminescence (ML) of non-irradiated polyvinylidene frouride (PVF_2) , polyethylene (PE) , polypropylene (PP), polystyrene (PS) , polymethylmethacrylate (PMMA) and polyethylmethacrylate(PEMA) have been studied from room temperature to 100^0C. It has been found that ML of polymers decreases with in increase in temperature and slightly shifts towards shorted time values. The ML intensity of polymers ceases completely near the melting point. At higher temperature the rate of discharge of newly created surfaces may be responsible for the decrease of ML in polymers.

SILICATE BASED LUMINESCENT MATERIALS FOR OPTICAL IMAGING

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We have recently developed inorganic luminescent nanoparticles ($Ca_{0.2}Zn_{0.9}Mg_{0.9}Si_2O_6$: Eu^{2+}, Mn^{2+}, Dy^{3+}), which are suitable for *in vivo* imaging and can avoid most of inherent problems encountered in classical optical systems (see figure 1 from [1]). The key parameter of this technology is based on a generation of persistent luminescence nanoparticles emitting in the red, which can be optically excited before *in vivo* injection. The persistent luminescence lasts for several hours and permits the removal of the background noise originating from *in situ* excitation.

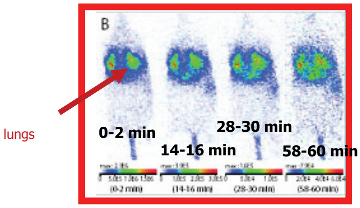

Figure 3. Persistent luminescence observed up to one hour after injection

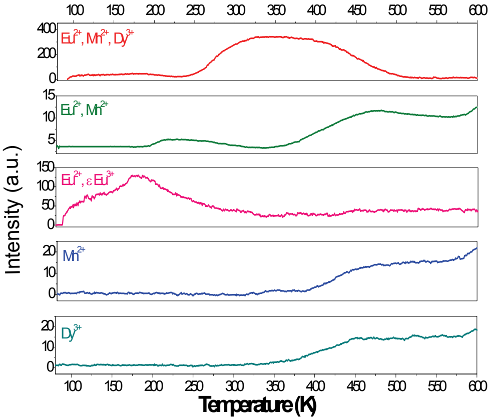

Figure 4. TL curves of Dy^{3+}-doped, Mn^{2+}-doped, Eu^{2+}-doped, Eu^{2+},Mn^{2+}-doped and Eu^{2+} , Dy^{3+} , Mn^{2+}-doped CZMSO NPs

In the $Ca_{0.2}Zn_{0.9}Mg_{0.9}Si_2O_6$ (CZMSO):Eu^{2+},Mn^{2+},Dy^{3+} composition, Mn^{2+} ion is the luminescent center, whereas Eu^{2+} and Dy^{3+} cations presumably act as UV sensitizer and trap center respectively.

Our purpose is to improve the persistent luminescence and to better understand the related mechanism. The persistent luminescence of these materials has been evaluated and thermoluminescence has been used. For instance TL glow curves of CZMSO are presented in figure 2. At the conference the effect of the matrices structure ($Ca_{0.2}Zn_{0.9}Mg_{0.9}Si_2O_6$ (CZMSO) in comparison with $CaMgSi_2O_6$ (CMSO)), and several dopants capability will be discussed.

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BIOCOMPATIBLE CALCIUM PHOSPHATES WITH RED LONG LASTING PHOSPHORESCENCE FOR *IN VIVO* IMAGING

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Calcium HydroxyApatite (HA) and TriCalcium Phosphate (TCP) are the two most well-known human biocompatible materials [1]. These compounds are the natural constituents of bones and teeth and as such, are widely used for the synthesis of human bones protheses. On the other hand, in these structures, calcium can easily be substituted by luminescent ions such as transition metal ions (Mn^{2+}) or rare earth ions (Eu^{3+}) for lighting applications.

These two properties of HA and TCP made them the candidates of choice for the application of Long-Lasting Phosphorescent (LLP) markers used in a new technique of *in vivo* imaging [2]. In this technique the luminescent marker is excited by a UV lamp only once (for several minutes) before being injected to the animal. The marker is a long-lasting phosphor emitting in the red region (λ>600 nm) so that its phosphorescence lasts for several minutes and can be detected through the animal living tissues.

Using a co-precipitation method and some annealing steps, HA and TCP powders of different structure were synthetised by playing with the ratio of Ca/P and the annealing temperature. Then manganese doping was introduced in order to obtain a broad band of luminescence from the $^4T_1$ -> $^6A_1$ transition of Mn^{2+}. In HA Mn^{2+} substitutes Ca^{2+} in a weak crystal field positions (Ca(1) and Ca(2)) leading to orange luminescence. In TCP, we found that Mn^{2+} subsitutes only Ca(5) which is the tightest site of the structure to produce a stronger crystal field around Mn^{2+} and emits red luminescence. Emission and excitation spectra were studied.

As HA:Mn^{2+} and TCP:Mn^{2+} do not present any intense absorption band matching with the emission spectrum of the UV lamp, Ce^{3+} co-doping was introduced to sensitize Mn^{2+} luminescence.

Long-lasting phosphorescence was studied. It was found that TCP compounds are much better candidates than HA for LLP *in vivo* imaging and Ce^{3+} co-doping improved LLP. The results will be discussed in relation with the structure of the materials.

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TRIPLET STATE LIFETIME AND ACTIVATION ENERGIES OF EPOXY RESIN MODIFIED BY CARBAZOLE

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The next generation of flat panel displays seem to be polymer electroluminescent devices. They have been extensively investigated in last years. High luminescence intensity, low drive voltage and broad emission spectrum are the most interesting properties of these materials. They are prepared from solution by spin coating method. It is cheap technique because it does not require expensive high vacuum equipment

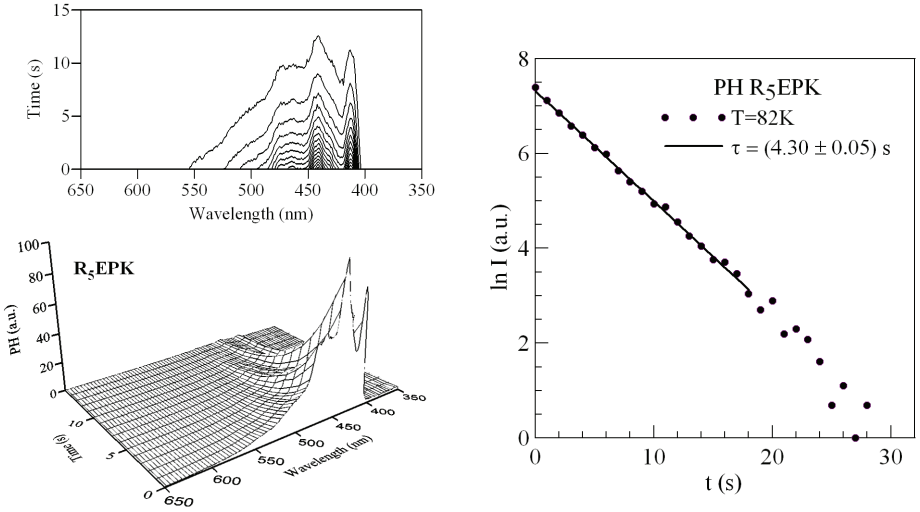

Fig. 1 Phosphorescence decay of R_5EPK thin film excited by 286 nm light at T = 82 K.

This paper presents results of phosphorescence (PH) temperature dependence studies performed with 9-(2,3-epoxypropyl) carbazole (EPK) added to epoxy resin(R) (R_5EPK - 5% weight content of the carbazole group in polymer). Spectrally resolved phosphorescence decay of R_5EPK in temperature 82 K is shown in Fig. 1. Lifetime of the triplet state (τ_P) of R_5EPK was calculated in the temperature range 80K – 200K on the basis of first order kinetic approach. The phenomenon of nonradiative deactivation of the excited aromatic molecule in the lowest excited triplet state to the ground state were studied. Lifetime measurements enabled us to determine activation energy distribution. An interpretation of the results in terms of interaction between solid-state matrix and carbazole group will be given.

INDENTATION HARDNESS OF GLASSES OF Cu-As-Se-I SYSTEM

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As a part of general physical characterization of chalcogenide glasses, mechanical properties of $Cu_x[(As_2Se_3)_{0.9}(AsI_3)_{0.1}]_{100-x}$ glasses with x = 5, 10, 20, 25 at. % were examined. The measurements were performed on bulk glass samples using indentation technique with Vickers diamond indentor. Martens hardness, indentation hardness, hardness value according to Vickers and Young's modulus were calculated from the indentation load-displacement curves. It was shown that all these parameters increase linearly with the increase of copper content. Since chalcogenide glasses are generally very brittle, copper addition is justified because of the mechanical properties improvement.

MECHANICAL AND THERMAL PROPERTIES OF ELASTOMERIC COMPOSITES FILLED WITH NANO-SILICA PARTICLES

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In this applicative contribution the reinforcing effect of nanosized silica filler (15 nm average size of primary particles) was studied. Four types of rubbers were used as network precursors: styrene butadiene rubber (SBR), natural rubber (NR), butadiene acrylonitrile rubber (NBR) and polychloroprene (CR). The effect of nano silica on the elastomeric composite properies was compared with the influence of micro-silica (28 μm average size). The cure characteristics, mechanical properties and thermal stability were estimated by oscillating disc rheometer, stress-strain measurements and thermogravimetric analysis, respectively. It was determined that natural rubber greatly improve the crosslinking process by shortening the time to optimum cure (t_{90}) and prolonging the setting-up time (t_{10}), which improves production efficiency and operational security. It was assessed that the tensile strengths of nano-silica samples were close to micro-silica composites, but the tear strength and modulus of nano-composites were better. The good interfacial interactions between the nano particles and rubber macromolecules influenced excellent mechanical properties, and enhanced thermal stability.

RADIOLYTIC SYNTHESIS AND CHARACTERIZATION OF THERMORESPONSIVE Ag/PNIPA HYDROGEL NANOCOMPOSITES

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The radiolytic synthesis of nanocomposites of silver nanoparticles (AgNPs) within thermoresponsive poly(N-isopropylacrylamide) (PNIPA) hydrogel was studied. PNIPA hydrogel was previously obtained by gamma irradiation induced polymerization and crosslinking. The *in situ* reduction of Ag^+ ions was performed using strongly reducing species, such as hydrated electrons and 2-propanol radicals, formed under the irradiation. PNIPA demonstrates a lower critical solution temperature (LCST) or transition temperature (T_{tr}) at about 32 ^{o}C in aqueous solution. Below this temperature, PNIPA is hydrophilic and dissolved in water. However, it becomes hydrophobic, and the polymer chains exist in a collapsed state and precipitate out from the aqueous solution as the temperature is increased above the LCST. Correspondingly, the crosslinked, three-dimensional PNIPA hydrogel exhibits phase separation and changes volume abruptly in response to the variations of the external temperature changes. Below the LCST, PNIPA hydrogel absorbs a lot of water and exists in a swollen state. As the temperature is increased above LCST, PNIPA gel shrinks dramatically and collapses in volume thermoreversibly. LCST of hydrogels, neat PNIPA and Ag/PNIPA nanocomposites, were determined gravimetricaly by swelling procedure at different temperatures and by DSC measurement. The swelling behavior of synthesized hydrogels in the water, at a room temperature, also was determined. Absorption spectra of Ag/PNIPA nanocomposites indicated the presence of typical surface plasmon absorption band of AgNPs, with peak maxima around 400 nm (particles with diameter less than 10 nm). XRD measurement showed the Bragg's reflections from crystal planes which corresponds to the *fcc* structure of AgNPs. Interaction between nanoparticles and polymer matrix was investigated by IR spectroscopy. By ICP measurement release of silver from hydrogel nanocomposites was investigated. Due to its unique swelling properties, materials based on PNIPA hydrogel has been utilized in many different areas such as catalysis, optics, electronics, pharmaceutics and biomedicine.

SYNTHESIS OF SILICA CORE / FERRITE SHELL PARTICLES FOR ENCAPSULATION OF ENZYMES

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Recently, a variety of nanomaterials have been defined as promising candidates for bioengineering applications because of the unique characteristics inherent to the nanoscale. For these purposes, assembling of distinct nanoparticles on the surface of silica spheres (i.e. formation of a core/shell structure) using different chemistries and techniques seems very promising. Monodispersed silica particles were synthesized via the hydrolysis and condensation of silicon alkoxide in alcoholic solutions in the presence of water and with ammonia as catalyst. These submicrometer spheres were utilized as templates for the assembly of different type of zinc-ferrite nanoparticles to obtain desirable shell structures. Structural characterization confirmed that the formation of desired core/shell structure requires the careful control of key processing parameters.

PLASMONIC OPTICAL ENHANCEMENT IN HYBRID DEVICES FOR BIO SENSORS

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We present two conceptionally different models to calculate electromagnetic field distributions in multilayer metal-organic structures used for bio sensoring [1].

The excitation of plasmonic oscillations at the surface of nanostructured devices can create strong local field enhancement as exploited in near-field optical microscopy [2] (NSOM/SNOM) and surface enhanced (resonant) Raman spectroscopy (SE(R)RS) [3].

In this contribution, we particularly investigate hybrid, metal-organic devices used for the detection of small amounts of proteins. Hybrid devices are promising in particular to combine advantageous electrical, optical and chemical properties of different metallic layers.

Our calculations are performed in a quasistatic limit to describe near-field effects at roughened metallic surfaces with multiple coatings.

The first model provides a good understanding of the transport of optical energy in such devices. It is based on a concentric multilayer structure system in full spherical symmetry, only allowing dipole solutions.

The second model, taking more realistic geometries via higher multipoles into account, gives an even more accurate picture of the enhancement effects. This is achieved by applying an image dipole method [4].

We compare the spatial and spectral distribution of common SE(R)RS electrodes with the novel Ag-Au hybrid device pointing out its advantages [1]. We briefly show the dependence of enhancement effects on the layer thicknesses to demonstrate the interplay of metallic and organic layers.

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LUMINESCENCE INDUCED BY ELASTIC AND PLASTIC DEFORMATION OF γ-IRRADIATED KCl CRYSTALS

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A large number of organic and inorganic solids emit light during their deformation and fracture. This physical process of light emission induced by any mechanical action on solids is known as mechanoluminescence (ML). The light emissions induced by elastic deformation, plastic deformation and fracture of solids are called elastico-ML, plasticoML and fractoML respectively. For a long time it was thought that mechanoluminescence appears only during fracture of solids. In 1960`s it was reported for the first time that ML also appears during elastic and plastic deformation of coloured alkali halide crystals. When a γ-irradiated KCl crystal is compressed slowly at a fixed strain rate, then initially the ML intensity increases linearly with deformation time, and later on it attains a saturation value. When the compression is stopped, then initially the ML intensity decreases at a fast rate and later on it decreases slowly with time. Considering the occurrence of ML owing to the mechanical interaction between dislocations and F-centres, expressions are derived for the dependence of ML intensity on different parameters such as strain, strain-rate, density of F-centres, temperature, size of crystals, etc. The expressions derived are able to explain successfully the different characteristics of ML. It is shown that several parameters of crystals can be determined from the ML measurements.

STRUCTURAL AND MAGNETIC PROPERTIES OF NANOPARTICLE $La_{0.7}Ca_{0.3}MnO_3$ MANGANITES OBTAINED BY MECHANOCHEMICAL PROCEDURE

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Mechanochemical procedure was used to produce mixed valence manganite $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) from corresponding metal oxides. The samples were characterized by using X-ray diffraction, scanning electron microscopy and magnetic measurements. The results showed that it is possible to produce single phase LCMO perovskite powders after 3 h of ball milling. Prolonging milling time, up to 15 h, results in decreasing of crystallite size, strain as well as stabilization of crystal structure. DC magnetic measurements, performed in different magnetic fields showed phase transition at temperature T_B which is assigned to blocking temperature of the single domain nanoparticles. M(H) measurements at constant temperature $T<T_B$, exhibit hysteretic curves, showing ferromagnetic character of the sample. The dynamic properties of 10 h ball-milled sample were investigated by AC susceptibility using the Neel–Brown and Vogel–Fulcher model for superparamagnetism. Structural and magnetic properties depending of milling time are discussed, and compared with the similar samples, obtained by different chemical routes.

APPLICATION OF Ti: SAPPHIRE LASER FOR EXCITATION OF LOCALIZED WAVE PACKETS

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Wave packets of Rydberg states are one of the examples of designing controllable quantum states of electrons. They are a good approximation for coherent states and demonstrate the properties of both quantum and classical motion. The problem of creating a localized packet is to populate the Rydberg states with high values of quantum numbers in all degrees of freedom. Laser pulse excitation is considered to be one of the possible ways of solving this problem [1]. We performed a numerical simulation study of population dynamics in a hydrogen atom driven by a laser pulse in order to estimate the possibility of Rydberg wave packet formation.

The model Schrödinger equations for population amplitudes were solved numerically in the finite, but large enough basis of hydrogen atom eigenstates of discrete and continuous spectrum. The continuum was represented by a sequence of states with equidistant values of the wave number k [1]. We consider the action of a circularly polarized field, hence, the transitions satisfying the selection rules $\Delta l = 1$, $\Delta m = 1$ are allowed only. The pulse duration of 48 fs and the central wavelength of 780 nm used in the calculations were taken to correspond to the parameters of the multiterawatt Ti:sapphire laser system [2]. The approximation of continuum by a sequence of closely-spaced discrete levels requires special measures to account for irreversible nature of atomic ionization (the ionization losses). This is done by introducing artificial level width providing dissipation in the system.

The suggested model, including discrete and continuum states with different values of orbital and magnetic quantum numbers and accounting for "horizontal" transitions within n-manifold of states, differing in l [1] and m, exhibits a sophisticated population dynamics under the action of a laser pulse, in which one can distinguish both transitions between discrete states, and cascade transitions between discrete and continuum states, sequentially increasing the values of orbital and magnetic quantum numbers. Thus a laser pulse with the amplitude of $4.59 \cdot 10^8$ V/cm provides almost total depopulation of the ground state and forming of the wave packet comprising the states with high values of n, l and m. However, in this case 72 % of the total population is lost due to ionization. The low-laying states are populated more significantly. It is explained by relatively low frequency of field. A train of pulses is expected to populate the Rydberg states with high values of n, l and m as sequent pulses with lower amplitude increase the quantum numbers in all degrees of freedom.

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SPECTROSCOPIC AND OSCILLATION PROPERTIES OF Nd^{3+} OPTICAL CENTERS IN SrF_2 CRYSTAL

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Spectroscopic properties of Nd^{3+} ions in SrF_2 crystal were investigated. The absorption and fluorescence spectra of different individual and clustered optical centers were observed depending on Nd^{3+} ions concentration (see Fig. 1). Two types of optical centers were found to predominate for neodymium concentrations below 0.5 at.%. The lifetimes of the high symmetry (Nd^{3+} - F^-) L-centers were measured and found to be two orders of magnitude longer than that for clustered $(Nd^{3+}$ - $F^-)_2$ M-centers (see Fig.2) at room temperature. The lifetimes of M-centers at different temperatures were measured and microparmeter of ion-ion interaction in Nd-pairs was determined (see Table 1). The laser properties of SrF_2:Nd^{3+} crystal with neodymium ions concentration of 0.5 at.% containing high symmetry tetragonal optical centers L together with low rombic symmetry clustered M-centers were investigated under diode laser pumping. Using temperature tuning of laser diode pumping wavelength two different lines centered at about 1037 nm and 1044 nm attributed to oscillation of different optical centers were obtained (see Fig. 3). The slope efficiency of 17% was obtained for short wavelength oscillations at 1037 nm without optimization.

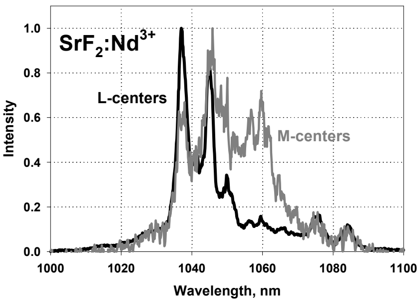

Fig. 1 Fluorescence spectra of L and M optical centers in SrF_2:Nd^{3+} crystal.

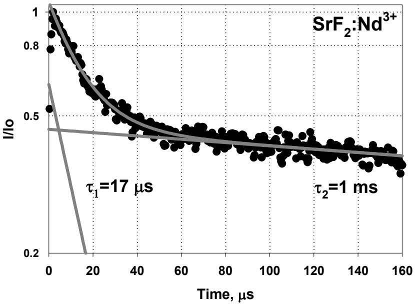

Fig. 2 Decay of L and M optical centers in centers in SrF_2:Nd^{3+} crystal.

Table 1.

SrF_2 : 0.5mol.% Nd^{3+} [Rmin = 0.409nm]			
T(K)	300	77	10
τ(μs)	17	115	237
C_{DA}(cm^6/c)	$2.75*10^{-40}$	$4.07*10^{-41}$	$1.96*10^{-41}$

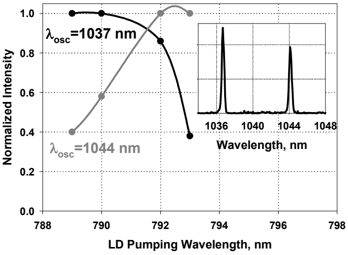

Fig. 3 Normalized intensity of oscillating lines vs LD pumping wavelength

NANO-SCALE PHOTONIC STRUCTURES

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Photonic crystals are artificially created periodic structures of dielectric materials, which are expected to play a significant role for future all-optical circuits. Among the different fabrication methods the self-assembly of colloidal microspheres provides a simple and inexpensive approach to the fabrication of 3D photonic crystals and we obtained some significant results. In this work we report on direct and inverse opal structures as well as on nanospheres activated by Er^{3+} ions. High quality synthetic opal photonic crystals were formed by controlled self-organisation of colloidal silica spheres. A sol-gel fabrication protocol was elaborated obtaining silica microspheres of 270 nm diameter with a polydispersivity less than 5%. We have demonstrated that large well-ordered crystals of synthetic opal can be produced starting from these spheres by vertical deposition or evaporation-assisted sedimentation. Transmission measurements permitted to estimate the peak broadening effect $\Delta\lambda/\lambda c = 0.07$ and the value of stop band depth of 40%. Er^{3+}-activated inverted opals were fabricated by the sol-gel process. The template was prepared using a vertical deposition technique and the void spaces of the opal template were then infiltrated by silica sol activated by erbium ions. The average dimension of the air-hollows was ~210 nm. The inverse opal exhibited violet regions, and the reflected light was easily observed by the naked eye, because the bright colour resulted from optical Bragg diffraction from the crystal planes. Stop band was between 260-300 nm, as a function of the incident angle used in the reflectance spectra. The inverse opal exhibits a main emission peak at 1540 nm and a quantum efficiency of 90% was estimated. Nanospheres were prepared by acid catalysis and seeded growth core-shell technique and quantum efficiency higher than 70% was demonstrated, making these systems perspective candidates for efficient luminescent markers and nanosensors. The core-shell fabrication process, moreover, allowed us to obtain a large quantity of monosize Er^{3+}-doped spheres, perfectly suitable as building blocks of ordered structures such as active photonic crystals.

THE USE OF ARTIFICAL NEURAL NETWORK (ANN) FOR MODELING OPTICL PROPERTIES OF HYDROTHERMALLY SYNTHESIZED ZnO NANOPARTICLES DESIGNED BASED ON DOEHLERT METHOD

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In the present work, the influences of synthetic parameters on the optical properties of hydrothermally synthesized ZnO nanoparticles were investigated. Multivariate experimental design was applied to study the growth behavior and optical properties of obtained nanoparticles. Doehlert experimental design allowed determining the influence of three parameters (Synthesis temperature; synthesis period; and, initial concentration of precursors) on the different properties of the obtained nanoparticles; including: crystallite size obtained from Debby-Scherer calculation, exciton energy and band-gap energy obtained from optical absorption spectra of synthesized nanoparticles. Experimental data were fitted using artificial neural networks (ANNs). The reproduced experimental data from mathematical model show a confidence within 86% and allows the simulation of the process for any value of parameters in the experimental range studied. Also, the saliency of the input variables was measured using the connection weights of the neural networks in which the relative relevance of each variable with respect to the others was estimated. Results showed that the crystallite growth of obtained nanoparticles intensifies by increasing in hydrothermal time and temperature. Increase in crystallite size influences the optical properties of the obtained nanoparticles. All obtained particles showed blue shift respect to bulk zinc oxide which could be related to small crystallite size of the obtained nanoparticles. The ANN results indicated that the exciton band edge which was observed in UV-Vis spectra of the obtained nanoparticles due to confinement effects, increase by increasing the crystallite size while the band gap shows shrinkage as shown in Fig. 1.

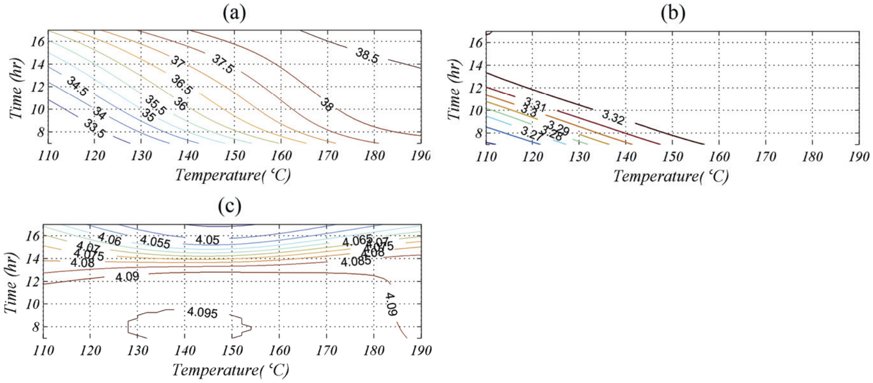

Fig. 1 Counter maps for ANNs simulation for modelled a) Crystallite size[nm]; b) Exciton energies[eV]; and, c) Band-Gap[eV] for initial 0.75mol Of $Zn(Ac)_2$ and 1.5mol NaOH concentrations.

MAGNETO-OPTICAL KERR EFFECT IN GLASS/Cu/SnO$_2$/Co/SnO$_2$ THIN FILMS

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We report the Kerr signal enhancement of a Co thin film incorporated into Cu/SnO$_2$/Co/SnO$_2$ quadrilayer structure deposited onto a glass substrate. We have investigated the effect of semiconductor cap and spacer layers on the magnitude of the polar and longitudinal Kerr signals. In order to design an optimized structure we have used the theoretical calculations, based on a 4×4 matrix method [1]. The polar and longitudinal Kerr signals were calculated as a function of the cap and spacer layers thicknesses. The results are shown in Fig. 1 for red light and an incident angle of 20°. In this figure, Cu and Co thicknesses were fixed at 40 nm and 20 nm, respectively.

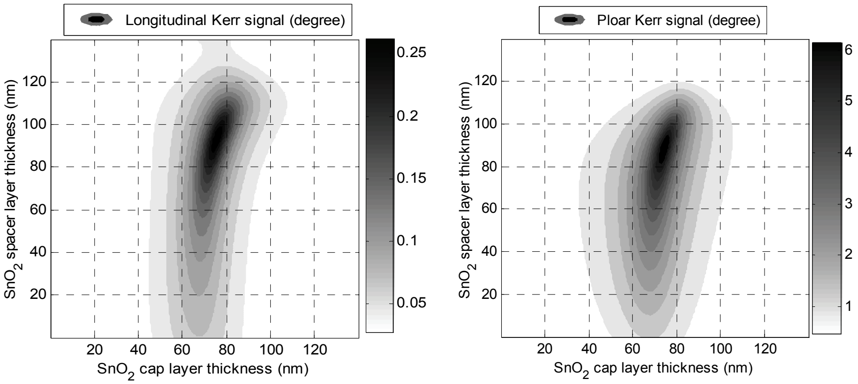

Figure 1: Dependence of the longitudinal (left) and polar (right) Kerr signals of glass/Cu/SnO$_2$/Co/SnO$_2$ films on the cap and spacer layers thicknesses.

Regarding the theoretical results, we have prepared samples using electron beam and conventional evaporation techniques. The magnetic behaviour of the samples has been investigated using the Kerr technique in polar and longitudinal configurations. The soft in-plane magnetic behaviour of samples indicated that they all have in-plane magnetization. The experimental results also confirmed the enhancement of Kerr signals predicted theoretically.

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OPTIMIZATION OF STRUCTURAL PROPERTIES OF TIO_2 COMPACT LAYER FOR 3D NANOSTRUCTURED TIO_2 BASED SOLID STATE DYE SOLAR CELLS

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Photovoltaic designs based on non-silicon nanostructured materials, which allows low cost production offer inexpensive and reliable, solar-based renewable power.

All solid state dye solar cells consist of a nanoporous interpenetrating network of a *n*-type material (TiO_2) a dye layer, like Ru organo-metallic compounds, that collect the light and transfer an electron to the n-type semiconductor and a *p*-type semiconductor that collect the holes (e.g.,Spiro-OMeTAD) [1]; in some cases dye and *p*-type semiconductor can be constituted by the same material (e.g. $CuInS_2$). The all inorganic 3D nanocomposite TiO2/$CInS_2$ solar cells have achieved energy conversion efficiency grater then 5% and because of the kind of technology implied it shows a promisingly possible integration with the building industries.

Performance of the solar cells could be sensibly influenced by the quality of the compact TiO_2 layer [2].

The aim of this paper is to investigate the influence of deposition conditions on the quality of compact TiO_2 thin films to be used in 3D nanocomposite TiO2/$CuInS_2$ solar cells.

An Ultrasonic Spray Pyrolysis (USPD) system using a piezoelectric-atomizing nozzle and nitrogen carrier gas was employed. TiO_2 thin films were deposited on glass or glass/FTO substrate using TAA-Di-isopropoxy titanium bis(acetylacetonate), as a precursor plus ethanol with different concentration.

The films are prepared at substrate temperatures 350 and 420 ^{o}C. After deposition samples are subjected on two steps annealing treatment: 1h in air at the deposition temperature and 1 h on 500 ^{o}C.

Investigations of the films were made by Raman, UV-VIS Spectroscopy, SEM, AFM and Contact-step Profiler.

Preparative parameters like solution concentration, quantity of spraying solution, noozle-to-substrate distance, applied power to the piezoelectric atomizer, solution and nitrogen flow rate are optimized to obtain uniform, pin-hole free and adherent films. Films were deposited with identical conditions and characterized in order to check their reproducibility. In order to improve further the structural quality of TiO_2 compact films the multi-layer structure were perform by adding spin coated TiO_2 compact films, before and after sprayed one.

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OBTAINED MESOPOROUS ALUMINA FROM ALUMINA HYDROXIDE NANOPOWDERS USING GLUCOSE TEMPLATE

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Mesoporous materials have been intensively studied during the last decade due to their excellent properties, such as high surface area and narrow range of porosity, which enabled them to be applied in a very wide range of applications. Alumina as mesoporous material has very broad possibilities of application in ceramic industry, in catalysis, as an adsorbent, biomaterial, reinforcement of metal–matrix composites etc. It is well known that beside α-alumina, as the most stable phase, alumina appears in a large variety of metastable crystallographic forms with very diverse and intrigant properties. The main subject of this work was to elucidate the conditions of obtaining mesoporous active alumina phase, γ and η alumina. Glucose, which has shown special abilities in creating amorphous mesoporous silica materials, was used as a template for creating mesoporous structure of alumina. Two groups of samples were prepared for the investigation of the effect of glucose on formation of alumina mesoporous structure. In the first group of samples, this organic additive was used as water suspension with aluminum hydroxide, AH, or aluminium oxohydroxide, AOH, nanopowders which were dried at 100°C in air to remove water and all other volatiles. The resulted solids were then heat treated up to 600°C, for a different time to remove the template. The molar ratio of Al^{3+}: glucose: H_2O in the suspensions was 1:0.1:35. The other group of mesoporous alumina was prepared in a similar way, but glucose was added in the Bayer liquor during synthesis of AH and AOH nanopowders (boehmite, pseudoboehmite, bayerite or gibbsite). These powders were synthesized via neutralization of the sodium aluminate solution using sulfuric acid. The powders were characterized using: FT-IR spectroscopy, BET, DTA/TG, XRD, and SEM. The obtained results showed that the use of glucose as a template had an effect on the increase of the surface area of mesoporous alumina (which was up to 500 m^2/g) and on narrowing the pore size distribution, where the mean size was approximately 5 nm. The effect of glucose on the increase of the surface area of mesoporous alumina is more pronounced for samples prepared by the second method. The phase compositon of mesoporous alumina depends on the composition of the starting powder and results have confirmed that bayerite as starting powder is favorable for obtaining η-phase with high surface area (374 m^2/g) even without glucose, but with wide pore distribution.

DYNAMIC-MECHANICAL AND OPTICAL PROPERTIES OF PMMA-Gd_2O_3 (Eu^{3+}) NANOCOMPOSITES

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This study reports research related to processing and characterization of polymer optical nanocomposites, which are very promising materials for optical fibers used as hybrid light guides cables. In the host matrix of PMMA the Eu-ion doped Gd_2O_3 nanophosphor powder was dispersed and nanocomposites were produced by mixing molder device. Composite samples were fabricated with various content of particles, which were dispersed using solution casting method. For comparison purposes, composites with pristine Eu-ion doped Gd_2O_3 nanophosphor powder were fabricated and tested.

The influence of processing parameters and particle content on their de-agglomeration and distribution degree in composites and, consequently, on the optical and dynamic-mechanical properties of nanocomposites were investigated. The structure and the particle size distribution were investigated by X-ray diffraction (XRD) microstructure of composite by scanning electron microscopy (SEM); the optical properties of pristine particles and obtained nanocomposites were investigated by laser-excited luminescence spectroscopy. Dynamic-mechanical analysis was performed in determination of mechanical properties of nanocomposites (storage modulus, loss modulus, damping ratio).

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SYNTHESIS AND CHARACTERIZATION OF NIOBIUM DOPED 1D TITANATE

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It is well known that one-dimensional (1D) nanostructured materials have a very diverse possibilities of application in respect to their bulk counterparts due to specific structural characteristics, such as high aspect ratio and large surface area. Titania based 1D materials (nanotubes, nanorods, nanowires, nanobelts) are one of the most promising semiconducting ceramic materials because of their wide range of potential applications in nanoelectronics, in optical and sensor devices, in solar cells etc. One of the most important challenges in obtaining 1D based titanate materials is to achieve precise control of the size, dimensionality, composition and crystal structure at nanoscale. Appropriate solution of this problem could be a powerful tool for the tailoring of the properties suitable for desired applications. A significant improvement in properties of 1D titanate could be attained by introducing different types of dopants into their structure. In this work Nb-doped one dimensional titanate structures were synthesized via simple hydrothermal procedure at 150°C for a different time and starting from two different solutions. The first starting mixture was highly alkaline solution of the commercial TiO_2 powder (Degussa P25) and $NbCl_5$ powder and the other was alkaline solution of previously synthesized anatase powder doped with proper amount of Nb ion. Finally obtained powders were characterized by BET, XRD, FT-IR spectroscopy and SEM with energy-dispersive X-ray spectroscopy, EDS. The obtained results confirmed successfully synthesized Nb-doped one dimensional titanate structures only after 1h of hydrothermal reaction. There was an obvious change in the FT-IR spectra of the shape and position of the band characteristic for octahedral building blocks which could probably indicate that Nb was introduced into the titanate structure. Doped 1D titanates obtained from P25 showed high increase in a value of specific surface area (even higher than 300 m^2/g) in respect to starting powder.

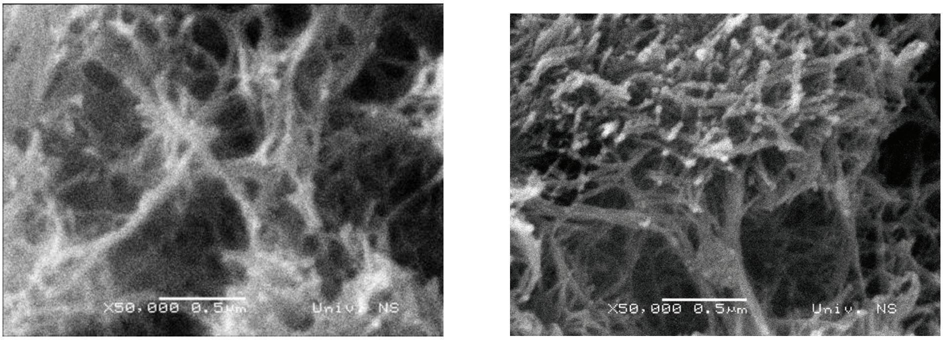

Fig.1. SEM micrograph of 1D titanate obtained from different starting solutions

NUMERICAL STABILITY ANALYSIS OF (3+1)-D GENERALIZED NONLINEAR SCHRÖDINGER EQUATION WITH DISTRIBUTED COEFFICIENTS

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We present numerical stability analysis of exact spatiotemporal periodic traveling wave solutions to the generalized (3+1)-dimensional nonlinear Schrödinger equation with distributed coefficients, using adaptive higher order split step Fourier method. Stable, oscillating and chaotic dynamics is observed.

RECONSTRUCTION OF THE OPTICAL DEPTH STRUCTURE FROM PHOTOTHERMAL RESPONSES

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The mathematical model is derived relating arbitrary variation in the depth-dependent optical absorption coefficient to observed temperature variations at the surface of a sample. The direct and inverse relations between the heat source profile and frequency spectra are investigated. Based on these results a reconstruction theory of optical depth profile from photothermal responses is presented. The performance of suggested approach is illustrated by numerical simulations using well-defined artificial samples with varying optical properties across the layers.

PHOTOTHERMAL CHARACTERIZATION OF ULTRATHIN FILMS AND COATINGS

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This paper describes applications of photothermal techniques for measurement of the thermal properties of ultrathin films deposited on substrates. The one-dimensional problem of heat waves propagation for a two layer system is solved assuming the surface absorption model of the optical excitation. The analytical solution is shown to be suitable for the implementation of normalized depth-profilometric methodologies for thermal properties measurement that eliminates some thermophysically nonrelevant proportionality factors in theoretical equations. The application of potential interpretation method based on derived model with respect to the on-line control of coating deposition processes is discussed.

KINETICS OF EXCITATION IN TL AND OSL DETECTORS

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Thermoluminescence (TL) optically stimulated luminescence (OSL) are widely known techniques, frequently used for characterization of traps and recombination centers (RCs) in insulating materials. Commercial applications include dosimetry of ionizing radiation and dating of archeological and geological objects. Prior to the measurement a sample is excited at appropriately low temperature to fill traps and RCs with charge carriers. Then, the sample is heated, usually with a constant rate (in TL) or stimulated by a strong light (in OSL). Then, the emitted luminescence is recorded. The luminescence is related to recombination of charge carriers, which were thermally or optically released from traps and then moved to RCs.

Theoretical description of these processes is usually based on two models: the model of localized transitions (LT) and the simple trap model (STM). The first one (the LT model) allows trapped charge carriers to recombine solely to adjacent RC. The second one (STM) assumes transition of charge carriers via conduction band. These transitions are delocalized. Recently [1] a more general model was proposed combining both localized and delocalized transitions. This is the model of semi-localized transitions (SLT). Analytic equations for SLT are constructed using enumeration technique which transforms concentrations of carriers to concentrations of states of localized trap - recombination centre (T-RC) pairs. The model allows explaining some unusual properties observed in TL measurements (e.g. the occurrence of very high frequency factors [2]).

This paper presents formulation and exemplary application of the SLT model to the analysis of excitation processes, which are very important to future analysis of TL and OSL output. It shows how various factors determine initial conditions for these measurements. Possible consequences for the analysis of TL and OSL in terms of standard kinetic models – LT and STM – are discussed also.

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LUMINESCENCE AND ENERGY TRANSFER FROM ACAI OIL IN POLYSTYRENE MATRIX

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We investigated the optical properties of the acai oil extracted from a Brazilian Amazon plant embedded in polystyrene (PS) matrix. By doing this, we expect to introduce new properties in the polymeric matrix and check their availability for the construction of light-emitting devices. Energy transfer experiments were realized using a confocal microscope adapted for scanning the luminescence on the sample surface with micrometer spatial resolution. Luminescence from the sample has been provided by huge amount of chlorophyll molecules found in the acai oil. Two main emission peaks were observed, one peaking at 621 nm and the second peaking at 654 nm. The higher energy peak corresponds to the fluorescence of the monomeric form of the chlorophyll molecules; otherwise the lower energy peak is due to chlorophyll fluorescence in aggregated form [1]. The energy spatial transfer coefficient equivalent to the photon migration length was measured using the confocal technique [2]. The photon migration length increases by increasing the oil concentration. The diffusion lengths were measured for specific wavelengths. The migration length is also larger at 654 nm compared to 621 nm, showing the energy transfer from higher energy states to lower energy states. For this reason, re-absorption by ground and excited states has played a crucial role in the energy propagation. The technique was very useful for investigation of energy transfer processes in chlorophyll molecules doped systems. The spatial distribution of the luminescence was measured, and the transfer among chlorophyll molecules was discussed. All these processes verified so far allows classify the system oil/PS as a good candidate to be employed in optical electronic devices.

Acknowledgements: The authors are grateful to CNPq and FAPEMIG for financial support and Prof. S. G. C. Moreira for the acai oil.

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CHARACTERIZING THE CARRIER DIFFUSION IN SELF-ASSEMBLED QUANTUM DOTS BY USING AN OPTICAL TECHNIQUE

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Many studies regarding InAs/GaAs self-assembled quantum dots (SAQD) reported that photoexcited or electrically injected carriers are generated in the barriers or in the wetting layer (WL) before their capture into the quantum dots (QDs) [1]. Evidently, during this capturing process, carriers experience migration in the barriers and WL. This fact demonstrates a great importance of the carrier transport processes besides capture into the semiconductor structures for the improvement of the optoelectronic and electronic QD-based devices [2,3]. Recently, new features on the enhancement of carrier capture rate due to an external applied field have been explained [4]. The InAs/GaAs SAQD samples were grown by the Stranski-Krastanov mode using molecular beam epitaxy (MBE) to achieve a p-i-n structure. The final arrangement of the sample was consisted of five layers of InAs dots separated by 20 nm of undoped GaAs. The dots had a density of $5x10^{10}cm^{-2}$. Metallic contacts with optical access were employed in the QD mesas with diameter of 400 μm in order to apply the electric field across the intrinsic region. A microluminescence surface scan technique has been developed in order to investigate the influence of external electric fields in the dynamics of carriers in InAs QDs [5]. The measurements were performed at 77 K with excitation at 632 nm from HeNe laser. The laser beam was tightly focused in a micro-sized spot on the sample surface by a microscope objective. Backscattered light collected from the sample is directed to an optical fiber attached to the spectrometer. The results reveal that the carrier diffusion increases with the direct external electric field. Eventually the diffusion decreases with the field after maximum value. The maximum value of the carrier diffusion and its energy dependence is highly important to understand the whole dynamics in QD devices.

Acknowledgements: The authors are grateful to CNPq and FAPEMIG for financial support.

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RARE EARTH DOPED FLUORIDE NANOPARTICLES FOR BIOLOGICAL LABELING AND IMAGING

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RE doped inorganic materials have demonstrated a huge application area (display, lasers and amplifiers for telecom…) and more recently in biological applications. Ignored from this area until few years ago, a lot of works are now devoted to synthesis and optical spectroscopic studies of RE inorganic nanoparticles for biological applications. On the contrary to other commonly used optical probes (dyes, Quantum dots, fluorescent proteins), RE doped materials even in nanometer scale are extremely stable under high powerful excitation (most of them are used as laser sources for industrial or military applications). Quantum confinement due to the size reduction is inefficient for sizes higher than 5-8 nm and their luminescence efficiency can be maintained; it is also insensitive to pH variation (unaffected in a pH ranging from 2 to 7.4) which is very important for biological applications and finally can be synthesized in a dispersible form in water or physiological buffer. Moreover, whatever the composition (oxide, fluoride….), nanoparticles (Nps) surfaces are easily modified (core shell structure or functionalized) which make them as potential very sensitive biosensors or biolabels. Concerning their biocompatibility, several works have already demonstrated the biocompatible character of the RE doped nanoparticles [1, 2]. One of the first studies on use of RE doped NPs in biological media has demonstrated the ability of RE doped NPs to control the cell internalization of Eu^{3+} doped phosphate NPs under Laser Confocal Microscopy [3].
Rare earth doped LaF_3 nanoparticles have been synthesized (RE= Eu^{3+}, Er^{3+}/Yb^{3+}, Tm^{3+}/Yb^{3+}). This host belongs, due to its low phonon cut-off frequency, to the most efficient one for upconversion process. Stable colloidal suspensions in water have been achieved. From light diffusion scattering and MET analysis, the mean diameter of the synthesized NPs lies between 20-35 nm. The spectroscopic study of Eu^{3+} doped NPs was conducted on particles dispersed in water. Emission from $^5D_2$, $^5D_1$ and $^5D_0$ states allows to demonstrate that main part of the emitting centers are protected from the environment (especially away from coupling with OH vibrations) keeping their high luminescence efficiency comparable with that of the single crystals. Time resolved spectra were measured as a function of Eu^{3+} concentration from 1% up to 40%. Energy transfer processes will be presented.
Under infrared excitation @980nm, either green, red or blue emissions are observed in codoped Yb^{3+} -RE^{3+} NPS depending on the power and the concentration (RE= Er^{3+}, Tm^{3+}). The upconversion as well as the concentration quenching processes will be discussed.

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PHOTOCURRENT GENERATED BY UPCONVERSION EMISSION EXCITED BELOW THE c-Si ENERGY GAP OF A SOLAR CELL

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A new concept for solar cells with an improved efficiency has emerged based on the use of rare earth doped materials as upconverters. Even in the best state of the art solar cells, sub-bandgap radiation which represents a large fraction of the solar energy is non absorbed by the semiconductor. In the research devoted to 3rd generation solar cells, one of the proposed solutions consists in the use of photon addition to increase significantly the solar cell efficiency. In a photon addition type system, a large gap PV cell absorbs the high-energy photons of the solar spectrum whereas the IR photons are converted into higher energy photons and returned to the cell using a simple mirror.

Optical infrared (IR) to visible conversion is commonly observed in Rare Earth (RE) doped materials. In Er^{3+} single doped hosts, the IR window @1530nm can be exploited which is of a great technical interest to improve the efficiency of the most common solar cells based on c-Si. The absorption transition from the Er^{3+} ground state to the first excited state exhibits quite important oscillator strength and allows also to observe upconverted emissions from the NIR to the UV by ETU or ESA (Excited State Absorption). The upconversion process is more effective when the phonon cut off frequency is low, as it is the case with halides. Among them, fluorides are the most appropriate for this purpose due to their chemical stability. In this work, we focused our interest in single doped Er^{3+} fluoride materials demonstrating a very high IR→NIR conversion efficiency suitable for enhancing the performances of widely used c-Si based solar cells.

Absolute conversion efficiency has been measured. Efficiencies (i.e., ratio of emitted visible light energy to absorbed IR energy) up to 12% and 17% have been obtained with the most part due to the NIR emission @1µm. The studied materials demonstrate upconversion efficiencies among the highest published so far up to our knowledge. In spite of the fact that the up-conversion processes in rare earth doped materials are extensively studied up to now, there exist a very few publications reporting on the efficiency measurements. Due to the inherent nonlinearity of up-conversion process, such measurements need rather sophisticated procedure. The setup and method will be presented in details.

The tests of a complete system (bifacial c-Si cell+upconverter) were performed in order to prove the feasibility of the proposed concept. A light-generated current is measured in a bifacial c-Si solar cell by a 1.53µm excitation (well below the c-Si absorption edge) while the IR radiation @ 1.53µm is not able to generate a current in the cell alone. A model has been developed to describe the complete system and the theoretical values of the short circuit current are in complete agreement with the experimental ones.

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ON THE MECHANISM OF GENERATION OF VERY HIGH FREQUENCY FACTORS IN THE SLT MODEL

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Since many decades the occurrence of extremely high frequency factors (of the order of 10^{20} s^{-1} and higher) in many thermoluminescence (TL) materials was a challenge to the theory based on standard kinetic models. According to solid state theory considerations, the value of frequency factor should not exceed 10^{14} s^{-1}. The explain the discrepancy several complex and sophisticated kinetic mechanisms were proposed. Recently, new model was suggested for TL and optically stimulated luminescence (OSL) phenomena. This is the semi-localized (SLT) transitions model [1] which offers a simple and natural explanation of the high frequency factors enigma. The model assumes the existence of occupied trap-recombination centre (T-RC) pairs. The mechanism was called cascade detrapping (CD) phenomenon.

During TL and OSL processes trapped charge carriers may recombine during localized (within the pair) as well as delocalized (outside the pair) recombination. Both cases may occur simultaneously. The CD mechanism is taking place when the activation energy for detrapping is higher for T-RC pair with trapped electron and hole, than a T-RC pair without a trapped hole.

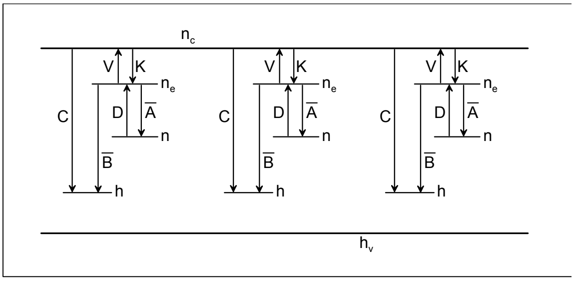

Figure 1: Energy band diagram for SLT model.

This paper examines various initial conditions leading to very high frequency factors. In particular, it is shown that specific excitation conditions may significantly change the value of estimated frequency factors. A comparison to earlier models and some experimental results is given also.

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NARROW GAP III-V MATERIALS FOR IR PHOTODIODES AND TPV CELLS

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Narrow gap III-V semiconductors are of interest from both the fundamental physics viewpoint and from viewpoint of IR optoelectronics. In recent years this class of materials has become the subject of extensive investigations because of the progress in developing infrared photodiodes, solar cells and thermophotovoltaic (TPV) devices for 2-5 μm spectral range. In this paper we present our results, including the growth of both GaSb-related and InAs-related materials and device investigation aspects. The chemical composition of GaInAsSb, GaAlAsSb, InAsSb, InAsSbP solid solutions was determined by X-ray spectral microanalysis. The crystalline quality of the grown epitaxial layers, the surface morphology and interface abruptness have been studied with PL, SEM, AFM, TEM, X-ray diffraction methods. The carrier density ***and mobility*** in the materials were determined through the study of the galvanomagnetic properties. An analysis of the GaInAsSb/GaAlAsSb and InAs/InAsSbP heterostructures performance through the investigation of optical and electrical characteristics was carried out. The spectral sensitivity distribution shows that for the GaInAsSb/GaAlAsSb heterostructure the half maximum wavelength ($\lambda_{50\%}$) of sensitivity determined by energy gap of the GaInAsSb active layer is 2.32 μm (Eg=0.53 eV) at room temperature. The monochromatic current sensitivity at the maximum of spectrum (λ=2.0-2.1 μm) is 0.8-1.0 A/W, which corresponds to a quantum efficiency of 0.6-0.7 without any antireflection coating. At the same time, for the InAs/InAsSbP heterostructure the half maximum wavelength ($\lambda_{50\%}$) of sensitivity is 3.5 μm at room temperature. The monochromatic current sensitivity at the maximum of spectrum (λ=3.1-3.4 μm) is 1.4-1.6 A/W, which corresponds to a quantum efficiency of 0.5-0.6 without antireflection coating. We have observed that the sulfide passivation of the III-V substrates before epitaxial growth could result in the increasing of quantum efficiency. Broad bandwidth, high-efficiency GaInAsSb/GaAlAsSb and InAs/InAsSbP photodiodes have been developed and investigated. Today, our research ***activities focus*** on TPV cells for the 1200-2500^{0}C temperature range (Eg=0.4-0.6 eV). Using the narrow gap III-V materials allows us to extend spectral sensitivity of TPV elements to longer wavelengths and to utilize efficiently thermal energy from sources with low temperatures.

The work is supported by the Russian Foundation of Basic Research (RFBR) under Grants No. 07-02-01359, No. 09-08-91224.

BIAS FIELD EFFECT ON THE DIELECTRIC AND PYROELECTRIC PROPERTIES OF (Pb,La)(Zr,Ti)O_3 TRANSPARENT FERROELECTRIC CERAMICS

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Temperature and bias field dependences of the dielectric permittivity ε and pyroelectric coefficient γ for transparent ferroelectric (Pb,La)(Zr,Ti)O_3 ceramics have been studied. . Ceramic samples were obtained by hot pressing. Pyroelectric coefficient γ was determined by a dynamic technique in the field-cooling and field-heating modes.

At zero field, the maximum of $\gamma(T)$ dependence is observed in the vicinity of the Fogel-Vulcher temperature but, at even small but finite bias fields, this maximum shifts to the position of the supposed critical point (which is in the vicinity of the permittivity maximum temperature T_m) and grows in magnitude. The latter increases up to the field corresponding to the critical point in the E-T phase diagram (it can be roughly estimated from the minimum in the $T_m(E)$ dependence [1]) and decreases at higher fields. Thus application of the biasing fields driving the system towards the critical point crucially enhances the pyroelectric response. These data support a quasicritical behavior of pyroelectric coefficient in relaxors at the critical point, revealed earlier for $Pb(Mg_{1/3}Nb_{2/3})O_3 – PbTiO_3$ single crystals [2].

This study is supported by the Russian Foundation for Basic Research (RFBR), grants 07-02-12165 OFI and 07-02-00099_a.

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SELECTED NANOMATERIALS FOR FIELD EMISSION DISPLAY APPLICATIONS

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The field emission display (FED) is one of the most promising technology on flat panel display market. Moreover, the materials and techniques applied in FEDs could be successfully used during different light emitting devices fabrication. Recently, one of the most interesting class of materials, because of their unique features are nanocrystallites. For example some nanocrystalline phosphors are brightness then conventional micrograin size phosphors. Also addition of indium-tin oxide nanocrystallites, during the fabrication process improves the properties of the ITO layers. In this work selected features of nanocrystalline, RE-doped phosphors and indium-tin oxide (ITO) nanocrystallites synthesized by modified Pechini method, as well as some aspects of FED fabrication process and application of RE-doped nanophosphors and ITO thin films in different light sources will be presented and discussed.

COMPARISION OF DIELECTRIC RELAXATION RESPONSE OF MESOGENIC LIQUIDS WITH DIFFERENT POLARITY

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Two mesogenic liquids composed of the molecules of similar structure and length, but of an essentially different polarity have been studied by dielectric relaxation spectroscopy. This method could be an excellent tool for comparison studies of dielectric relaxation response of mesogenic liquids giving the information on the orientational molecular dynamics of the mesogens in the isotropic (I) and nematic (N) phases. The experimental data on two mesogenic liquids composed of molecules of a quite similar structure and different polarities: *n*-heptylcyanobiphenyl, C7H15PhPhCN, 7CB (molecular dipole moment (μ=5D) and 4-(*trans*-4′-*n*-hexylcyclohexyl)isothiocyanatobenzene, C6H13CyHxPhNCS, 6CHBT (μ=2.5D) are presented here. The temperatures of the I-N phase transition for the two compounds are very close to each other (*T*NI) 316.6 (0.2 K). It is shown that regardless of the differences in polarity of 7CB and 6CHBT molecules and their abilities in dipolar aggregation, the values and temperature dependences of the relaxation time (corresponding to the rotational diffusion of the molecules around their short axis) are very close to each other, in both the isotropic and nematic phases of the liquids studied. Also, in the isotropic phase of both compounds, at the same temperature, the dielectric absorption maximum was found to be at the same frequency of the probing electric field. It means that the conclusion concerning the dielectric relaxation was somewhat unexpected. The results presented in this paper clearly show that from the molecular dynamics point of view, as observed by the dielectric relaxation spectroscopy in the isotropic liquids and the nematic liquid crystals, the polarities of the molecules play a secondary role only. The two compounds studied, composed of molecules of essentially different polarity, exhibit the same way of returning to the equilibrium state after perturbation of that equilibrium by the probing electric field. This relaxation process proceeds mainly with an exponential time dependence, as a normal Brownian rotational diffusion, and the relaxation time value appears to be not influenced by the intermolecular interactions.

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ANGULAR MOMENTUM CONSERVATION IN PHOTONIC LATTICES

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We investigated analytically and numerically orbital angular momentum of light propagating in fully periodic and radially periodic optically induced photonic lattices. We considered both fixed and interacting lattices, in copropagating and counterpropagating beam geometries. For fully periodic lattices, interacting with the light, the transfer of angular momentum from the vortex beams to the photonic lattices is demonstrated, leading to the conservation of angular momentum. In the fully periodic fixed lattices, angular momentum is never conserved; however the pseudoangular momentum is conserved. On the other hand, the transfer of orbital angular momentum in radially periodic (interacting or fixed) photonic lattices is absent, so that the angular momentum is always conserved.

SOME PROBLEMS IN MODELING OF LASER INTERACTION WITH TRANSPARENT AND ABSORPTIVE MATERIALS

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Optical damages in materials and material resistance to beam radiation has been a topic of numerous models and experiments. This area borders to several other developed areas (fracture theory, plasma interaction with materials, thermal models with phase transitions, fractal theory and similar). In this work, modeling of some areas of laser operation (visible, IR, various pulse lengths), differing by several orders of magnitude, has been performed. Considering different approaches to observation of the beam-material interaction and of the ejected particles monitoring, some unsolved questions arose. Two different standing points of material observation, from damages and from ejected material, have been showing differences of fundamental nature. Results have been analyzed from those questions point of view and compared to experimental results.

In this work, the interaction of laser beams (of well known lasers, like Nd^{3+}:YAG, CO_2, but also alexandrite and others) with optical materials (in broader sense of view) and accessories has been done. As an experimental part, some damages have been analyzed by optical and electron microscopies, as well as EDX, which confirm material content change or preservation. The shapes of damages depend on the laser working regime, pulse width, mono- or multi-pulse expositions. Cumulative effects are the subject of investigation of many authors. In the terminology of optical damages, there are precise defined protocols for "laser damage", but they differ in both investigation types and the "damage" term application. Obtained results on various materials could enable analyses of several types including the data on the source itself, of materials resistance to optical beams, and of research by other developed fatigue tests as well. For some approaches, calculations which represent numerical implementation for given geometries and chosen pulse shapes, have been performed. Besides them, interpretations which would be commonly deduced, based on the models of obtained record processing, has been given [1–3].

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STRUCTURAL AND MAGNETIC PROPERTIES OF MECHANOCHEMICALLY SYNTHESIZED NANOCRYSTALLINE TITANIUM MONOXIDE

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Nanosized titanium monoxide, TiO powders were prepared by mechanically assisted synthesis. A mixture of commercial Ti and TiO_2 (anatase) powders with molar ratios of 1:1 was milled for 0.5 and 1 h under nitrogen atmosphere. The samples were further characterized by XRD, SQUID measurements and by thermo gravimetric analysis (TGA). The temperature dependency of the magnetic susceptibility is characterized by the significant contribution from the Pauli paramagnetism due to conduction electrons. The low value of the band gap determined from the temperature dependency of the magnetic susceptibility makes it possible to assign the mechanochemically synthesized titanium monoxide to narrow-gap semiconductors.

This work was financially supported by Serbian Ministry of Science and Environmental Protection (Project No. 141027).

STRUCTURAL AND MAGNETIC PROPERTIES OF MECHANOCHEMICALLY SYNTHESIZED NANOSIZED $YTiO_3$

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In this work we investigated magnetic and structural properties of novel nanosized $YTiO_3$. The sample was prepared using the mechanochemical treatment. A mixture of comercial Y_2O_3 powder and mechanochemically synthesized TiO in a molar ratio 0.5:1 was milled for 30, 60 and 90 minutes under nitrogen atmosphere. X-ray diffraction revealed that the crystal structure of $YTiO_3$ is a pseudo-cubic perovskite with an orthorhombic distortion (the GdFeO3-type distortion). Relevant structural and micro-structural parameters were refined from the XRD data using full profile Rietveld's method within *Pbnm* space group. The sample was further characterized by the SQUID measurements in the temperature range 2-300 K and by the thermo gravimetric analysis (TGA). The relation between magnetic, structural and micro-structural properties was discussed.

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INFLUENCE OF Mg-DOPING ON SYNTHESIS OF SOL-GEL DERIVED BST THIN FILMS

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Solid solutions of $Ba_{1-x}Sr_xTiO_3$ (BST) type are very attractive for application in information technology but also in microwaves for electrically controlled devices. In contrast to the bulk ceramics or fine powders, the structure and properties of ferroelectric thin films are well known to exhibit a number of deviations. Characterization techniques that provide information about the structure of thin films are thus useful. Raman spectroscopy is such an important method.

In the present study thin films of a $Ba_{0.6}Sr_{0.4}TiO_3$ solid solution were prepared by the sol-gel-type chemical solution deposition method. Apart from other characterization techniques used like thermal analysis, X-ray diffraction, SEM and EDS, we report results of Raman spectroscopy investigation of MgO-doped $Ba_{0.6}Sr_{0.4}TiO_3$ thin films grown on stainless steel substrates. The influence of y=1, 3 and 5 mol.% MgO doping on synthesis, microstructure and crystalline structure of BST thin films was studied.

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PHOTOLUMINESCENCE OF NANOCRYSTALLINE SOL-GEL-DERIVED (Ba,Sr)TiO$_3$ THIN FILMS

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Ferroelectric (Ba$_{0.6}$Sr$_{0.4}$)TiO$_3$ (BST) thin films were subjected to an intensive study in the last decade due their potential use in monolithic microwave integrated circuit used for decoupling capacitors, tunable microwave filters, and phased array antennas. Ferroelectric oxides are of particular interest, that offer the possibility of novel, yet simple devices that take advantage of their electro-optical and non-linear optical properties.

In the present study photolumunescence of the nanosized (Ba$_{0.6}$Sr$_{0.4}$)TiO$_3$ (BST) thin films doped with Co and Mn was studied. The BST thin films were obtained by the modified sol-gel method that has the advantage of large area deposition, in addition to its low cost and convenience process control. The thin films were deposited on silicon, and stainless steel substrates by spin coating and crystallized by the conventional thermal annealing at temperature T=600 – 700 ^{0}C. Formation of the perovskite structure was confirmed by X-ray diffraction method. Conservation of the chemical composition was investigated by energy dispersive spectroscopy.

The visible luminescence has been observed in BST:Co and BST:Mn thin films at room temperature. Results on luminescence excitation and emission in barium strontium titanate thin films are discussed in the present paper.

Acknowledgements: The authors wish to acknowledge Polish Ministry of Education and Science for financially supporting the present research from the funds for science in 2006-2009 as a research project N507 098 31/2319

LUMINESCENT SPECTRA OF YTTRIUM OXYAPATITE OBTAINED BY UREA ASSISTED REFLUX METHOD

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The luminescent characteristics of yttrium oxyapatites doped with europium ions obtained by using reflux method assisted by urea subsequent degradation were investigated in this paper. The SEM investigations of these powders show their a very specific rope-like morphology.. The structure of yttrium apatite realized by incorporation of the Eu^{3+} ions, as luminescent active centers has been shown the most important reflections of an hexagonal phase of yttrium oxide silicate-yttrium oxyapatites, obtained as a consequence of the Y^{3+}ion stabilization.. This fact has a significant influence to the position of the Eu^{3+}luminescent spectra, showing a slight shifting towards the blue area in comparison to the typical spectra of other yttrium-silicate phases.

CHARACTERIZATION OF NORMAL AND INCLINED GaSb NANOCONES BY MUELLER MATRIX ELLIPSOMETRY

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Self organized nanostructures open up for efficient and low-cost production of materials with new and interesting properties, with applications in electronics, optics and life sciences. A major challenge for controlling and understanding growth processes of such structures is the characterization of nanometer sized structures. Low energy ion sputtering of GaSb with normal incidence results in densely packed normal nanopillars, while oblique ion incidence results in densely packed inclined nanopillars, pointing in the direction of ion incidence. We demonstrate that ellipsometry can be used as a non-destructive tool to characterize such structures, with possibilities for in situ use. The optical properties of the inclined GaSb nanocones are highly anisotropic, requiring the use of generalized ellipsometry or Mueller matrix ellipsometry.

THE STRUCTURING OF SEALING COMPOSITE MATERIALS BASED ON ETHYLENE DIENE TERPOLYMER

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The temperature and frequency insensitive damping and elasticity are of significance to extend the availability in the industrial uses. There exists considerable demand for "damping materials" to suppress vibration and noise in industrial fields. The basic mechanical principles on which sealing and damping materials are based can vary wildly between different applications and operating environments. Dynamics or pressure within a system may compel the use of more complex sealing profiles or composite seal assemblies, consisting of multiple materials that, in combination, can offer the required properties. Many differing grades of material, with significantly varying properties, may belong to a single material designation. Synthetic elastomer materials used in sealing systems generally consist of an organic polymer and inorganic reinforcing filler systems. Elastomers based on ethylene-propylene-diene terpolymer rubber have proven to be useful barrier materials in the automotive, electrical and construction industries. In this contribution the properties of oil-extended ethylene-propylene terpolymer based materials filled with different filler content (nano sized furnace carbon black and micro sized chalk) intended for automotive window seal component production was studied. The paraffin process oil was used as a plasticizer. The compounds containing blowing agent were expanded in hot air at 205°C. Microcellular samples were obtained either by curing in salt or in hot air. The mechanical properties of prepared materials including tensile strength, elongation at break, hardness, and compression set, before and after ageing, were analyzed. A dynamic mechanical analyzer was used to perform bending tests with dual cantilever fixtures over a temperature range from at 6 frequencies. The dependences of storage modulus (E′) and damping-energy dissipation component (E”) were analysed. The morphology of samples was characterized by scanning electron microscopy (SEM). The images were taken on the gold sputtered surfaces of s. It is estimated that with increasing filler loading the values of sample hardness increased while compression set and tensile strength decreased. The samples with high filler loading have higher E′ value over the whole range of temperatures in comparison with composites with small filler content. It was found that the addition of chalk in small concentrations, has a positive contribution to modulus, and does not change tensile strength and elongation at break. The scanning electron micrographs of cryo-cracked sample surface observations indicated the uniform filler dispersion.

THE CHARACTERIZATION OF GROUNDWATER PARTICULATES FROM SCANNING ELECTRON MICROSCOPE AND ELEMENTAL MICRO-ANALYSIS

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The colorant microbiological material was obtained from samples of iron-oxidizing/depositing bacteria, colonies of bacteria, and examination of the structures under scanning electron microscope and elemental micro-analyses can be summarized. Acceptable comparison of particle size analysis was obtained from SEM (JEOL- JSM-6460 L) and Mastersizer 2000. Groundwater deposits revealed appearance of carbon in samples with increased relative error of oxygen; the appearance of magnesium is found in samples with increased relative error of titanium. Deviation of phosphorus decreased in dark silted material (Figure).

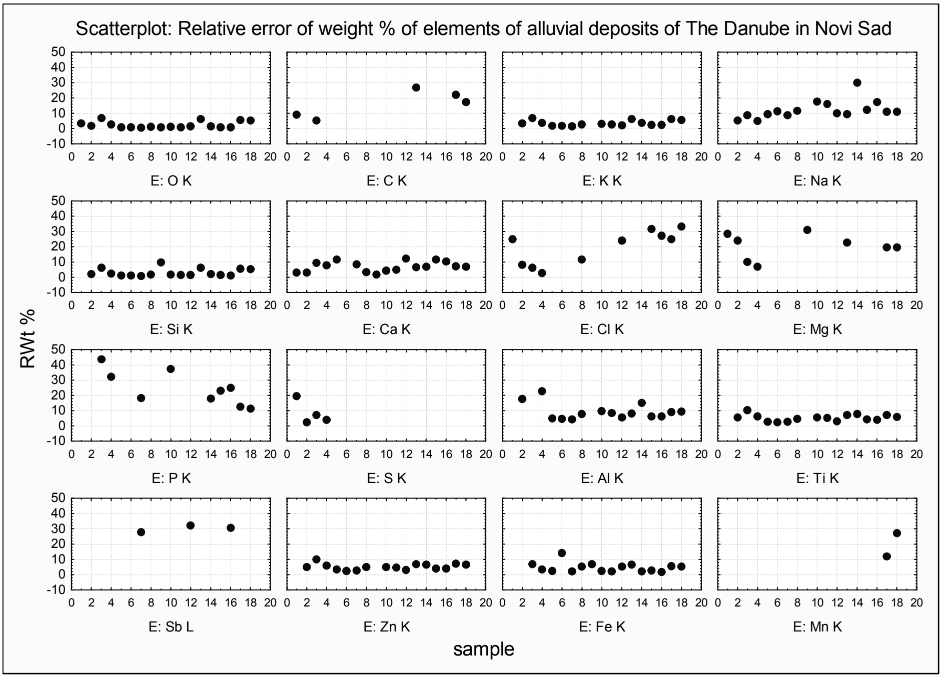

Figure 1. Categorized graph-Scatterplot of relative error of weight fraction (%) of different elements of groundwater drainage deposits- <u>ochre</u> occuring in drainage wells of The Novi Sad city nearby The Danube. Relative weight (sigma weight (%)/weight (%)) was presented by the categorized scatterplot graph (Statistica 8) in order to provide systematization of EDS analyzed parameters of spectrum point analyses (Oxford Instrument INCA-X-sight software).

METASTABLE PROCESSES IN PROTEINS

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The Scott's model of protein Hamiltonian we transformed to metastable form by means of double coherent unitary transformation. It turned out that in metastable Hamiltonian number of quasi particles is not conserved due to the forming of pairs of excitations. The energies of pairs are found and their population is quoted. It is interesting that elementary excitataions of metastable state behave similarly as exctitations of molecular vibrations field as well as excitations of electromagnetic field.

THERMAL LENS SPECTROMETRIC MEASUREMENTS OF METAL COLLOIDS IN SOLUTIONS

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Metal colloids dispersed in solutions play an important role in material science as well as in several technological and environmental processes and applications. They not only display novel catalytic properties in many chemical reactions but also change the optical parameters of materials which are a function of the metal nature, morphology of colloid particles and the state of their aggregation [1]. Due to the ability of influencing the physical and chemical properties of a wide range of materials, the metal colloids are commonly used in sensors for volatile organic chemicals, in DNA chips, data storage media, photonic devices, and also for fabricating magnetic and nanofluids [2-4].

Various methods are used for preparing metal colloids including laser ablation [5], photochemical [2] and chemical methods [6]. Transmission electron microscopy and atomic absorption spectrometry [2] are most frequently used for metal colloid detection and characterization but other techniques such as thermal lens spectrometry (TLS) was also used to monitor the process of metal colloid preparation [6].

In this work the possibility of exploiting the formation of metal colloids for detection of low concentrations of heavy metals was investigated. TLS [7] technique was applied for detecting metal colloids in solutions at 457.9 nm (100 mW excitation power). The colloids were prepared in a flow-injection (FIA) system by injecting a solution of metal ions into a flowing carrier stream and mixing it with a solution of a reductant (BH_4^-) in a mixing coil. Combination of FIA and TLS provides low limits of detection, which are at the levels of a few ng/mL as demonstrated for example for Ag. The measurement procedure is simple, fast and performed at a single wavelength. The described technique could therefore serve as a sensitive and universal detection scheme for metal ion detection in systems such as ion chromatography and capillary electrophoresis.

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LUMINESCENCE OF Tb^{3+} IONS IN SOL-GEL DERIVED YAG:Tb^{3+} POWDERS

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The rare earths (RE^{3+}) activated garnets are well known as efficient lasers or luminescent systems. In these systems it is well established that RE^{3+} concentration affects the static (spectra) and dynamic (emission kinetics) optical properties due notably to the discrepancy between the ionic radii of the dopant ion and the replaced host ion, or to the inhomogeneous distribution of this dopant over the structure. Nevertheless, such effects can be strongly dependent on the distance between the RE^{3+} ions and the crystal structure. Depending on these distances, direct ion-ion interactions induce energy transfer between the active ions which results generally in the accelerating of the luminescence decay of the considered emission. Cross-relaxation mechanisms based on long range multipolar interactions have been extensively used to explain the self-quenching of the Tb^{3+} emission arising from $^5D_3$ in compounds where the Tb-Tb separation is relatively low [1]. Consequently in such systems, the luminescence is green originating mainly from $^5D_4$. Due to the predominance of exchange interaction in the $^5D_4$ de-excitation process [2,3], the quenching of $^5D_4$ emission occurs generally at concentrations much higher than that considered for $^5D_3$. For equivalent sites in the material, the $^5D_4$ fluorescence decays often in exponential manner in this large concentration range.

We report in this work spectral properties of YAG:Tb^{3+} analyzed either under UV or blue selective excitation. Despite that sol-gel technique is known as a powerful technique for the preparation of materials where the active ions are homogeneously distributed, the kinetics of the $^5D_4$ emission decays are observed to be drastically different when excitation occurs either at the centre or on the wings of the excitation lines suggesting inter-site energy transfer; notably, two decay components were recorded in Tb^{3+}: $^5D_4 \rightarrow {}^7F_5$ emission.

Besides the evaluation of microscopic rate constants for $^5D_3$-$^5D_4$ cross-relaxation mechanism, the obtained results are discussed considering the possible occurrence of Tb^{3+} pairs in YAG.

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INVESTIGATION OF LASER SURFACE PROCESSING OF STEEL AND NICKEL BASED SUPERALLOY

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Investigation was carried out on steel and nickel based superalloy samples. After thermomechanical treatment and adequate preparation, Nd:YAG laser processing was applied. Laser energy was up to 50 mJ, pulse duration 532 nm and 1064nm, and pulse repetition and number of pulses varied. The samples were exposed to the laser shock peening process and laser ablation. Changes in samples microstructure were observed by optical microscope, scanning electron microscope and energy-dispersive spectrometry, and analyzed as well. Aim of investigation was to identify the structural microconstituents and determine their influence on the mechanical properties of materials. Microhardness was measured and difference in the structure of steel and nickel based superalloy arisen by processes of laser shock peening and laser ablation was discussed.

EFFECT OF NB AND CR ON IRON AND NICKEL BASED SUPERALLOYS MICROSTRUCTURAL CHANGES

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The investigations were carried out on superalloys different chemical compositions, the common being that except of dominant content of Ni, Fe, Cr, Co and Mo, they consist W, Mn, Si C, Al as well. Iron based superalloy is alloyed with Nb. The yield strength, tensile strength and elongation were determined by tensile strength tests, and the interaction of pulsed Nd:YAG laser beam with iron and nickel based superalloys samples were analyzed by a scanning electron microscope (SEM) and an energy-dispersive x-ray spectrometry (EDS). In this paper, the effect of Nb and Cr on the microstractural changes arrisen by laser beam action was discused, with the aim to determine the optimal regime that provides good chemical and mechanical properties of researched superalloys.

NOVEL PROPERTIES OF PES FABRICS MODIFIED BY CORONA DISCHARGE AND COLLOIDAL TiO_2 NANOPARTICLES

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The prospects of excellent technical and economical results, as experienced in different sectors of industry worldwide, were stimulating efforts to apply nanotechnologies more widely in the processing of high-added value textile materials. Engineering of fiber surface from the standpoint of its functionality, in combination with well known surface characteristics of nanometer-sized particles can provide long term durability and stability of desired effects. Recent studies indicated that UV protection as well as self-cleaning effects can be tailored by depositing the non-toxic and inexpensive TiO_2 nanoparticles (NPs) onto textile fibers, without changing the bulk properties of the fiber and deterioration of textile appearance. However, the application of colloidal TiO_2 NPs to polyester (PES) fabrics is problematic due to hydrophobic surface of fibers and poor binding of TiO_2 NPs. Therefore, the aim of this study was to highlight the possibility of using the corona discharge at atmospheric pressure for the surface activation of PES fabrics in order to improve interaction with colloidal TiO_2 NPs which were synthesized by acid hydrolysis method without using stabilizers.

Chemical changes on the surface of PES fibers were followed by SEM-EDS, Raman spectroscopy and XPS. The UV protection efficiency of modified fabrics was evaluated by measuring transmission spectra and further calculation of UV protection factor (UPF). Self-cleaning properties of the PES fabrics were tested by irradiation of blueberry juice stains for certain time intervals whereas the photoactivity of PES fabrics was examined by degradation of methylene blue.

The fabrics modified by corona and TiO_2 NPs showed high self-cleaning and UV protection efficiencies. They provide very high UPF values, which correspond to UPF rating of 50+ designating the maximum UV protection. In addition, the total degradation of methylene blue was achieved already after six hours of UV irradiation and this ability was preserved and even improved after repeated degradation cycles.

The financial support for this work was provided by the Ministry of Science of Republic of Serbia (projects 142066 and TR 19007).

P3HT:PCBM BULK HETEROJUNCTION SOLAR CELLS

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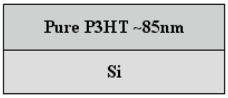
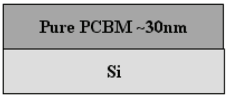
The performance of organic solar cells based on the blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) is strongly influenced by blend composition and thermal annealing conditions. For high-efficiency solar cells, a nanoscale interpenetrating network with crystalline order of both constituents is the desirable architecture for the photoactive layer. To that end, recent studies have focused on how to tailor and control the morphology of the P3HT:PCBM blend, the material combination that has led to the highest power conversion efficiency values reported thus far (4-5%) [1].

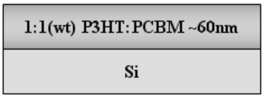
Three monolayer samples of P3HT, PCBM and P3HT:PCBM were studied by spectroscopic ellipsometry. Spectroscopic ellipsometry is an optical technique mainly used for the determination of film thickness and optical constants (n,k) of thin film structures [2]. We will demonstrate the use of ellipsometry as a powerful and sensitive metrology means of monitoring blend morphology, phase separation as well as crystallinity.



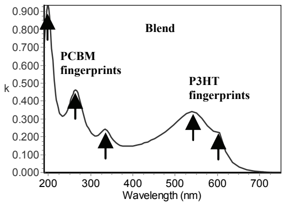
1st sample

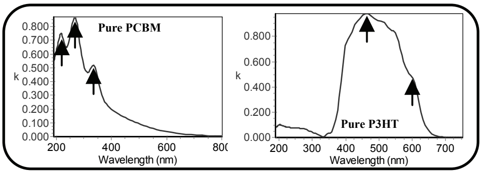


2nd sample



3rd sample





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DATA RECORDING BY FLUORESCENT PHOTOSENSITIVE NANOCRYSTALS

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Three-dimensional optical memories have generated considerable interest for their potential application to high-density optical data storage. Fluorescent photosensitive materials such as fluorescent photosensitive glasses [1] and fluorescent photosensitive glass-ceramics have interesting properties useful for 3D optical data storage [2-4].
The paper explains the significance of rare-earth host interaction for engineering optical data storage medium. A fluorescent photosensitive glass-ceramics containing nanocrystals with rare earths ions was realized and analyzed by SEM, TEM, HRTEM and photoluminescence spectroscopy. The measurements reveal the presence of nanocrystals having dimensions in the range of tens of nanometer. Using low power laser pulses and an adequate aperture of focusing lens, bits as small as 500 nm in diameter (Fig. 1) were written.

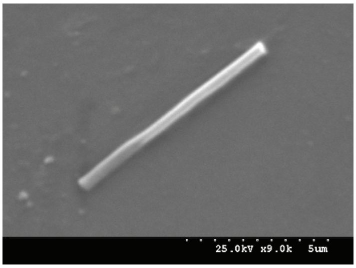

Figure 1. SEM image of a recorded line

A new media based on fluorescent photosensitive glass-ceramics has been developed. Large operating tolerance on writing laser power makes this material a good candidate for systems capable of high data storage densities.

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POLYMER COMPLEX SOLUTION SYNTHESIS OF $(Y_xLu_{1-x})_2O_3$:Eu^{3+} NANOPOWDERS

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In the last two decades extensive research has been performed on the development of inorganic nanophosphors with improved physical properties and strong emission in the visible spectral range. They gained a special place in material science research due to numerous applications ranging from the solid state lightening and novel flat displays to high resolution X-ray detectors and sensors in biomedicine. For these reasons, research in novel or improved synthesis methods are important.

In our previous work we investigated the luminescence properties of europium doped mixed Y_2O_3-Gd_2O_3 and Lu_2O_3-Gd_2O_3 nanocrystalline phosphors using polymer complex solution method (PCS) based on polyethylene glycol (PEG) fuel. We observed that all powders have strong red emission with long decay time that remained preserved even after high pressure-high temperature treatments [1].

In the present work we expand our investigation on Y_2O_3-Lu_2O_3 nanopowders (set of 5 samples $(Y_xLu_{1-x})_2O_3$, x = 0, 0.25, 0.5, 0.75, 1) doped with europium. Detailed information on their phase, morphology and crystallinity are obtained using X-ray powder diffraction, SEM and TEM while detailed optical characterization is done with photoluminescence spectroscopy techniques.

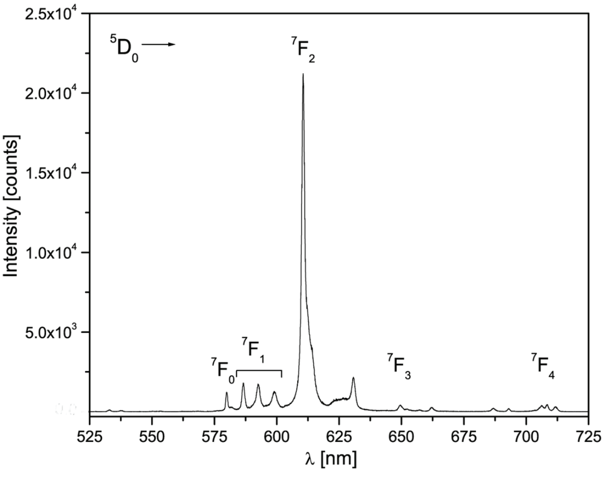

Figure 5 Emission spectra of $(Y_{0.5}Lu_{0.5})_2O_3$:3at%Eu nanopowder (λ_{ex} = 466 nm)

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Gd_2O_3:Eu^{3+} NANOPARTICLES PREPARED USING COMBUSTION SYNTHESIS: INFLUENCE OF DIFFERENT FUEL TYPES AND ACTIVATOR CONCENTRATIONS ON PARTICLE MORPHOLOGY AND LUMINESCENCE PROPERTIES

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In present work we explored the possibility of obtaining nanocrystalline powders of europium-doped Gd_2O_3 using polymer complex solution synthesis technique. Two series of nanocrystalline Gd_2O_3:Eu^{3+} have been prepared: 1) for different composition of fuel (PEG with molecular weight MW = 200, 1000, 2000, 4000, 12000, 20000, 100000, 300000, 1 million) and 2) for different activator concentration using PEG 200 as fuel (0.1, 0.5, 1, 3, 5, 7, and 10 at % of Eu^{3+}). The first set of samples served to determine the influence of the fuel on the luminescent characteristics of obtained phosphors, as well the impact it has on the structure and morphology of the constituting nanoparticles. The second set of samples is used to explore the activator concentration effect on optical properties of the phosphors in correlation with the decay profiles of the Eu^{3+} emission. Decease in the lifetime of $^5D_0$ level with increasing Eu concentration is obvious after doping of 3 at%.

Samples were characterized with XRD, BET, electron microscopy (SEM / EDX, and HRTEM) and luminescence spectroscopy.

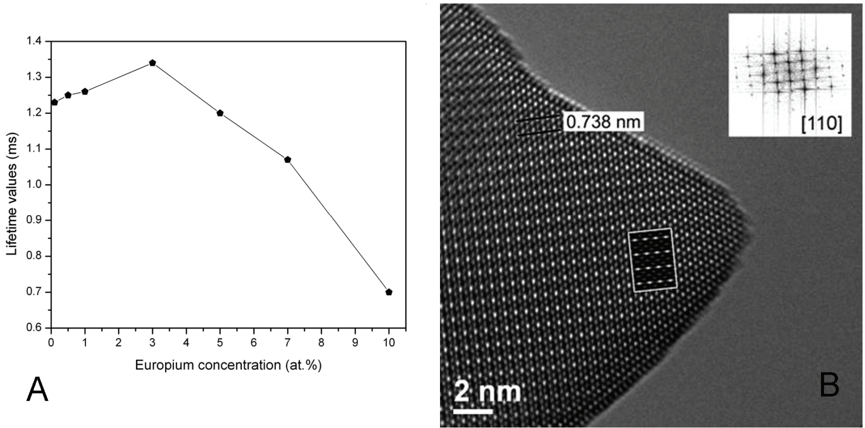

Figure 6 A) Lifetime values of Gd_2O_3:Eu^{3+} are presented as a function of the activator concentrations. B) HRTEM image taken from one Gd_2O_3:Eu^{3+} nanoparticle with the FFT plots indicate the crystal in a [110] zone axis orientation. The simulated image is added as an outlined input.

POLYMER COMPLEX SOLUTIONS SYNTHESIS TECHNIQUE FOR RARE-EARTH-DOPED Lu_2O_3 NANOPOWDERS

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Rare earth luminescent materials have attracted much attention for their applications in artificial lights, X-ray medical radiography, lamps and display devices, for high-power solid-state lasers, etc. Among them rare-earth sesquioxides are well recognized host materials due to good chemical stability, adequate thermal conductivity and high light output. Recently, lutetium oxide is regarded promising host for detectors of ionizing radiation of high stopping power and high performance, with application in X-ray imagery. This is ascribed to its exceptionally high density (~9.42 g/cm^3) combined with the high *Z* number of Lu (71), which endows Lu_2O_3 with high stopping power for ionizing radiation [1]. In addition, its cubic crystal structure makes possible the preparation of transparent ceramics starting from the nanopowder. This is actually of great importance as the high melting point of this compound, around 2763 K, makes it difficult for single crystal growth with standard crystal growth methods.

In present work we explored the route for simple and energetically efficient production of rare earth (Tb^{3+} and Sm^{3+}) doped Lu_2O_3 crystalline nanopowders based on polymer complex solution method. In this type of synthesis, polyethylene glycol (PEG) is used both as fuel for the combustion reaction and as nucleation agent for the crystallization process. Samples were characterized with XRD technique, electron microscopy (SEM/EDX and TEM) and luminescence spectroscopy (steady state and luminescence lifetime). Obtained results confirmed that applied synthesis technique is able to produce highly crystalline, pure phase, luminescent nanopowders of Lu_2O_3.

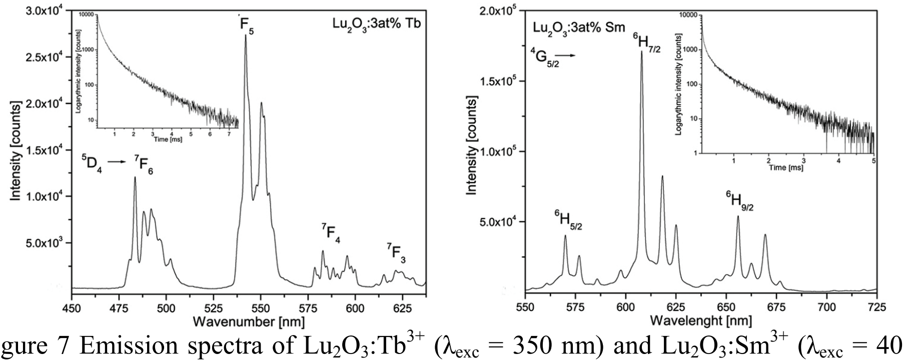

Figure 7 Emission spectra of $Lu_2O_3:Tb^{3+}$ (λ_{exc} = 350 nm) and $Lu_2O_3:Sm^{3+}$ (λ_{exc} = 406 nm) with fluorescence decay curves as insets.

[1] Q.Chen, Y.Shi, L.An, J.Chen and J. Shi, J Am Ceram Soc 89(6), 2038-2042 (2006).

FABRICATION AND CHARACTERIZATION OF SAMARIUM AND TERIBIUM ACTIVATED TiO_2 ANATASE NANOPARTICLES

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Stefano POLIZZI[2], Davide CRISTOFORI[2] and Miroslav D. DRAMIĆANIN[1]

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Luminescence of rare-earth ions has been attractive topic due to the potential applications in the various fields. We investigated doping of the anatase TiO_2 phase with trivalent samarium and terbium ions aiming to obtain biocompatible material exhibiting phosphorescent emission. To produce these materials in the form of nanopowders, the sol–gel synthesis route has been adopted, starting from the rare-earth nitrates and titanium (IV) isopropoxide.

We investigated the process of crystallization of Sm^{3+} and Tb^{3+} activated TiO_2 gel and how it influences the luminescence behavior of the material. Fourier transform infrared spectroscopy is used to monitor decomposition of organic phases while transforming gel into powder form while anatase TiO_2 phase is confirmed with X-ray diffraction measurements. Thermal analysis is done with TGA-DTA techniques. The microstructure of calcinated samples has been observed using electron microscopy techniques (SEM and TEM) and the powder average particle size of around 10 nm is found from transmission electron microscopy. Luminescence measurements are employed to investigate emission spectra and emission decays of rare earth activators in the anatase matrix.

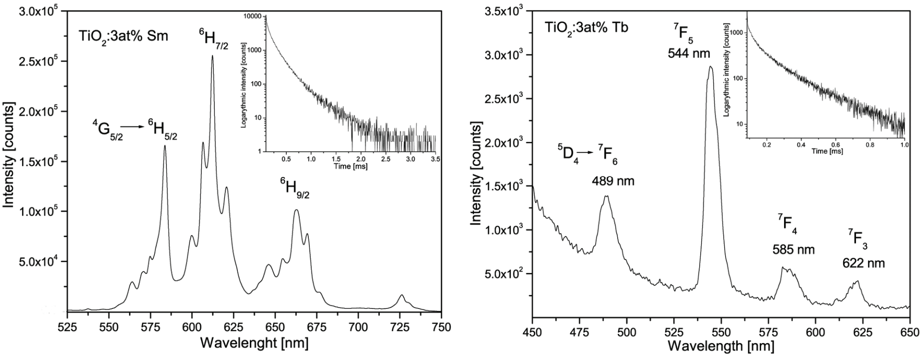

Figure 8 Emission spectra of $TiO_3:Sm^{3+}$ (λ_{exc} = 406 nm) and $TiO_2:Tb^{3+}$ (λ_{exc} = 350 nm) with corespondent fluorescence decay curves given as insets.

List of authors