The 7th International Conference on the Physics of Optical Materials and Devices
&
The 4th International Conference on Phosphor Thermometry

BOOK OF ABSTRACTS

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ICOM&ICPT 2024

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&

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Becici, Montenegro, 26th to 30th of August 2024

Dear Colleagues and Friends,

It is our great pleasure to welcome you to The International Conference on the Physics of Optical Materials and Devices AND the International Conference on Phosphor Thermometry – ICOM&ICPT 2024. The conference is organized by the Society for science development of Serbia (Serbia), l'Institut de Recherches de Chimie Paris (France), and the Otto-von-Guericke-Universität Magdeburg (Germany). This meeting is the continuation of a series of ICOM conferences organized every three years starting with Herceg Novi, Montenegro in 2006 and 2009; Belgrade Serbia in 2012, Bečići, Montenegro in 2015, Igalo in 2018 and in Belgrade, Serbia in 2022. The last editions of ICPT were organized in Glasgow, UK (2018), online in 2020, and in Magdeburg, Germany (2022).

The ICOM&ICPT Conference brings together scientists and technology users who investigate or develop materials for optical applications. The conference presents the state of the art in preparation methods, optical characterization, and usage of optical materials and devices in various photonic fields. This year 9 keynote, 23 invited lectures, 79 oral and 75 poster presentations will be presented in the following sections: Light for sensing, Thin Films and Composites, Exploring Luminescent Systems, Persistent Luminescence Materials, Persistent Luminescence Mechanisms, Tools and Applications of Persistent Phosphors, Design of Optical Thermometers, Phosphors for bio-applications, New Optical Phenomena, Optical Thermometry, Applications of Rare Earth Emissions, Tuning Optical Properties.

We hope that ICOM&ICPT 2024 will be fruitful in terms of scientific exchange and that it will reinforce the existing collaborations between the participants and promote new ones in the future. We would like to acknowledge financial support given by numerous organizations.

Organizers of the ICOM&ICPT 2024 wish you a nice time during the conference in Bečići!

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K-1

Lanthanides working together

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Recent trends in science policy show a shift from recognizing brilliant individuals to stressing the importance of team work. The field of lanthanide luminescence made this transition decades ago. Old phosphors as $Y_2O_3:Eu^{3+}$, BAM:Eu^{2+} or $Gd_2O_2S:Pr^{3+}$ rely on a single type of lanthanide ion but new luminescent materials demonstrate that cooperating lanthanides can achieve more. In this presentation we focus on the role two types of interactions: (1) Cooperative effects and (2) Cross-relaxation in lanthanide-doped luminescent materials.

Cooperative absorption, emission and energy transfer were pioneered in the 1970's [1]. After an introduction to cooperative effects in lanthanide spectroscopy, we focus on cooperative energy transfer from a single lanthanide to two or even three neighboring lanthanide ions. Evidence for cooperative energy transfer processes is challenging but can be obtained by modelling luminescence decay curves using the shell model [2]. In addition, correlated photon counting can serve as evidence for cooperative energy transfer and quantum cutting [3].

Cross-relaxation is partial energy transfer between neighboring ions of the same or different type. It is often undesired as it can effectively quench emission at elevated concentration, e.g. in Pr^{3+}-doped phosphors. It can also be beneficial: cross-relaxation is at the heart of photon avalanching which recently experiences a revival in photon avalanching nanocrystals [4]. Here we use cross-relaxation between neighboring Ho^{3+} ions to probe ion diffusion in $NaYF_4$ core-shell nanocrystals and offers a sensitive method to probe the sharpness of core-shell interfaces. By measuring luminescence decay curves of the Ho^{3+} $^5S_2$ emission the diffusion of Ho^{3+} from the doped core into the undoped shell can be monitored as a function of time and temperature.

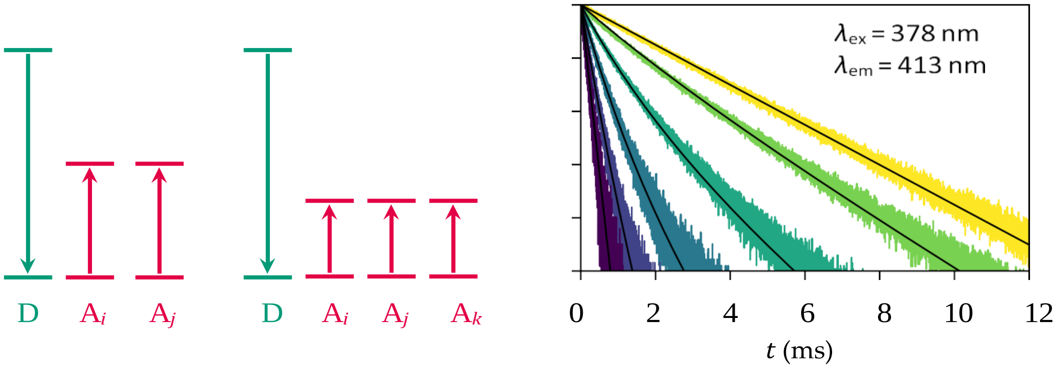

Figure 1 – (left) Cooperative energy transfer from one donor to two or three acceptors. (right) Decay curves of Tb^{3+} $^5D_3$ emission in $LaF_3:Tb^{3+}0.1\%$, Ce^{3+} x% (x= 0, 20, 40, 60, 80, 100). Drawn lines are fits for a cooperative energy transfer process from Tb^{3+} ($^5D_3$-$^5D_4$) to two Ce^{3+} ions ($^2F_{5/2}$-$^2F_{7/2}$)

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K-2

WATER'S HIDDEN DENSITY DANCE

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The emergence of luminescent nanothermometry during the last decade opened the possibility of measuring thermal flows at spatial scales below 1 μm, unreachable by conventional electrical methods. Diverse phosphors capable of providing remote detection through their light emission properties have been examined, e.g., polymers, DNA or protein conjugated systems, organic dyes, quantum dots, and trivalent lanthanide (Ln^{3+}) ions incorporated in organic-inorganic hybrids, multifunctional heater-thermometer nanoplatforms, upconverting, downconverting and downshifting nanoparticles [1].

In recent years, luminescence nanothermometry has entered a more mature stage. Although new classes of thermographic phosphors continue to be reported (e.g., covalent organic frameworks and single-ion magnets) we are perceiving a gradual shift in the emphasis of the technique. The research efforts are now focused on establishing comprehensive theoretical backgrounds and standardization procedures (both in data acquisition and processing and in measurement methodologies), discussing the reliability, repeatability, and reproducibility of the technique, and developing new applications [1].

In the lecture, we will discuss the intricate relationship among temperature, pH, and Brownian velocity in a range of differently sized upconversion nanoparticles dispersed in water. These nanoparticles, acting as nanorulers, offer insights into assessing the relative proportion of high-density and low-density liquid in the surrounding hydration water, validating the two-state model. These findings underscore the significance of the surface of suspended nanoparticles for understanding high- to low-density liquid fluctuations and water behavior at charged interfaces [2,3].

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SELECTION RULES OF NON-RADIATIVE TRANSITIONS AND THEIR CONSEQUENCES FOR LUMINESCENT MATERIALS

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Usually, photoluminescence is concerned with an optimization of the spontaneous radiative decay pathway, whose foundations were already laid down by the advent of (cavity) quantum electrodynamics and led to the vibrant field of photonics. In contrast, the non-radiative pathway, i.e. the coupling of the transition dipole moment to vibrational modes, has only got into a closer focus since the early 1970s [1]. One major finding was the energy gap law for multi-phonon transitions with a limited temperature dependence [2], while broad-band emission is thermally very labile due to a so-called non-radiative crossover [3]. Theoretical approaches to the non-radiative channel have ever been tackled but often require very sophisticated techniques and still do not satisfactorily agree even in the order of magnitude with experimental data. An interesting impetus was given by Burshtein in 2010 [4] that, after pioneering works by Orlovskii, Pukhov and others [5] as well as Ermolaev and Sveshnikova [6], indicated that non-radiative transition rates should also be related to transition oscillator strengths. From a quantum field theoretical perspective, this would be very intuitive and implies that many control parameters known for radiative transitions should also hold for non-radiative transitions. Such an understanding is key to the design of luminescent thermometers [7], but could even open up new avenues to control the quantum efficiency of phosphors in general.

Within this lecture, I will give a brief historical account on major theoretical and experimental breakthroughs in the understanding of radiative and non-radiative decay in phosphors and demonstrate how theoretical approaches to the non-radiative transition can be explicitly tested with Boltzmann and crossover-type thermometers [8]. Selected examples among various (in)organic emitters demonstrate what are critical experiments in the proof of selection rules of non-radiative transitions [9], what other impacts there are besides the energy gap law and how this can be used to additionally tailor the performance of luminescent materials.

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K-4

HOW TO ENGINEER LANTHANIDE LUMINESCENCE QUENCHING TEMPERATURE AND LANTHANIDE CHARGE CARRIER TRAP DEPTHS IN COMPOUNDS

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The methods how to locate the lanthanide ground and excited states in the bandgap of compounds, and also relative to the vacuum level are now well-established. Those locations are known as vacuum referred binding (VRBE) energies or charge transition level (CTL) energies. Recently, the methods were further validated using data on the quenching of 5d-4f emission [1] and on thermoluminescence glow peaks from either electron or hole release from lanthanides [2]. The limitations of the methods became also clearer. Temperature and the presence of defects affect the CTL energies and therewith the quenching temperature and the temperature at the glow peak maximum. This on the one hand makes predictions less reliable but on the other hand enables to engineer properties. The latest results from [1,2] on VRBE and CTL energies will be shared in this work.

Several engineering tools will be discussed. 1) By a proper combination of two different lanthanides in a compound, one may design the electron-trap depth, the hole trap depth and also the recombination center and therewith the recombination luminescence. When the charge carrier releasing lanthanide creates a glow peak just above room temperature, the phosphor may be suitable as afterglow phosphor where the afterglow color can be tuned from the ultraviolet to the infrared. When the glow peak is well-above room temperature it may function as a storage phosphor. Various examples will be provided to illustrate those engineering aspects. 2) By means of solid solutions, the VRBE at the conduction band bottom or/and valence band top can be altered. This provides an additional engineering tool to alter quenching temperature and trap depths. 3) One may also combine a lanthanide with a transition metal element like Cr^{3+} or with a $6s^2$ element like Bi^{3+} to further broaden the engineering tool box. Again examples will be shown.

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K-5

Near-infrared luminescent materials and their light sources applications

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Near-infrared (NIR) light sources play an important role in NIR spectroscopy technologies, which are widely applied in night-vision, food analysis, biomedical imaging, etc. NIR-emitting phosphor-converted LEDs (pc-LEDs) have attracted considerable research interests because of their small size, tunable broadband emission, and high efficiency. However, the development of efficient and broadband NIR-emitting phosphors remains a significant challenge. In this talk, we will introduce some recent advances in our group on the design, discovery and performance optimization of the NIR phosphors.
Moreover, there is also an ongoing challenge to improve the output power of NIR pc-LEDs, however, due to the "efficiency droop" of blue chips and the poor thermal conductivity of organic silicones, it ultimately hinder improvements in the output power of NIR pc-LED light sources. Recently, our group develops translucent MgO:Cr^{3+} ceramics and utilizing them in a laser diode (LD) -pumped pc-NIR light source that emits an unprecedented output power exceeding 6 Watts. Some further work on the bulk phosphor materials for NIR-pc-LD is also in progress and we will introduce some design principle in this field.

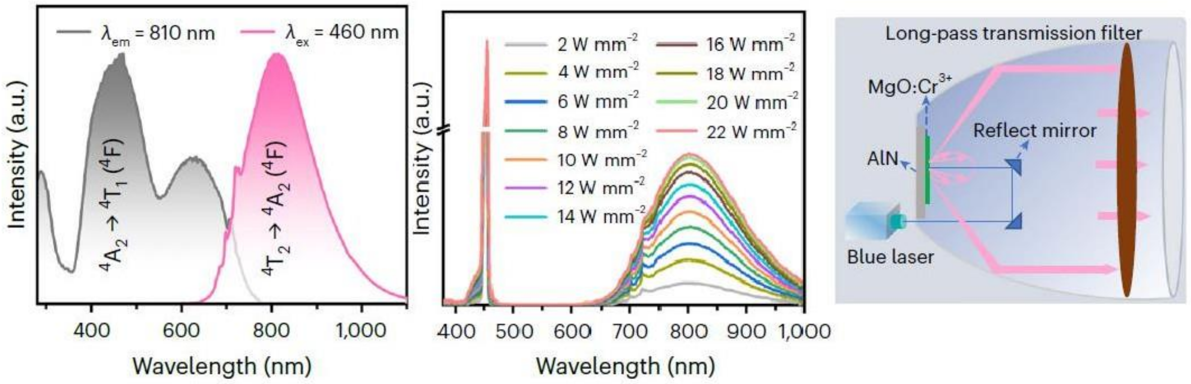

Figure 1. Near-infrared

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K-6

INFLUENCE OF LASER-GENERATED HEAT ON THE CHARACTERISTICS OF INDIVIDUAL CRYSTALS AND NANO-POWDERS

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There are two primary approaches to characterizing materials. One involves maintaining low temperatures to prevent changes, while the other entails heating samples using various methods, including lasers, to induce alterations. Laser-induced heating, particularly with nanoparticles, results in localized changes around the laser's focal point. The susceptibility of samples to heating largely hinges on their melting temperatures. Raman spectroscopy, employing laser excitation, can induce structural modifications on the sample surface due to local heating. Sometimes, these alterations can lead to sample decomposition, altering the Raman signal. Such changes manifest as shifts in phonon line positions and widths on the spectrum, along with the emergence of new lines stemming from permanent alterations in the sample.

In this keynote address, we will explore the temperature sensitivity of investigated samples and their diverse responses based on sample preparation techniques and types. Specifically, we will examine the effects of two distinct lasers—femtosecond and continuous Raman—on single crystals of BiGeO and BiSiO. Special emphasis will be placed on the impact of continuous Raman laser irradiation on the properties of CoO-doped ZnO nanoparticles, depending on sample preparation methods, as well as on Fe_2O_3-doped and MnO-doped ZnO nanoparticles, alongside pure MnO samples. All sample types underwent laser heating, with their changes monitored using Raman spectroscopy during the heating process. To effectively track alterations in peak positions and intensities, formation of new phases, uniformity of changes, resonance phenomena, or thermal degradation, supplementary methods such as XRD, AFM, and infrared spectroscopy were employed depending on the nature of the samples.

K-7

NIR PERSISTENT LUMINESCENCE OF Er^{3+} IN REAGG PHOSPHORS AND THEIR THERMOMETRIC PROPERTIES

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Due to rapid advancements and enhanced accessibility of InGaAs detectors, the third biological window (BW-III, 1500-1800 nm) has emerged as a focal area because of its superior properties, including reduced scattering coefficient, improved spatial resolution, and deeper tissue penetration. This study builds upon groundbreaking developments in the ratiometric Boltzmann thermometer (YAGG:Ce^{3+}-Er^{3+}) within BW-III, focusing on the thermal coupling of Stark sublevels of the $^4I_{13/2}$ level. This research explores the impact of {A} site substitution, specifically the replacement of Y^{3+} with Lu^{3+} and Gd^{3+}, on the

Er^{3+}:$^4I_{13/2}\rightarrow{}^4I_{15/2}$ Stark sublevels and the performance of thermometers. Significant variations in Stark splitting among various hosts are revealed through meticulous analysis involving deconvolution of temperature-dependent peaks and construction of Stark energy sublevel diagrams. Notable are the relative sensitivity (S_r) values for the VII/I mode of logarithmic intensity ratio thermometry in LuAGG: Ce^{3+}-Er^{3+}, reaching as high as 7.26% K^{-1} at 100 K and 0.73% K^{-1} within the crucial physiological temperature range of 25-60 °C. The introduction of additional Cr^{3+} doping in *RE*AGG: Ce^{3+}-Er^{3+} (*RE*=Lu, Y, and Gd) has resulted in impressive persistent luminescence characteristics, indicating strong potential for these materials in various biological applications.

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K-8

Luminescent Coordination Polymers or MOFs as Temperature Sensors

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Temperature is a basic physical parameter that is essential in both science and industry areas. One of most promising non-invasive technique to measure the temperature relies on ratiometric luminescent thermometers where the absolute temperature is optically determined *via* the measurement of the intensities of two transitions of distinct emitting centers. If the first studies on luminescence thermometry refer to inorganic compounds such as oxides, fluorides or sulfides, metal-organic frameworks (MOFs) recently appeared as promising candidates.[1,2] MOFs are crystalline hybrid materials built-up from metal ions as nodes linked by bridging ligands. They have attracted great interest due to their versatile chemistry, high surface areas and chemical functionality. The luminescence of MOFs can be generated in different ways, by using luminescent metal nodes (such as lanthanide cations), luminescent organic linkers, or luminescent guest species (organic dyes, metal complexes...). Consequently, many combinations are possible to elaborate ratiometric MOF luminescent thermometers.

Currently, many efforts are focused on lanthanide-based luminescent MOFs (Ln-MOFs), which are built on Ln^{3+} ions or clusters. The organic linker are chromophore molecules which absorb in the UV range, acting as sensitizers for Ln^{3+} ions *via* an energy transfer from their triplet excited state energy to the emitting energy states of Ln^{3+} ions. Therefore most of Ln-MOFs reported to date for luminescence thermometry are based on the Eu^{3+}-to-Tb^{3+} emission ratio between the transitions $^5D_4 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_2$ of the Tb^{3+} and Eu^{3+} ions, respectively. Here, we will propose a small overview of our recent results on mixed Eu-Tb MOFs luminescents thermometers, and we will discuss the different strategies to modulate the thermometric performances, such as operating temperature range or relative thermal sensitivity.[3]

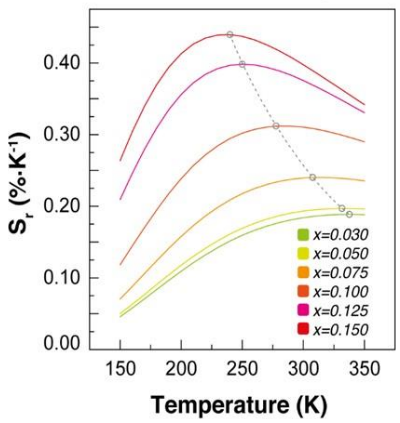

Figure 1: Relative thermal sensitivity for the mixed compounds $[Tb_{1-x}Eu_x(CH_3COO)(1,3\text{-bdc})(H_2O)]$ in the 150–350 K range.[3]

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K-9

Recommender System for the Discovery of New Inorganic Compounds

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In this study, we explore the development of a recommender system designed to efficiently identify chemically relevant compositions (CRCs) of previously unknown inorganic ionic compounds [1,2]. Utilizing the Inorganic Crystal Structure Database (ICSD), our tensor-based recommender system evaluates over 23 billion chemical compositions across five-element ionic systems. Remarkably, our approach achieves high success rates without relying on prior knowledge or first-principles calculations. The recommendations generated have led to the successful synthesis of novel oxides and nitrides [3,4], highlighting the system's efficacy in accelerating materials discovery. Additionally, our recommender system predicts optimal processing conditions for these new compounds by leveraging a dataset derived from parallel synthesis experiments [5-7]. This methodology not only enhances the discovery pipeline but also sets a new standard for computational materials science, combining vast data handling with practical experimental applications.

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TRANSITION METAL IONS FOR LIGHTING AND THERMOMETRY - THEORETICAL MODELING

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Combination of complementary calculation techniques – first-principles and crystal field calculations – is a powerful tool for getting a deeper understanding of complicated interrelations between the structural and electronic properties of a host material, on one side, and energy levels of a dopant, on the other side. The first-principles calculations allow for calculating the electronic band structure of solids, whereas the crystal field models give a possibility of calculating the crystal field splittings of the multielectron energy levels of impurities. Such calculations, if performed for large groups of isostructural materials or isoelectronic impurities, can help in revealing certain correlations, sometimes not obvious, between local structure and optical properties. Numerous examples focused on the Mn^{4+}- and Cr^{3+}-doped phosphor materials for lighting and thermometry will be discussed in detail, with an emphasis on tunabilty of the spectral positions of the emission peaks and their intensity by varying host's chemical composition [1-5].

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I-2

HIGH RESOLUTION THERMOMETRY IN FLUID FLOWS BASED ON IMAGING ISOLATED SUBMICRON PHOSPHOR PARTICLES

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Understanding mixing in turbulent flows is crucial to study the formation and dispersion of pollutants in the atmosphere, for example the formation of condensation trails past airplane engines, but also to control chemical reactors or design the thermal management of electric and thermal propulsion systems. Turbulent flows are characterized by strong spatial and temporal variations of state variables such as temperature. In turbulent flows of interest, which span sometimes meter-wide regions, the smallest time and spatial scales of variations can below 10^{-4} s and 10^{-5} m, requiring measurement systems able to resolve both small and large scales. While microscope-based nanothermometry can be used to resolve micron-scale, it is limited to small working distance and sub mm region.

To achieve high spatial resolution over wide region, we propose to introduce sub-micron luminescent particles into the studied fluids and to image their luminescence using macroscopic objectives (M<1). Nanosecond pulse lasers are used for luminescence excitation to form sharp images of the particles without motion blur. In this way, the imaged particles are distributed in the 3D space at the instant of the laser pulse and form an intricate web of local thermometers. Each thermometer which is randomly distributed can be localized with sub-pixel resolution by determining the center of its diffraction limited image as shown in Fig. 1 a).

To determine the particle temperature, a ratiometric method is used, either based on two spectrally filtered or two gated images of the luminescence upon a single excitation pulse. Those exploit changes in the emission spectrum or in the decay time of the luminescence, respectively. However, unlike traditional ratiometric measurement, the pixelwise intensity distributions on the luminescence images are not directly divided. Instead, the diffraction limited image of the particle is individually fitted by a 2D gaussian function, and the intensity of each image determined from mathematically integrating this function before division.

To push the measurements boundaries further, it is possible to determine the position of the particle in 3 dimensions by imaging the particle from multiple cameras. In addition, by tracking the displacement of the particles between different instant, not only the temperature is measured but also the local flow motion, as shown in Fig. 1 b).

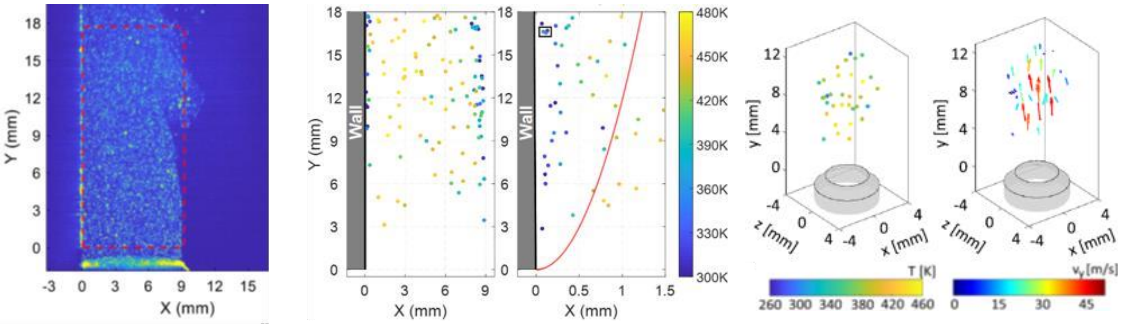

Figure 1 –Temperature measurements in a hot gas flowing past a cold wall adapted from [1] left, 3D temperature and velocity measurements in a turbulent jet reproduced from [2], right.

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RARE EARTH-DOPED GLASS MATERIALS FOR SOLID-STATE LIGHTING: RECENT ADVANCES

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Solid-state lighting (SSL), identified as the fourth generation of illumination technologies, has undergone rapid evolution over the last three decades due to its commendable attributes of high efficiency and environmental protection. Among the SSL devices, phosphor-converted light-emitting diodes (LEDs) and laser diodes (LDs) are frequently utilized in many different contexts, including remote illumination, industrial production, projection displays, and car headlights. The commercial white LEDs have been prepared by using yellow-emitting phosphor (YAG: Ce^{3+}) coated on InGaN blue/n-UV chips. Due to the encapsulating material for the LED there are some drawbacks such as poor thermal stability, high correlated color temperatures (CCT) and low color rendering index (CRI). To overcome these issues many efforts have been made to produce novel optical materials that do not require encapsulation, such as glass/ceramic/glass-ceramics doped with rare earth (RE) ions or single crystals. Among them, RE-doped glasses can serve as the best alternative materials with their high transparency, high thermal stability, homogeneous and intense emission, easy shaping in different forms, low cost, and epoxy resin-free manufacturing.

In this talk, we will provide an overview of recent progress and developments in singly and multi-RE-doped glasses through down-shifting and up-conversion processes. Key topics covered include the synthesis and characterization of RE-doped glasses, their optical properties, and their applications in SSL systems. Additionally, recent advances in fabrication techniques are discussed, along with strategies for enhancing the efficiency of these materials.

I-4

Modeling Excited States in Solids: Advancing Accurate Simulation of Luminescence Spectra

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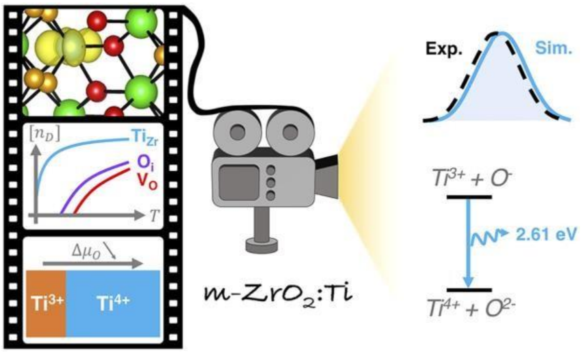
Luminescence in solids is a critical phenomenon underpinning various technologies, from LEDs to scintillators in medical imaging. Smart control of the luminescence also enhances strong integration toward devices than may dramatically lower our environmental impact. However, developing new devices with optimized materials and properties is all except cost effective. It is exactly at this place that theoretically oriented scientists become essentials. Indeed, if one is able to develop a computational approach able to simulate the luminescence of a material (intrinsic or with a dopant), it may guide towards predicted materials with optimized properties to be synthetized in a shorten amount of time.

Our work presents a comprehensive computational model for simulating luminescence in solid-state materials. By integrating quantum mechanical methods, we may accurately predict the electronic and optical properties of luminescent centers.

We first established the pivotal role of point defects on the optoelectronic properties on different materials using defect formation energies technics. Then, we were able, using the so-called constrained-DFT to determine the luminescence triggered by a specific activator. The combination of both technics allowed us to dichotomy different geometric sites allowing us a fine understanding of the process occurring at the excited state. The fine reproduction of the vibrational properties (i.e. Raman and IR) allows us to couple the vibrational contributions to the electronic transitions, allowing us to simulate a vibronic fine spectrum.

In this presentation, I will show that we are able to get simulated luminescence spectra in very good agreement in terms of energy and intensity with respect to experiment using different computational approaches. It enables the design of new materials with optimized luminescent properties, paving the way for a strong symbiosis between experimentally and theoretically oriented scientists.[1-4]



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I-5

Persistent phosphors enable the study of uncommon divalent lanthanides

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Lanthanides are frequently employed in various applications. Some of them, like Eu, Sm, Yb, and Tm, are relatively easy to stabilize in a divalent state.[1] However, others like Dy^{2+} or Nd^{2+} have exclusively been stabilized in a few halides or organometallic compounds and often only after gamma- or hard X-ray irradiation.[2]

As an alternative, certain luminescent oxides, sulfides, and nitrides can host metastable states for divalent lanthanides. These persistent luminescent materials, such as $SrAl_2O_4$:Eu,Dy [3] or $CaAl_2O_4$:Eu,Nd, [4,5] store part of the excitation energy and release it gradually through delayed luminescence. This is achieved via an electron transfer from the activator to the Ln^{3+}-codopant, resulting in metastable Ln^{2+}. These materials hence offer a unique opportunity to study the luminescence and absorption spectra of these uncommon Ln^{2+} ions.

Here we report on the optical properties of metastable Nd^{2+}, Sm^{2+}, and Dy^{2+} codopants in $SrAl_2O_4$. These are investigated using diffuse reflectance and luminescence spectroscopy. This study further reveals the role of these codopants as electron trapping defects in persistent phosphors and provides an experimental approach that offers insights into charge trapping mechanisms in luminescent materials without having to resort to more complex or less accessible experimental techniques.

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Plasmonic Heating Within the Biological Windows

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Plasmonic nanoparticles can be used as actuators to induce a local thermal increase upon illumination. Most applications under development based on this light-heat conversion must occur in aqueous media, including the promotion of local chemical reactions or photothermal therapy. In this second case, besides water, the environment may also have additional components, such as melanin, haemoglobin, lipids, etc. From the optical perspective, the relevance of the composition of the environment relies on the different ways in which it can attenuate excitation light that, instead of reaching the nanoparticle, can be lost along the way in absorption or scattering events. Besides a reduced penetration depth of light, such events would induce heating all along the optical path and uncontrolled illumination areas. For this reason, the development of optically activated nanoparticles for such applications benefit from being excited within the biological windows, which are the wavelength ranges in which light attenuation is lower in tissues.

Depending on the specific tissue several windows have been described, but we will focus on the most common ones, defined as BWI (650 – 950 nm), BWII (1000 – 1350 nm) and BWIII (1450 – 1900 nm). To obtain good photothermal plasmonic nanoparticles with dimensions compatible with biomedical applications in BWII and BWIII is still a challenge. We have addressed it developing water-dispersible ITO nanoparticles with plasmonic response in BWIII, and gold nanostars with plasmonic response in BWII. While both strategies present photothermal heating in the range on interest, they also account for limitations that will be discussed.

Regarding BWI there´s already a good availability of plasmonic nanoparticles with large heating efficiencies (between 70% and 90%), including gold nanorods and nanostars. Hence, we will discuss the possibility of measuring local temperature through luminescent nanoparticles ($CaF_2:Nd^{3+}$) specifically developed to overlap in excitation with the heaters and present good thermal sensitivities in BWII. In this way, the emitted signal containing thermal information is minimally distorted by the heaters. Still, thermal accuracy requires the development of measurement strategies, which we will discuss and test in proof-concept experiments specifically designed so we can discuss the differences between local temperature and macroscopically measured temperature.

I-7

LUMINESCENCE-BASED 3D THERMAL IMAGING

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Luminescence nanothermometry is a remote sensing technology that allows studying phenomena "from within" in a minimally perturbing way. The use of nanometric probes – from dye molecules to luminescent nanoparticles – ensures minimal disturbance of the system to be observed, while setting the conditions for submicrometric spatial resolution. Given its characteristics, luminescence nanothermometry is a prime tool to monitor the thermal state of microelectronics and hot spots in catalytic reactions, investigate complex phenomena like Brownian motion at the nanoscale, and even peer into the metabolism of cells or the health of larger complex organisms. Nonetheless, a key limitation of this technology has been the lack of three-dimensional mapping capabilities. This is particularly crippling in the biomedical context, where access to 3D thermal information would allow better understanding the progress of inflammation events and diseases, as well as provide insight into thermoregulatory mechanisms.

In this talk, a 3D luminescence thermometry approach will be presented, which fills this technological gap. Specifically, the approach is based on the use of Ag_2S nanoparticles and machine learning algorithms, which are able to extract simultaneous information about location and thermal state of the nanothermometers in biological tissues.

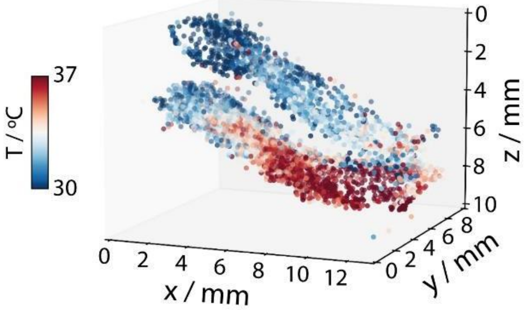

Figure. 3D thermal image obtained from luminescent Ag_2S nanothermometers embedded in tissue phantom.

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I-8

Photonic effects on lanthanide luminescence

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Intro

Color conversion by lanthanide-doped materials often relies on complex excited-state dynamics. Dopant centers absorb and emit light, but may also decay nonradiatively or transfer energy to other dopants. The emission efficiency and emission color of a material depends on the competition between these different pathways, determined by the associated rate constants.

Radiative transitions between energy levels of a lanthanide center, whereby a photon is emitted, have typical rate constants of the order of 1 ms^{-1}. The exact value depends on the lanthanide considered and the specific transition, as well as on the host material. Beyond these intrinsic materials parameters, radiative decay rates are also influenced by the *photonic environment* of the emitting center. For example, radiative decay is accelerated—or slowed down—simply by changing the refractive index of the surrounding of the emitter center or by introducing a reflective surface nearby.

Summary of presentation

This presentation will overview *challenges and opportunities associated with photonic effects* on radiative decay rates. For example, suppressing radiative decay makes competing energy-transfer processes more likely, which can lead to more efficient color conversion.[1] Alternatively, systematic experiments in different photonic environment can be used as a spectroscopic trick to quantify radiative and nonradiative decay constants.[2,3] **Figure 1** shows unpublished data on upconversion dynamics based on this concept. Conversely, lanthanide-doped nanoparticles can be used as nanosensors that probe local electromagnetic fields created by photonic structures.[4] Finally, photonic effects on light emission may introduce challenging cross-sensitivities when lanthanide-doped nanoparticles are used as sensors for other parameters, such as temperature.[5]

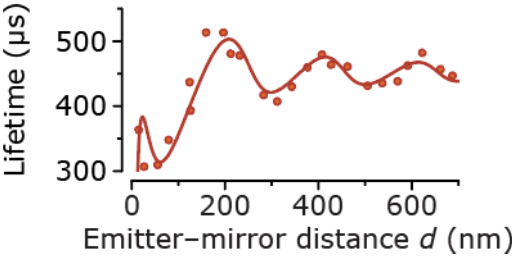

Figure 1 — The lifetime of the red upconversion luminescence from $NaYF_4:Er^{3+},Yb^{3+}$ nanoparticles, when placed at different distances from a mirror. The mirror changes the local density of optical states (solid line) experienced by the nanoparticles.

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I-9

Development of Hole Detrapping Persistent Phosphors

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Persistent phosphors, which show continuing luminescence even after the ceasing of excitation light, have been widely used as luminous paint in many products. The persistent luminescence is generally caused by 1. Carrier generation, 2. Carrier trapping, 3. Storage, 4. De-trapping and 5. Luminescence processes in Figure 1.[1] The detrapping carrier is determined by the relationship of trap depths by electron and hole traps. In the condition that the electron trap depth ($E_{\mathrm{e\_trap}}$) is shallower than the hole trap depth ($E_{\mathrm{h\_trap}}$), the electrons are firstly detrapped and the electron detrapping persistent phosphors can be obtained. If $E_{\mathrm{h\_trap}} < E_{\mathrm{e\_trap}}$, the hole can be firstly detrapped and the hole detrapping persistent phosphors can be obtained. Common persistent phosphors like Eu^{2+} and Ce^{3+}-doped materials are classified as the electron detrapping persistent phosphors. On the other hand, it is expected that Eu^{3+}-doped phosphors are caused by the hole trapping and detrappng due to the photo-reduction process ($Eu^{3+} \Leftrightarrow Eu^{2+} + h^+$).

Recently, we successfully demonstrated that the hole-ionization process in Eu^{3+}-doped oxysulfide phosphors using thermoluminescence techniques and developed a new red persistent phosphor of Eu^{3+}-Pr^{3+} co-doped La_2O_2S based on the hole-trapping and detrapping mechanism [2]. In the presentation, the design concept of the hole detrapping persistent phosphors will be discussed.

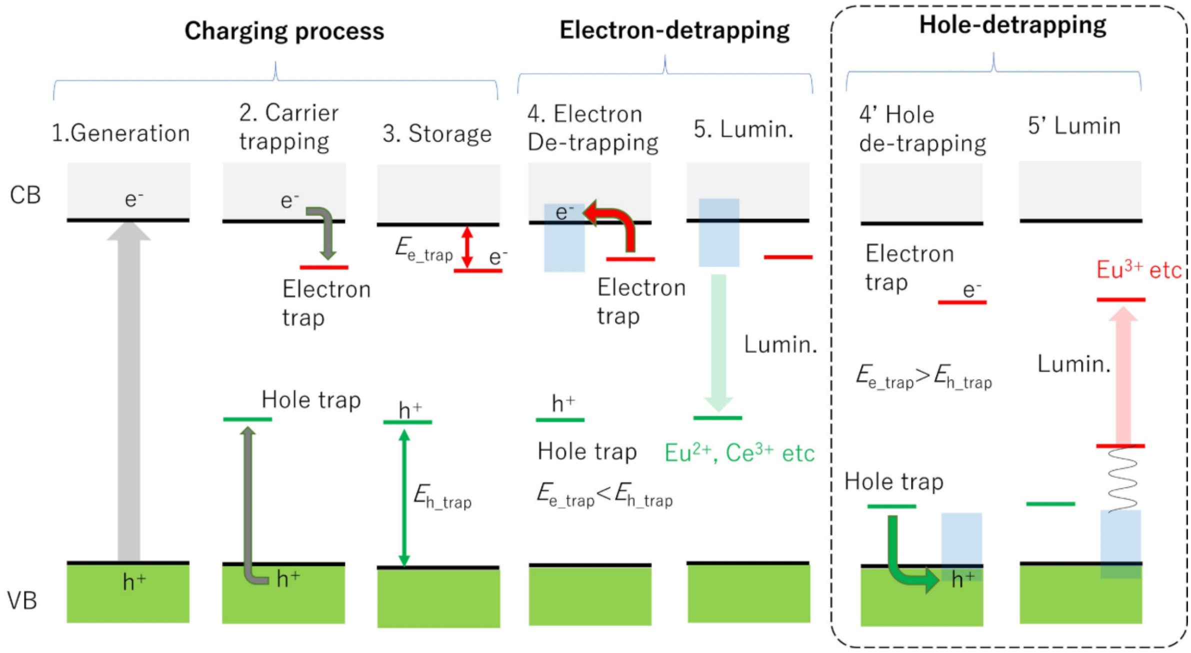

Figure 1. Persistent luminescence mechanism with different processes (Generation, trapping, storage, electron detrapping or hole detrapping, luminescence). [1]

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I-10

MECHANOLUMINESCENCE PROPERTIES OF $LiTaO_3$:Pr AND RELATED MATERIALS

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Mechanoluminescence (ML) is a fascinating phenomenon, exhibited by numerous solid materials as the emission of light upon mechanical stress and physical deformation [1]. Some materials also exhibit such a phenomenon during sonication at a high frequency.

Mechanoluminescence (ML) properties of the $LiTaO_3$ host material with a trigonal R3c structure with variable concentrations of praseodymium (Pr) activator ions (1% (S1), 3% (S2), and 5% (S3)) were examined in this work. Three distinct ML experimental setups, namely, friction-induced mechanoluminescence (F-ML), impact-induced ML (I-ML) [2], and stress-induced ML (S-ML), are utilized to examine their ML properties. F-ML measurements demonstrate the ML spectra of $LiTaO_3$:Pr, which have emissions in green, red, and IR regions. I-ML measurements exhibit their fast detection capabilities of applied mechanical impact with excellent ML recoverability at various impact kinetic energies. S-ML experiments reveal a remarkable superposition of emitted S-ML intensity curves with the time-dependent applied force. Additionally, we also studied light emission from $LiTaO_3$:Pr during exposure of low (20 kHz) and high (3.3 MHz) frequency ultrasonic waves. After being charged at ~270 nm, the phosphor emits light with three prominent peak bands at 511 nm, 618 nm, and 892 nm, as observed in both photoluminescence and mechanoluminescence spectra.

Photoluminescence results exhibit identical emission spectra for each sample associated with the Pr^{3+} ions. Among them, the S3 sample exhibited the best ML properties and reproducibility due to the appropriate ratio of deep and shallow traps and luminescence centers, as suggested by the thermoluminescence spectra. A part of ML emission from $LiTaO_3$:Pr also lies in an infrared biological window, which is another unique feature explored in this study. The outcomes validate $LiTaO_3$:Pr as a promising candidate for the fast, sensitive, and remote detection of diverse mechanical stimuli in various industrial and biological applications. In addition, the presented study offers a comprehensive roadmap for understanding of the correlation between mechanoluminescence and the energy distribution of trap depths. [3]

Acknowledgments: This work was partially supported by the Polish National Science Center project No: 2019/33/B/ST8/02142.

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I-11

From demonstration to application: Considerations for high-speed phosphor thermometry in high transient heat flux environments

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Lifetime-based phosphor thermometry has been demonstrated in a wide variety of surface temperature measurement environments due to its relative ease of implementation and robustness to background interference when compared to other optical temperature measurement methods. To be useful from a quantitative model-development perspective, further analyses must complement the measurements to assess the diagnostic, both in terms of precision and bias. Here, we discuss our recent work in these areas for the application of assessing potential heat flux reduction offered by temperature-swing thermal barrier coatings (TBCs) in internal combustion engines.

Simulations have shown that the temperature-swing of a TBC-coated piston during typical diesel operation may span a range from 450 K to over 1200, with temperatures changing as rapidly as a few Kelvins every 20 µs. To address this unique requirement, a new thermographic phosphor for surface temperature measurements, Pr:YAG, was investigated. 100 single-shot measurements were acquired in a tube furnace from room temperature to 1200 K. The emission lifetime of Pr:YAG was found to decrease continuously from 7 µs at room temperature to 200 ns at 1200 K, and measured single-shot temperature precision was better than 2 K over the entire range. A methodology developed using weighted linear regression statistics that enables in-situ single-shot temperature precision estimates in transient environments where it cannot be experimentally determined agreed within 1 K of the experimental results.

Aside from diagnostic precision, bias must also be accounted for. In particular, for surface phosphor thermometry, the effect of the phosphor layer must be analyzed. High-speed phosphor surface temperature measurements were performed on 4140 steel substrates installed in the cylinder head of an optically-accessible internal-combustion engine. Four substrates were studied, each coated with a phosphor layer of different thickness ranging between 6 µm and 47 µm. The measured temperature swings during combustion were shown to be heavily impacted by the presence of the phosphor coatings, increasing by roughly a factor of 2 - 2.5 when increasing the thickness from 6 µm to 30 µm. A technique was implemented which utilizes the temperature data in combination with a heat transfer model to provide estimates of the corrected temperature swing and heat flux in the absence of the phosphor coating. It was shown that even a 6 µm phosphor coating could lead to an order of magnitude increase in the temperature swing relative to the uncoated 4140 steel substrate. To evaluate the accuracy of the approach, the corrected phosphor heat flux estimates were compared to heat flux estimates determined using two different state-of-the-art high-speed thermocouples. Reasonable agreement between the different diagnostics was obtained, indicating that despite its' intrusiveness, phosphor thermometry can be a reliable surface temperature and heat flux diagnostic for transient high heat flux environments if proper care is taken to account for the impact of the phosphor layer on the measurement.

The fully characterized phosphor thermometry diagnostic was then applied to study the effect of novel TBC materials on the temperature-swing and heat flux in the optical engine under four different operating conditions. The results were compared to the uncoated 4140 steel substrates and the heat loss reduction offered by each TBC was quantified.

TAILORING THE OPTICAL PROPERTIES OF 2D MATERIALS VIA FERROELECTRIC SUBSTRATES

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2D Transition Metal Dichalcogenides (TMDs) exhibit a unique combination of atomic-scale thickness, direct bandgap, and favorable electronic and mechanical properties, which make them interesting for the next generation of optoelectronic devices. Due to its atomic thickness nature, 2D-TMDs provide the possibility of engineering its properties by means of its surrounding environment. In particular, ferroelectric-driven electrostatic doping has been previously demonstrated [1,2]

Here, we investigate the interplay between ferroelectricity and light on the optoelectronic properties of monolayer MoS_2 deposited on the polar surface of a periodically poled lithium niobate crystal. Our findings unveil a photoinduced charging process strongly dependent on the ferroelectric domain orientation, in which light induces charge generation and transfer at the monolayer-substrate interface. This highlights the significant role of light excitation in ferroelectrically-driven electrostatic doping in MoS_2, and the possibility of spatial modulation of the charge carrier density, thereby tuning the optical response of the 1L-MoS_2

The results suggest prospects for novel optoelectronic and photonic application involving monolayer 2D-TMDs by combining light-matter interaction processes and the surface selectivity provided by ferroelectric domain structures.

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I-13

SIZE-DEPENDENT LANTHANIDE ENERGY TRANSFER AMPLIFIES UPCONVERSION LUMINESCENCE QUANTUM YIELDS

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Optical upconversion from lanthanide-doped nanoparticles is promising for a variety of applications ranging from bioimaging, optogenetics, nanothermometry, super-resolution nanoscopy and volumetric displays to solar cells. Despite remarkable progress made in enhancing upconversion to fuel these applications, achieving luminescence of upconversion nanoparticles (UCNPs) that is comparable to or higher than the bulk counterparts has been challenging due to nanoscale-induced quenching effects. Here we demonstrate a size-dependent lanthanide energy transfer effect in a conceptual design of hexagonal sodium yttrium fluoride ($NaYF_4$) core–shell–shell $NaYF_4$@$NaYF_4$:Yb/Tm@$NaYF_4$ UCNPs with depleted surface quenching. We show that precise control over the domain size (or the thickness of the middle shell doped with ytterbium (Yb) and thulium (Tm) from 1.2 to 13 nm) increases the lanthanide energy transfer efficiency (from 30.2 to 50.4%) and amplifies the upconversion quantum yield to a high value of 13.0 ± 1.3% in sub -50 nm UCNPs (excitation: 980 nm, 100 W $cm^{-2)}$, which is around fourfold higher than the micrometre-scale hexagonal $NaYF_4$:Yb/Tm bulk counterparts. Spectroscopic studies and theoretical microscopic modelling reveal that long-range lanthanide energy transfer (>9.5 nm) takes place and underlies the observed size-dependent phenomena. Demonstration of size-dependent lanthanide energy transfer and upconversion quantum yields at the nanoscale transforms our long-existing conceptual understanding of lanthanide energy transfer (size independence), thereby having important implications for applications of lanthanide nanophotonics and biophotonics. [1]

Reference

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I-14

Sensor fusion luminescence thermometry

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In luminescence thermometry, some of the frequently used indications are luminescence intensity ratio (LIR) or changes in luminescence lifetime (τ), bandwidth (Γ), or peak energy (line shift, ν).[1] Here we propose a Sensor fusion by inverse-variance weighting method as a replacement of multiple linear regression, as a simpler and more direct method. In sensor fusion for luminescence thermometry each indication is observed as an individual sensor. Since each indication has a different uncertainty, the contribution of each measurement to the fused estimate is weighed accordingly. Note that each indication is not perfect in accuracy. The fused estimate of temperature is calculated from the individual means of Gaussian distributions of each sensor, weighed by their variances.[2] The sensor fusion method in luminescence thermometry is demonstrated in Figure 1.

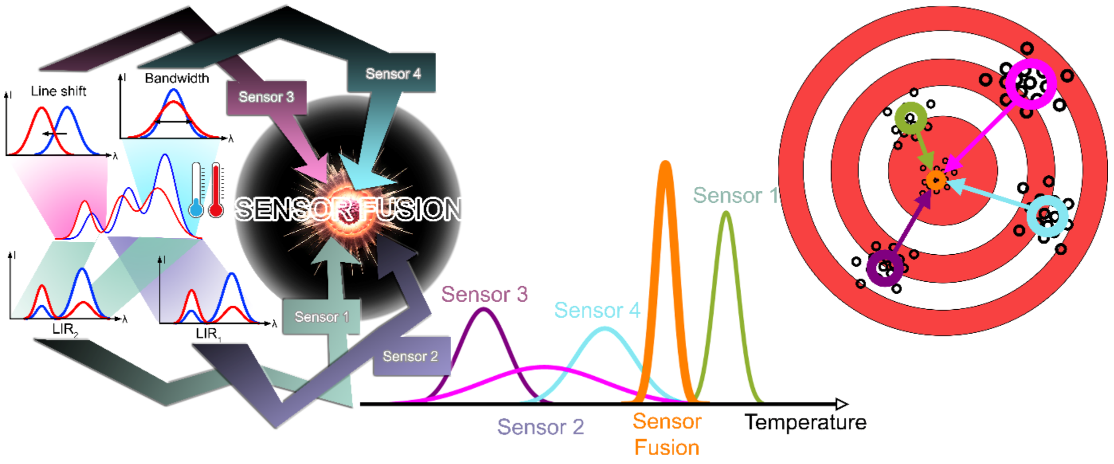

Figure 1. Sensor fusion in luminescence thermometry on an example of 4 sensors – indications: (1) LIR$_1$, (2) LIR$_2$, (3) Line shift, (4) Bandwidth, extracted from the temperature-dependent spectra; their Normal distributions and estimates on the temperature scale together with the fused Gaussian distribution, and how the method can be demonstrated by shooting at the target.

The sensor fusion method always results in reduced variance – uncertainty, i.e. the precision is increased, i.e. the temperature resolution is improved. The accuracy, however, is not necessarily improved, and the methods for improving accuracy lie outside of the scope of this paper. If there is a correlation between individual sensors then this has to be taken into account in the above equations. The sensor fusion in luminescence thermometry was tested on an Mn^{5+} doped sensor probe.[3] As theoretically predicted the fused precision is always better than the individual indications, thus sensor fusion is an adequate method for improving temperature sensing capabilities of phosphor materials in luminescence thermometry.

Acknowledgment

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I-15

Persistent phosphor thin films: Processing and optical environment matter

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Persistent phosphors, typically rare earth- or transition metal-doped inorganic oxides, exhibit unique delayed and long-lasting luminescence, known as afterglow, which is highly valuable for design and night signalization applications. Persistent nanophosphors, in particular, present exciting opportunities for anticounterfeiting, data storage, and imaging displays due to their ability to be processed into shapable and transparent thin coatings.[1] However, their potential is significantly limited by the challenges in tuning their properties and their relatively low storage capacity. In this context, we present a novel transversal approach to tune the afterglow properties of persistent nanophosphor thin films by modifying their optical environment in a controlled manner, without altering their composition. First, utilizing the versatility of the sol-gel method, we fabricated layered persistent nanophosphor garnet films exhibiting remarkable time-dependent chromaticity.[2] Additionally, we took advantage of $ZnGa_2O_4:Cr^{3+}$ nanoparticles colloidal stability to design transparent films in which TiO_2-based scattering centres could be embedded.[3],[4] Using this methodology, we achieved a substantial increase (approximately 3.5-fold) in afterglow intensity and a notable acceleration in the charging speed of persistent luminescence. These features are attributed to the synergistic effect of efficient charging and improved outcoupling. Our transversal approach provides a promising pathway for developing persistent nanophosphor coatings with intense and novel properties, crucial for designing dynamic anticounterfeiting tags.

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PUSHING THE LIMITS: THE 25-1225 K WIDE-RANGE LUMINESCENCE THERMOMETRY

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Luminescence thermometry has emerged as a pivotal technique for temperature sensing across a diverse range of applications, from materials and health sciences to environmental monitoring and beyond [1]. One of the biggest challenges currently is achieving high relative thermal sensitivity combined with a possibly wide range of temperatures even surpassing 1000 degrees [2].

Within this presentation, we will show a series of materials doped with Pr^{3+} ions developed for luminescence thermometry. Through a comprehensive analysis of the underlying luminescence mechanisms, we elucidate the unique properties of the chosen lanthanoid ion that make it an exceptionally useful candidate for temperature sensing both at cryogenic and at high temperatures. Tracing the interplay between the host matrix and Pr^{3+} ions, we explain its influence on the chosen phosphors' luminescence properties crucial in thermometry. Finally, experimental results will be shown for $Ca_3Sc_2Si_3O_{12}$:Pr, demonstrating its capability to measure temperature from 50 to 1225 K, maintaining relative thermal sensitivity > 0.5 %/K over almost the entire range.

Finally, we shall discuss the practical implications of our findings for the planning and execution of future research in this domain. By exploiting the unique advantages offered by Pr^{3+} activator, researchers can overcome important challenges associated with wide range temperature measurements. We believe that our results expand the possible ways of designing luminescent thermometers with such specific characteristics.

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RECENT ADVANCEMENT IN DEVELOPMENT OF COMPOSITE COLOUR CONVERTERS BASED ON EPITAXIAL STRUCTURES OF Ce^{3+} DOPED GARNET COMPOUNDS

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Development of the Planar-Chip-Level Conversion (PCLC) approach for white LEDs (WLEDs), where the phosphor is free-standing and separated from the LED chip [1], requires the investigation of novel durable phosphors which can be excited with high power blue/UV LEDs or lasers. For this purpose, it is urgently needed to design and investigate the new high structural quality and in the form of single crystals (SCs) and single crystalline films (SCFs) [2, 3].

This report presents the review of our last achievement in the development of multilayered composite luminescent materials based on the single crystalline films (SCFs) and single crystals (SCs) of garnet compounds using the liquid-phase epitaxy (LPE) growth method and application of these composite materials for industrial solid-state lighting. Namely, the report gives the brief review of the results in the development of ***single- and multi-layered film converters*** for WLED based on the (i) SCFs of $(Gd,Lu,Tb)_3Al_5O_{12}$:Ce garnets, grown by the LPE method onto undoped YAG substrates [3-5]; (ii) the SCFs of $(Gd,Lu,Tb)_3 Al_5O_{12}$:Ce garnets grown on the Ce^{3+} doped YAG and LuAG SC substrates [6-8].

The results of investigation of the luminescent and photoconversion properties (correlated color coordinates (CCC), color rendering index (CRI), luminous efficacy (LE)) of different composite converters based on the mentioned SCFs and SCs with different and substrate thicknesses and Ce^{3+} concentrations were presented. In turn, the variation in the thickness or activator concentration in each element of the composite converter allows obtaining almost any shade from green to orange emission on the chromaticity diagram. The obtained results were analysed with the aim of choosing the best compositions for WLED converters with the highest CRI and LE values.

Acknowledgment

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I-18

Unraveling luminescence behavior of $3d^3$ ions in solids: Navigating from crystal-field theory to first-principles analysis

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Phosphors activated by $3d^3$ ions are increasingly gaining prominence in the field of solid-state lighting due to their efficacy as red photon emitters. This presentation aims to underscore pivotal factors crucial for designing commercially viable red-emitting phosphors. Our focus lies in comprehending the electronic energy levels of $3d^3$ ions in both free-state and crystal-field environments, utilizing a semi-empirical data mining technique [1]. Moreover, we propose a robust first-principles approach (as illustrated in Figure 1) to enhance the description of excited ^2E and $^4T_2$ states in $3d^3$ ions, enabling accurate predictions of the structural, electronic, and optical properties of red-emitting phosphors doped with these ions. This proposed calculation scheme has demonstrated success in Mn^{4+}-doped K_2SiF_6 and Cr^{3+}-doped $Ca_3Y_2Ge_3O_{12}$ phosphors [2,3]. Additionally, it distinctly unveils the physical-pressure/chemical-stress induced excited-state crossover in $K_3MF_6:Cr^{3+}$ (M=Al, Ga) from a first-principles perspective. Furthermore, we delve into the thermal stabilities of the Mn^{4+}/Cr^{3+} emissions within the studied hosts, analyzing their thermal activation energies for the first time via the calculated configuration coordinate diagrams (an example of which is depicted in Figure 2). Ultimately, based on these findings, we offer practical recommendations for fine-tuning the emission wavelengths and intensities of Mn^{4+}/Cr^{3+}-doped red-emitting phosphors [4].

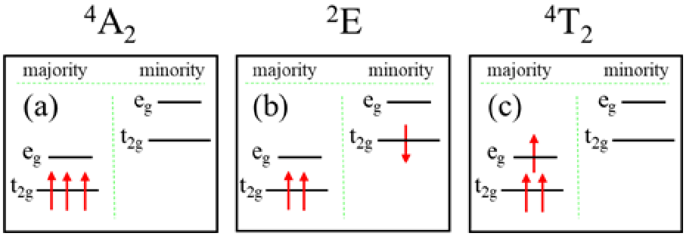

Fig. 1. Single-particle schematic diagrams of (a) the $^4A_2$ ground state and (b) the ^2E and (c) $^4T_2$ excited states of $3d^3$ ion in an octahedral environment.

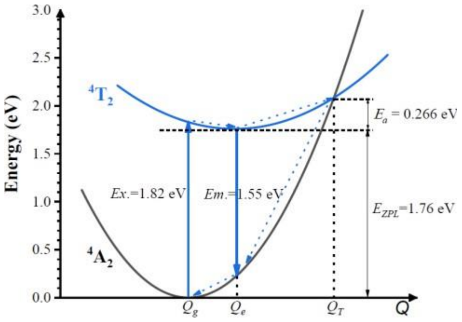

Fig. 2. Schematic depiction of the calculated configuration coordinate diagram of Cr^{3+} ions in $Ca_3Y_2Ge_3O_{12}$.

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HIGH-RESOLUTION SPECTROSCOPY FOR LUMINESCENCE CRYOTHERMOMETRY AND MAGNETIC FIELD SENSING

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Luminescent methods for remote measurements of important physical quantities such as temperature and magnetic field are being intensively developed [1,2]. In luminescent thermometry, the temperature range 100 – 800 K has been well mastered to date. It should be noted that detection of lower temperatures is relevant in crystallographic measurements at the synchrotron, aerospace research, and for modern quantum technologies.

We have undertaken investigations into the potential of high-resolution spectroscopy to measure low temperatures and magnetic fields using luminescence of lanthanide ions in inorganic crystals. We studied the applicability of luminescent Boltzmann ratiometric method [1,3] for measuring the temperatures in the range 3.5 – 60 K.

Luminescence spectra excited by the radiation of different diode lasers were acquired on an experimental setup built on the basis of a Bruker IFS 125 HR high-resolution Fourier spectrometer providing the minimal width of the instrumental function 0.0006 cm^{-1} (18 MHz) in the whole working spectral range (2500–16000 cm^{-1}) [4]. A set of luminescence line pairs in the spectra of $K_2YF_5:Er^{3+}$ [5], $LYF_4:Er^{3+}$ [6], and $LYF_4:Ho^{3+}$ crystals was investigated in the temperature range 3.5 – 120 K to verify the fulfillment of the equation $I_2(T)/I_1(T)=\exp(-\Delta E/kT)$ fundamental to Boltzmann ratiometric thermometry, ΔE being the energy interval between the initial luminescence crystal-field levels 2 and 1. Several line pairs with ΔE from 4 to 84 cm^{-1} were selected to realize Boltzmann ratiometric thermometers with maximum absolute sensitivities at the temperatures from 2.9 to 60 K, respectively.

We show that even lower temperatures (0.1 – 1 K) can be detected by measuring the intensities of hyperfine components in the luminescence spectra of Ho^{3+} in $LYF_4:Ho^{3+}$ crystals. The splitting of hyperfine components in an external magnetic field delivers a possibility to measure magnetic field strength with accuracy up to $\delta B \approx 17\ \mu T$ [4]. To convert these achievments into practical applications, we suggest to isolate selected lines and to use a contemporary Fabry-Perrot interferometer instead of a big and expensive broad-band high-resolution Fourier spectrometer.

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I-20

RARE-EARTH DOPED SESQUIOXIDE NANOPHOSPHORS MADE BY LASER SYNTHESIS

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Development of new techniques using optical probes needs application of ever smaller particles of luminescent materials, and to accomplish high-quality, truly nanoscaled particles, new methods of preparation and optimization of the nanophosphors are still of high interest. Among a number of preparation methods for true nanoparticles, laser synthesis (laser supported material evaporation and subsequent vapor condensation) is particularly promising, since it yields perfect, highly pure, non-agglomerated, spherical nanoparticles with a narrow size distribution [1]. Such nanoparticles have a peculiar property of the ones produced from vapor condensation - metastable phases formed on the path to fully crystalline materials [2]. Therefore, it is crucial to know, how the metastable states influence the phosphor’s emission, as well as to devise syntheses for obtaining a high degree of crystallinity of the materials.

This report deals with the production technology and characteristics of RE-earth doped sesquioxide nanoparticles fabricated by means of an Yb-doped fiber laser. The technique was shown to efficiently produce weakly agglomerated nanopowders with particle sizes ranged at about 15 nm and with a narrow size distribution. The structural, morphological and luminescent properties of the nanomaterials obtained were investigated employing SEM, TEM, BET, FT-IR, XRD, light absorption and luminescence analysis. During the research methods to fabricate the nanoparticles whose phase and luminescence depend on the particles size as well as to prepare highly stable water and alcohol suspensions of the nanoparticles were developed.

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I-21

NEAR-INFRARED PERSISTENT LUMINESCENCE PHOSPHORS

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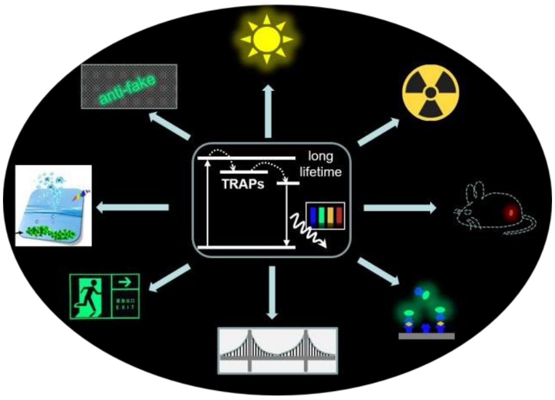
Persistent phosphors become novel unique optical tools because of their advances in long term temporal separation of the excitation/emission process. Now, they have been applied from simple night vision labels to advanced biomedical applications. The past few years have witnessed great progress in the development of bulk phosphors, but the existing achievements just supported the research on key scientific and engineering questions for understanding the complicated photo-ionization reaction of trap site and impurity centres in the macroscopic aggregation state. Perspicuously, it is more significant to investigate the species and quantities of traps, carrier' delocalization and migration processes, even the route of tuning the optical, electrical and magnetic properties of Persistent phosphors at the nanometer scale. After all, there is a huge difference between these two chemically structural states. In the past 10 years, we work on the control of afterglow property via the lattice defect engineering. In this presentation, we will cover the recent progresses on persistent phosphors by highlighting the tuning of energy traps of known materials, tailor of migration dynamics of carriers, discovery of new persistent phosphors and applications. These results represent important steps in the development of persistent phosphors as novel optical tool set in diverse fields.



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INFLUENCE OF ORBITAL HYBRIDIZATION ON THE INTENSITY OF THE HYPERSENSITIVE TRANSITION AND NONLINEAR OPTICAL EFFICIENCY IN RE ACTIVATED COMPOUNDS

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The influence of orbital hybridization on the intensity of the hypersensitive transition in isostructural vanadate, arsenide and phosphate systems is discussed. We show the same mechanism is also responsible for the efficiency of second harmonic generation (SHG). Is well-known that SHG is a nonlinear process in which a crystal converts lower frequency radiation to higher frequency. The bonding covalence within the acentric anionic groups, that are the basic structural moiety of the crystal framework (such as PO_4, AsO_4, VO_4, SiO_4, GeO_4, etc.), is chiefly responsible for the SHG activity. The importance of orbital hybridization on the SHG efficiency is exemplified by the striking difference in optical nonlinearity between isostructural titled compounds. While the vanadate is efficient, the phosphate shows no SHG activity, although the calculated SHG coefficients (pm/V) for both compounds are non-zero. The difference in the SHG efficiency has been clarified by examining the electronic band structure of these compounds. Our analysis supports the polarizability of $(XO_4)_3$- (X = P, As, V) over local site distortion effects as the intensity enhancing mechanism of the $^5D_0 \rightarrow {}^7F_2$ transition. The connection between the mechanism of hypersensitivity and second harmonic generation (SHG) is discussed.

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DYNAMIC TESTING WITH THERMOGRAPHIC PHOSPHOR DIGITAL IMAGE CORRELATION

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During an accident, coupled thermal-structural responses can decrease material strength and increase the risk of damage. To accurately capture these phenomena, simultaneous strain and temperature measurements are required, but traditional measurements of a material's thermo-mechanical performance are limited to homogenized, global stress-strain data combined with a single point temperature measurement from a thermocouple. As an alternative, thermographic phosphor digital image correlation (TP+DIC) is a synergistic combination & elevation of two optical diagnostics: phosphor two-color ratio thermography and DIC strain. This technique uses functional ceramics – thermophosphors – as a DIC speckle pattern. Temperature is inferred from phosphorescence, and simultaneous strain is inferred from DIC. TP+DIC has potential to provide full-field data with a single experimental set-up but has only been demonstrated from T = 30 °C – 150 °C and strain rates of 10-1 s-1 [1].

This work will extend the applicability of TP+DIC to higher temperatures and faster strain rates by exploring different strategies: 1) a setup-agnostic calibration for fielding TP+DIC, 2) a phosphor-ink pattern for large deformations, 3) testing in dynamic set-ups – such as a split Hopkinson pressure bar.

TP+DIC in dynamic environments will be compared to complimentary, non-contact, high-speed (GHz) single point IR pyrometry and lower speed (kHz) full-field IR camera thermography, which has been successfully demonstrated and can be used for benchmarking [2].

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O-1

Ratiometric Fluorescence Optical Fiber Enabling In-situ and Real-time Temperature Monitoring

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Thermal evolution is essential for improving the performance and monitoring the status of Li-ion batteries (LIBs). However, it is a challenge to design efficient and facile sensing materials for the detection of the in situ temperature of a working LIB. Herein, a ratiometric fluorescence optical fiber is developed and real-time temperature monitoring is performed with a measurement accuracy of 0.12 °C, and the feasibility based on this polymer optical fiber composed of $NaLaTi_2O_6$:Yb/Er phosphors is verified in a pouch-type battery. During the charging and discharging cycles, the in situ temperature is instantaneously conveyed, revealing the internal situation of LIBs. This article further dwells on the thermal characteristics in constant current (CC)/constant voltage charging and CC discharging processes at different C-rates and the battery failure when operated at low temperatures (0 °C). This work demonstrates an innovative strategy for operando solitary temperature monitoring conducted by ratiometric fluorescence optical fiber.

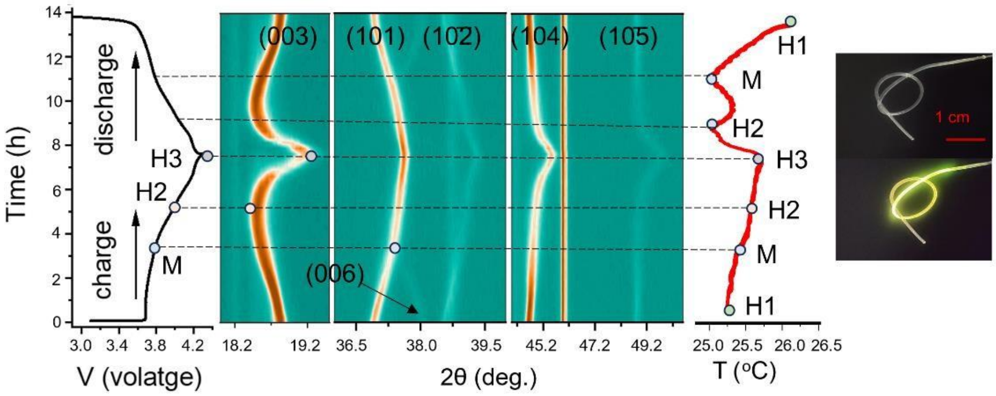

Figure 1. *Operando* temperature monitoring in the pouch-type battery via as-fabricated NLT optical fiber.

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O-2

RAMAN AND HIGH-RESOLUTION LUMINESCENCE SPECTROSCOPY OF RE DOPED $Gd_{1-x}Lu_xAlO_3$ SINGLE CRYSTALLINE FILMS

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The development of the microimaging technique using X-ray or synchrotron radiation in industry requires the use of scintillation screens with high spatial resolution [1, 2]. Therefore, scintillation screens based on single crystalline films play an important role in detectors used for 2D/3D imaging in X-ray synchrotrons with spatial resolution in the micron and submicron range [1]. Single crystalline films of rare-earth doped $RAlO_3$ perovskites (R= Lu, Gd, Tb) and solid solution on their base are very good candidates for these applications due to their high density and high values of effective atomic numbers Z_{eff}.

The development of scintillation materials with emission in the visible range, e.g. SCF of the $Gd_{1-x}Lu_xAlO_3$ perovskite doped with Eu^{3+}, Tb^{3+} and Ce^{3+} ions, with careful optimization of the composition (x-value) to minimize the lattice mismatch and to obtain high optical quality needed for X-ray imaging, has already been implemented in the European Synchrotron Radiation Facility (ESRF) as part of the project to develop new scintillating screens for X-ray imaging detectors [3-6].

In this paper we present Raman and high-resolution luminescence spectroscopy study to characterize the cross-section of the $Gd_{0.6}Lu_{0.4}AlO_3$:Eu SCF/YAP SC, $GdAlO_3$:Eu SCF/YAP SC and $LuAlO_3$:Ce SCF/YAP SC, especially, the region known as *transition layer* i.e. in the range close to the interface between SCF and SC substrate. Expecting the mechanical stress in this region we want to check its influence on vibrational and optical properties and possible compensation of stress regarding to composition of mixed perovskite $Gd_{0.6}Lu_{0.4}AlO_3$:Eu SCF/ YAP SC.

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O-3

DETECTION OF RADIATION-INDUCED FRENKEL DEFECTS IN FUNCTIONAL METAL OXIDES VIA OPTICAL AND EPR METHODS

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High tolerance to harsh radiation environment encourages the exploiting of wide-gap metal oxides as laser media, detectors/dosimeters of radiation, materials for lighting and various nuclear technologies. In particular, several binary and complex metal oxides (in the form of single crystals or transparent polycrystalline ceramics) are at present in the list of promising window materials for the projected *D-T* fusion facilities. As is generally accepted, the irradiation-induced degradation of many functional oxide materials (incl. optical materials) is predominantly caused by the creation/accumulation of interstitial-vacancy Frenkel pairs via elastic collisions of incident energetic particles with material nuclei.

The radiation damage caused by fast neutrons, protons or ~MeV-GeV swift heavy ions has been studied in α-Al_2O_3, MgO and $MgAl_2O_4$ crystals via optical absorption, electron paramagnetic resonance (EPR) and cathodoluminescence methods [1-5]. The revealed correlation between the characteristic EPR signal and a relevant elementary optical absorption band (via the decomposition of complex spectra into Gaussians) has allowed to track both, the accumulation with irradiation dose and a further thermal stepwise annealing of different Frenkel defects: an oxygen vacancy with one/two trapped electrons − the classical F^+ and F centers; oxygen interstitials in different charge states in corundum [2] as well as the F^+, F centers and complex cation-related defects in $MgAl_2O_4$ [3, 4]. In addition, several novel EPR-active defects have been detected in a neutron-irradiated mineral spinel (a set of the so-called trapped-hole *V*-centers [1]) and α-Al_2O_3 (double charged F_2 dimers). The experimentally measured annealing kinetics of the F and F^+ centers in α-Al_2O_3, MgO and $MgAl_2O_4$ crystals have also been modelled in terms of diffusion-controlled bimolecular reactions.

The accumulation of Frenkel defects with ion fluence as well as the recovery from radiation damage in neutron-irradiated corundum single crystals have also been analyzed via the spectra of steady-state and time-resolved cathodoluminescence. The correlation between the concentration of radiation defects and the luminescence intensity of self-trapped excitons (the 7.6-eV intrinsic emission band) and Cr^{3+} impurity center emission has been demonstrated [5]. The limitations of the use of specific luminescence bands for the detection and accumulation of a number of single and dimer *F*-type Frenkel defects with irradiation dose are considered as well (the case of neutron irradiation is also discussed in [5]).

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O-4

MACHINE LEARNING ASSISTED THERMOMETRY OF Mn^{5+} DOPED $Ca_6Ba(PO_4)_4O$ PHOSPHOR

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In this study, a principal component analysis (PCA) approach was applied to a dataset of Mn^{5+} doped $Ca_6Ba(PO_4)_4O$ temperature dependent luminescence emission spectra with the aim of improving temperature resolution of this Mn^{5+} based luminescent thermometer. PCA, a technique for linear dimensionality reduction, reorients the data onto a fresh coordinate system in such a manner that the primary principal components axes, having the greatest variance within the data, becomes readily identifiable and used as thermometric parameter. Conventional approaches in luminescent thermometry, such as luminescence intensity ratio (LIR), band shift analysis, and multiparametric methods, were also applied to Mn^{5+} doped $Ca_6Ba(PO_4)_4O$. This facilitated a direct comparison of their results with those achieved through the PCA machine learning technique, which demonstrates superior temperature resolution in comparison to the traditional methods – with average value for resolution of 0.135 K in 290 K to 375K temperature range and average resolution of 0.074 K in physiological range (303 K to 318 K).

Acknowledgment:
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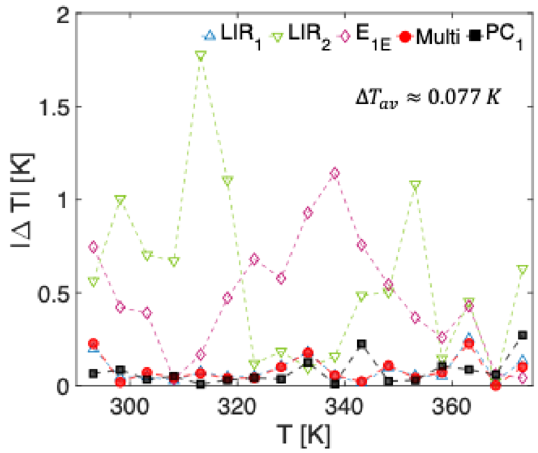

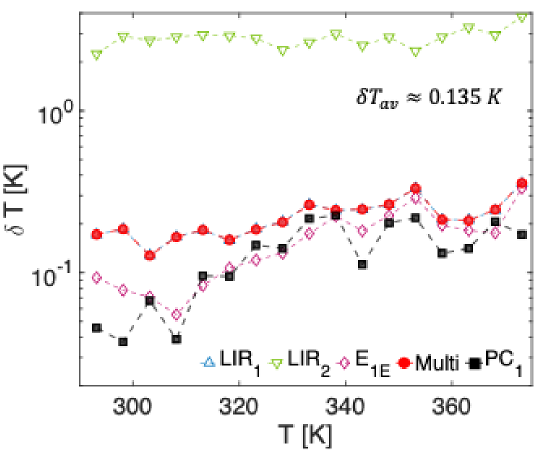

LUMINESCENCE MECHANOCHROMISM OF HYBRID COPPER IODIDE MATERIALS

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Achieving mechanoresponsive luminescent materials exhibiting high-contrast luminescence response to mechanical forces, is required for the development of technological applications.[1] At the same time, stimuli-responsive materials based on copper element are of great interest for developing cost-effective and efficient luminescent materials.[2] In this context, we report here our investigations on the study of luminescent mechanochromic materials based on copper(I) compounds.[3] In particular, we have recently reported a copper iodide material that exhibits a dramatic switching in emission intensity and color, from red to bright green, upon liquid-to-crystal transition triggered by mechanical stimulations.[4] This reversible phase transition taking place at room temperature relies on the intriguing ability of the studied copper complex to form a supercooled metastable liquid state, as illustrated in Figure 1. In addition to the contrasted emission color changes, a 20-fold increase in the photoluminescence quantum yield is measured reaching the high value of 87 %. The mechanochromic response is also very sensitive, as low mechanical forces induce complete phase transformation.

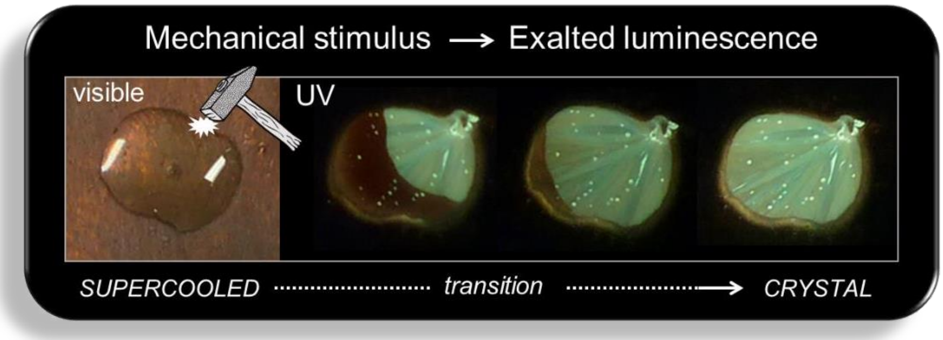

Figure 1. Photos of the supercooled liquid phase at room temperature under visible light and after mechanical stimulation (hammer) under UV showing the progressive photoluminescence switching.

The mechanism at the origin of the photoluminescence switching was investigated through X-ray diffraction experiments and Raman analyses of the metastable liquid state, combined with DFT calculations. The important luminescence changes can be attributed to modifications of the molecular structure of the complex in the different phases.

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O-6

Can Imaging Ellipsometry Beat the Diffraction Limit?

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Spectroscopic ellipsometry is non-invasive, non-destructive, non-contact, and can allow a user to determine several film properties simultaneously. The technique is fast and requires no sample preparation. It is also precise, reproducible, very sensitive to thin films even below to 1 nm. Since approximately a decade these advantages have been combined with imaging systems, -spectroscopic imaging ellipsometers (SIE)- which in addition to vertical sample structure determination now allows to gather vertical information on geometry and material.

It will be shown that spectroscopic imaging ellipsometers e.g. [1], can determine the number and size of inhomogeneity areas smaller than 50 x 50 nm^2 can be determined with an imaging ellipsometer on a field of view of e.g. a few µm by a few µm. First it will be discussed, which information can be delivered by spectroscopic ellipsometry for nanostructured samples with inner boundaries. The continuity conditions for the tangential components of the electric and magnetic field, as well as for the normal components of the displacement field and the magnetic flux have to be fulfilled.

In the contribution it will be first discussed, how ellipsometric measurements with an imaging ellipsometer shall be interpreted

1) in the case of no depolarization and with depolarization.
2) in the presence of subwavelength defects or structures (Au) of an areal size of e.g. 50 x 50 nm and 10 nm height on Si can be easily detected by SIE, provided the two ellipsometric angles ψ and Δ are measured with an accuracy of $\approx 0.01°$. This result proves that the well known sensitivity of ellipsometry on the thickness of vertical overlayers can be extended also to the horizontal dimensions[2,3].

Comparative measurements with electron microscopes will be presented, which show the potential for optical, nondestructive, and production line compatible defect analysis.

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O-7

Operando Luminescence Thermometry of Propane Dehydrogenation Catalysis

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Catalytic propane dehydrogenation (PDH) is an industrial route towards the production of propylene, a major chemical building block from which fuels, chemicals and materials can be made. Unfortunately, the formation of carbon deposits (coke) on the catalyst material results in gradual activity loss. Catalytic performance, including activity and selectivity, is often regained in an oxidative regeneration step.[1] During catalysis as well as catalyst deactivation and regeneration, the local temperature is expected to influence events on the catalyst surface that affect the overall catalyst performance and its long-term stability. The endothermic dehydrogenation process over a typical Pt-Sn/Al_2O_3 PDH catalyst can result in a locally lower temperature at the catalyst surface, while the exothermic regeneration process can result in strongly increased local temperatures. Potentially, information on the local temperature can be used to adjust the regeneration procedure in order to reduce irreversible catalyst degradation. In this work, we have developed *operando* non-invasive luminescence thermometry to gain insight in the local temperature of the PDH catalyst under working conditions.

Lanthanide-doped crystals, such as $Y_2O_3:Eu^{3+}$ can, serve as temperature-sensor materials at elevated temperatures of >100°C. The luminescence originating from two thermally coupled energy levels changes as a function of temperature.[2] There are many factors that complicate accurate and precise temperature sensing. Laser-induced background fluorescence causes difficulties for the precise determination of the luminescence intensity originating from the temperature sensor. In addition, the relative intensities of the bands in the Eu^{3+} spectrum are not only sensitive to temperature changes. Sample discoloration due to coking results in considerable temperature readout artefacts. We show that fluorescence rejection with time-gating using an intensified CMOS camera, together with a discoloration correction, allowed for more accurate temperature sensing during PDH catalysis at 580°C, thereby assessing the effect of the promotor (Sn) on the catalytic behavior of the supported Pt metal nanoparticles.

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O-8

Visible/NIR luminescence for nanothermometry with transition metal doped oxides nanoparticles

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Temperature (T°) is one of the most common physical quantities and significantly contributes to chemical reactivity and biological processes. Nanothermometry by luminescence is related to temperature measurements at nanoscale with high spatial and temporal resolution using nanoparticles (NPs). The temperature dependence on luminescence can be expressed by the evolution of one or more parameters such as: shift in the emission peak position, band shape, peak broadening, intensity variation, polarization evolution, or lifetime (Fig. a). [1]

To address this challenge, we are focusing our interest on matrices of transition metal-doped oxides, known for their chemical robustness and ability to withstand high temperatures (20-300 °C) that are envisioned in applications. To meet the requirement for spatial resolution, we are seeking probes that are uniformly dispersed and as small as possible to optimize this spatial resolution. One of the preferred approaches in this work is microwave synthesis, which allows us to obtain small crystalline particles (~ 10 nm) while adopting an environmentally friendly synthesis approach.

It is imperative that the probes exhibit a high relative sensitivity (>1% K^{-1}) over the studied temperature range. To achieve this threshold over an extended T° range, recent approaches are converging towards exploring evolution ratios between two parameters. For instance, by studying the ratio between two emission peaks evolving differently with T° (as seen in Fig. b). In this perspective, we focus on transition metal-doped oxides, for example, with Mn^{2+} and Cr^{3+} ions (visible emission). [3] Upon excitation in the UV (275 nm), these materials respectively emit at 500 nm (for Mn^{2+}) and 700 nm (for Cr^{3+}) (Figure b). It is propose to apply this approach with nanoparticles as well as with other luminescent ions emitting in the visible to NIR range.

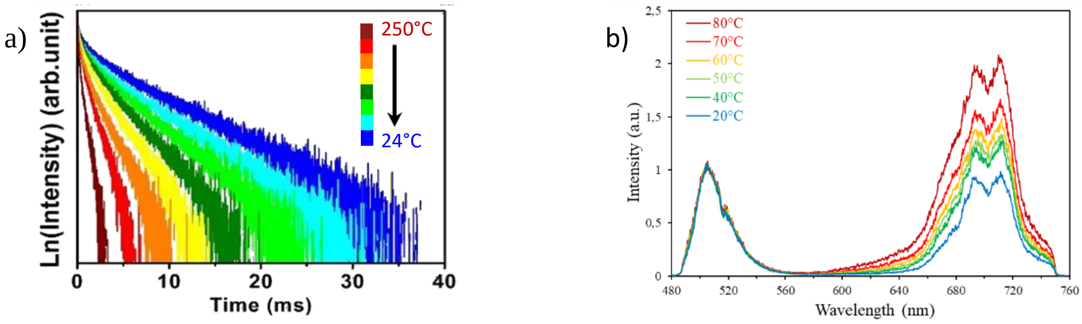

Figure: a) Lifetime evolution in function of temperature for ZGO:Cr^{3+} NPs (ex. à 430 nm). [2]
b) Emission spectra in function of temperature ZGGO:Mn^{2+},Cr^{3+} ultra small NPs in water.

The temperature range within which the nanothermometer is considered effective presents a significant challenge. The aim of the work is to develop a sensitive nanothermometer either close to room temperature for hyperthermia treatment applications or over a broader range, ideally covering from 20 to 300 °C for catalysis applications. To meet this requirement, we explore doping or atom substitution in the matrix with ions such as Ge^{4+}, Si^{4+}, Sn^{4+}. These exchanges indeed have repercussions on the matrix size and its interaction with temperature.

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O-9

Mn^{2+} as a local luminescent probe for unusual ligand field effects

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The influence of the surrounding ligand field on the luminescence of broad-band emitters is particularly well studied in the case of the $4f^{n-1}5d^1 \leftrightarrow 4f^n$ transitions of Eu^{2+} ($n = 7$) and Ce^{3+} ($n = 1$) [1]. However, the $3d^5 \leftrightarrow 3d^5$ transitions of Mn^{2+} are also strongly influenced by the ligand field. In contrast to the number of microstates in the $4f^65d^1$ configuration of Eu^{2+}, the density of excited states of the $3d^5$ HS ion Mn^{2+} is much more limited over the UV and visible range and thus, allows the clear assignment of ligand field transitions in an octahedral field [2].We show that a careful analysis of high-resolution photoluminescence excitation and emission spectra of a Mn^{2+}-doped sample can be used do gain detailed information about the ligand field strength and the subtle effects of covalency of the metal–ligand-bond for uncommon ligands. The concept is explicitly demonstrated for the weakly coordinating layer-like borosulfates $Zn_{1-x}Mn_x[B_2(SO_4)_4]$ (x = 0, 0.03, 0.04, 0.05, 0.10) [3]. The samples show orange emission at 590 nm, which is an unusually short wavelength for octahedrally coordinated Mn^{2+} similar to halidoperovskites and structural relatives thereof [4]. An in-depth analysis of the transition energies, however, revealed exceptionally high Racah repulsion parameters with values close to those of the free Mn^{2+} ion combined with moderate crystal field splitting thus allowing to place this type of ligand between chlorido and fluorido ligands within the spectrochemical series. Overall, this makes the photoluminescence of Mn^{2+} a simple yet valuable tool to probe such unusual electronic effects in uncommon and versatile compounds with a strong connection to the original works of ligand field theory back in the early 1960s [5].

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O-10

Electronic, optical, and photovoltaic properties of the orthorhombic $NaBiS_2$ compound: a highly perspective photoferroic material

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Density Functional Theory (DFT) calculations were performed to investigate the electronic, optical, and photovoltaic properties of $NaBiS_2$ compound with orthorhombic structure. The aim was to assess its viability for applications in ferroelectric-photovoltaic solar cells. Exchange and correlation electronic effects were approximated using Tran and Blaha's modified Becke-Johnson potential, in its semiconductor variance form. The compound was determined to possess a direct band gap of 1.2 eV, with an absorption coefficient exceeding 10^5 cm^{-1} for photon energies greater than 2.2 eV. Notably, the material displays significant optical anisotropy. Optical absorption within the visible range primarily arises from electron transitions from the S $2p_{x,y}$ to the Bi $2p_{x,y}$ states. Under sunlight, the photoconversion efficiency (PHCE) reaches a peak of 20% for a film thickness of approximately 5 μm. This efficiency surpasses that of $MAPbI_3$ perovskite, a ferroelectric-photovoltaic material with the highest experimental power conversion efficiency (PCE) to date, by 4%. These findings, in conjunction with previously reported estimates of ferroelectric polarization and charge carrier mobility [1], unveil the unexplored potential of orthorhombic $NaBiS_2$ for integration into photovoltaic and solar cell devices [2].

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O-11

A NOVEL FLUID DENSITY MATCHED TEMPERATURE-SENSITIVE PHOSPHORESCENT PARTICLE FOR SIMULTANEOUS MEASUREMENT OF TEMPERATURE AND VELOCITY

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Based on inorganic temperature-sensitive phosphorescent materials, particle tracing technology offers a potential method for non-contact simultaneous acquisition of temperature field and velocity field in thermal fluids [1]. However, the poor particle tracking ability of inorganic phosphorescent materials due to their high density limits their application in low-speed flows [2]. To overcome this limitation, this study developed a method for preparing temperature-sensitive phosphorescent tracking particles with matched fluid density. Firstly, using emulsion polymerization, phosphorescent microspheres with hollow structures were prepared by mixing phosphorescent materials, organic polymers, dispersants, and emulsifiers under controlled stirring and temperature. The shell of these microspheres consists of organic polymers and inorganic temperature-sensitive phosphorescent materials, allowing the tracking particles to retain temperature measurement functionality while possessing good fluid density matching characteristics and flow field tracking ability. Quantitative control of the particle diameter and average density can be achieved by adjusting the mixing ratio of phosphorescent materials to organics, stirring time, and stirring temperature. The prepared particle diameters range from 57μm to 120μm, with average densities between 0.5 and 1.5g/cm^3, and operating temperatures ranging from 0 to 200 °C. After temperature-phosphorescent signal calibration, suspension residence time measurement in liquids such as water and glycerin, and flow field measurements validation, the prepared tracking particles demonstrated excellent fluid density matching characteristics and flow field tracking ability. Finally, an application demonstration of simultaneous measurement of temperature field and velocity field was conducted in a bottom-heated liquid. The results show that the developed density-matched temperature-sensitive phosphorescent tracking particles can achieve simultaneous measurement of temperature field and velocity field in low-speed thermal flows, providing a feasible solution for non-contact synchronized acquisition of temperature field and velocity field in thermal fluids.

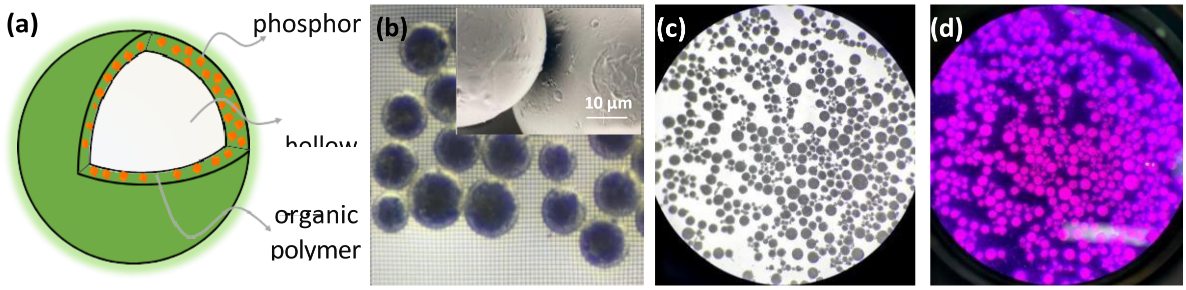

Figure 1: (a) Schematic diagram of fluid density-matched temperature-sensitive phosphorescent tracking particles, (b) SEM micrograph of tracking particles, (c) Tracking particles under non-excited state, (d) Tracking particles under excited state.

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O-12

THREE-DIMENSIONAL SURFACE TEMPERATURE MEASUREMENT UTILIZING LIFETIME-BASED PHOSPHOR THERMOMETRY

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A three-dimensional (3D) surface temperature measurement based on thermographic phosphor was proposed in this study. A 385nm UV light was used as the excitation light source, and two high-speed cameras were used as detectors. The phosphor MFG is mixed with the binder HPC and sprayed onto the tested 3D surface. The natural texture generated by the surface roughness of the phosphor coating was used as a feature for cross-correlation calculations. The digital image correlation algorithm is used to match these feature positions in the phosphorescent images from the two cameras. The influence of angles of excitation light and detector were studied. The results indicate that that the lifetime-based temperature measurement has good accuracy when the angle between the excitation light and the detector is controlled within 85 °. Finally, the method was validated on the pressure surface of a twisted turbine second-stage blade. By comparing the measurement results with the thermocouples, it has been proven that this research method can achieve temperature measurement on 3D surfaces, and the measurement accuracy can be maintained within 1.6%. The spatial accuracy of the method was obtained by comparing with the measurement results of a laser 3D scanner, revealing that the maximum absolute error of the 3D reconstruction is within 0.383mm, with a relative error of less than 0.01%. This study proposes a promising 3D surface temperature measurement method, which is expected to be widely used in Gas turbine blades, IC engine cylinders, complex curved heat exchangers, and other fields due to its non-contact measurement, low susceptibility to infrared radiation interference, high measurement accuracy, and ability to withstand harsh environments.

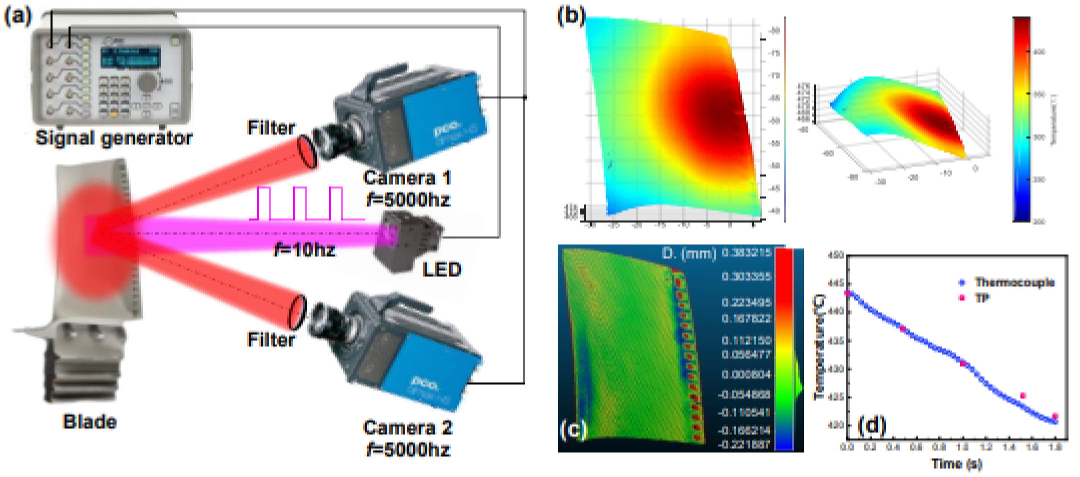

Figure 1. (a) Measurement setup, (b) Measured 3D temperature,(c) Deviation of 3D reconstruction, (d) Comparison of 3D phosphorescence-based temperature measurement and thermocouple measurement.

O-13

Towards thermographic Shake-The-Box: Combined three-dimensional flow thermometry and velocimetry using thermographic phosphors

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As turbulent flows are intrinsically three-dimensional (3D), their study greatly benefits from volumetric measurement techniques. Compared to one- or two-dimensional methods, 3D methods are not as prone to ambiguities, e.g., when investigating the extend of flow structures. One quantity measured the most in flow investigations is velocity. However, if a flow is not isothermal, scalar quantities like temperature are of great interest, too. Here, we present an improved version of thermographic particle tracking velocimetry [1] to measure flow velocity and temperature based on thermographic phosphor particles.

For 3D flow velocimetry, many tracer particle-based techniques have been developed. Typically, micron-sized tracer particles are seeded into a flow, small enough to follow its motion faithfully. They are illuminated by pulsed light sources and their Mie scatteringemission is imaged by a set of cameras. Each camera provides a different view of the in-flow particle distribution, allowing tomographic reconstruction or triangulation of particle positions.From this, shot-to-shot 3D particle displacements and velocities are calculated. In our recent publication [1], we combined such velocity measurements with phosphor thermometry to obtain joined velocity and temperature results. For this, the tracer particles were illuminated byan additional UV laser and their luminescence response was recorded in a two-color intensity ratio setup. Hence, different emissions of the same particles were used to extract flow velocityand temperature information. Now, the concept is evolved by using state-of-the-art camera calibration, particle triangulation, and double-frame tracking of particle displacement by combining in-house phosphor thermometry with Volume Self-Calibration (VSC) [2] and two-pulse Shake-The-Box (STB) [3] algorithms implemented in LaVision DaVis 11. Results produced using this improved processing pipeline from data recorded in a turbulent heated free jet embedded in a coflow at ambient temperature are shown in fig. 1. Compared to the former processing, the camera calibration error is reduced by 67%, the processing time is cut by 81%, and the temperature precision is improved by 30%. This is an important step towards combined flow thermometry and velocimetry with high spatial resolution from single-shot recordings.

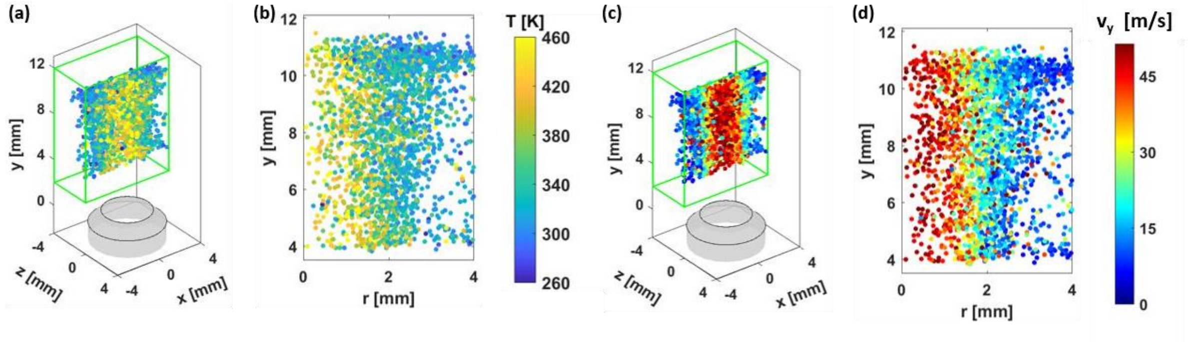

Fig 1: Particles in false colors according to measured temperature (a, b) and axial velocity (c, d) in cut-open 3D and height versus radial distance from jet axis plots. Results from accumulated single shots.

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O-14

EXPERIMENTAL AND THEORETICAL STUDIES ON THE APPLICATION OF DICYANIDOPLATINATES(II) AS OPTICAL THERMOMETERS

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It is a well-known fact, that in the field of materials science, including research on materials for magnetic, optical, and electronic devices, temperature is one of the key environmental variables to control. In this regard, many researchers explore emission-based optical thermometry as a quick, accurate, highly spatially resolved, and minimally disruptive method of its assessment by incorporating luminescent agents in the development of new materials, especially Single-Molecule Magnets (SMMs).[1,2] Following this trend, we employed C^N-cyclometalated dicyanidoplatinate(II) complexes as molecular luminescent thermometers in the design of $\mathrm{Dy^{III}}$-based SMMs, as our previous works proved the effectiveness of policyanidometalates in the latter use.[3] We report a novel family of coordination polymers, $\{[\mathrm{Dy^{III}(MediPhPO)_2(NO_3)}][\mathrm{Pt^{II}(CN)_2(L)}]_2\}\cdot n(\mathrm{solvent})$ (L = 2-phenylpyridine, 2-(4-bromophenyl)pyridine, 2-(4-methyl-phenyl)pyridine). The Pt(II) complexes not only provide bright temperature-sensitive luminescence but also form the coordination skeleton necessary to ensure the magnetic anisotropy of Dy(III) centers. Both magnetic and optical properties were thoroughly examined experimentally and theoretically. The latter was performed through *ab initio* methods for the magnetism, while the temperature dependence of emission spectra was simulated in the whole measured range through TD-DFT calculations using the ESD module of the ORCA software package (Fig. 1).[4] The results indicate, that the presented complexes are excellent stand-alone molecular thermometers for the next generation of multifunctional opto-magnetic materials.

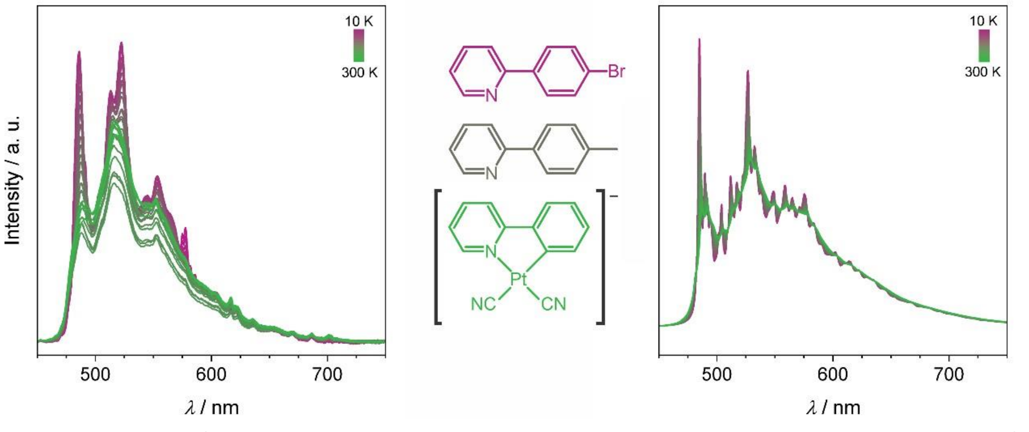

Fig. 1. Experimental (left) and simulated with Franck-Condon approximation (right) spectra for the complex with 2-phenylpyridine, together with the chemical structures of the compounds.

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Study on the Photoluminescence and Persistent Luminescence in the Rhombohedral Pyrochlore $M_{1.99}Mn_{0.01}La_3Sb_3O_{14}$ (M = Mg, Zn, Ca, Mn)

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Persistent luminescence (PersL) materials show continuous light emission ranging from seconds to hours after ceasing the excitation, and they are applied in various fields, such as light-emitting diodes, anticounterfeiting, and bioimaging.[1-3] Transition metal manganese (Mn),with several oxidation states, is an efficient activator in PersL. Mn^{2+} emits from green to red, depending on the coordination environment, while Mn^{4+} offers deep red to near-infrared emission.[4] However, the coexistent emission of Mn ions with different valence states has rarely been reported.

The trap carrier of the rhombohedral pyrochlore with the general formula $AA'_3BB'_3O_{14}$ has been well studied in terms of its structure.[5-6] $M_2La_3Sb_3O_{14}$ (M = Mg, Zn, Mn) give ordered structures, whilst $Ca_2La_3Sb_3O_{14}$ is disordered between Ca^{2+} and La^{3+}. It has already been shown by low-temperature, time-resolved spectroscopy that the difference in site-selective luminescence is caused by the substitution of La^{3+} by Eu^{3+} in the ordered Mg and disordered Ca analogues .[7] However, PersL has not been previously reported in these structures.

Here, we present 4 Mn-doped $M_2La_3Sb_3O_{14}$ (M = Mg, Zn, Ca, Mn) materials with different optical properties. Green and red photoluminescence (PL) have been recorded in the Mg, Zn, and Ca hosts, while green PersL can only be observed in the Mg and Zn analogues. Due to the concentration quenching effect, the PL emission was hardly observed for $Mn_2La_3Sb_3O_{14}$. We indicate the presence of oxygen vacancies by electron spin resonance (ESR) spectroscopy and perform thermoluminescence experiments to suggest a possible mechanism for PersL by investigating the trap levels in these systems.

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O-16

MOLECULAR FRAMEWORKS BUILT OF LUMINESCENT RUTHENIUM(II) POLYCYANIDOMETALLATES FOR OPTICAL THERMOMETRY

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A sensitive optical response to temperature variation, which can be acquired via luminescence, e.g., the colour of emission, band intensity, or emission lifetime, is one of the highly desired functionalities in modern materials science [1]. Coordination compounds based on cyanido transition metal or lanthanide complexes constitute a group of promising emissive materials and a great starting platform in the construction of high-performance luminescent thermometers [2]. Moreover, such materials can possess additional attractive features such as chirality-related phenomena like second harmonic generation (SHG) or circularly polarized luminescence (CPL) [3,4]. Herein, we focus on the strongly emissive heteroleptic ruthenium(II) polycyanidometallates in combination with f-block metal complexes as well as organic ligands or cations. Our work is motivated by the intrinsic optical properties of the tetracyanidoruthenate(II) complexes, which were found to be exceptionally sensitive to external factors making them potential versatile molecular building blocks in the construction of photoluminescent sensors, including optical thermometers [5].

Here, we present examples of emissive supramolecular frameworks built of $[Ru^{II}(bpy)(CN)_4]^{2-}$ ions and complexes of f-block metals or polar cations. Particular emphasis is placed on a system incorporating $[Ru^{II}(bpy)(CN)_4]^{2-}$ anion and chiral derivative of quinuclidine - $(3OH\text{-}Me\text{-}ABCO)_2[Ru^{II}(bpy)(CN)_4]$ (ABCO = 1-Azabicyclo[2.2.2]octane; bpy = 2,2'-bipyridine). The above-mentioned compound combines strong thermosensitive MLCT emission with SHG activity and red emission originating from the two-photon absorption (TPA) phenomenon.

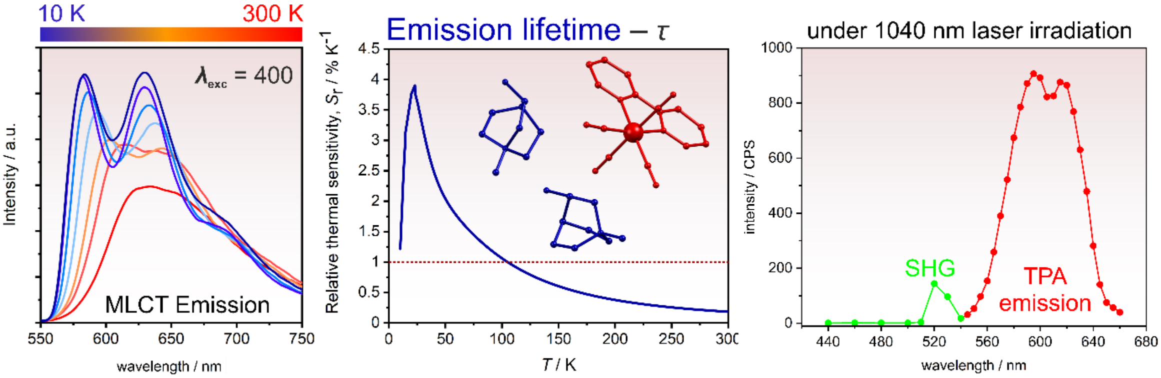

Figure 1. Optical characteristics of $(3OH\text{-}Me\text{-}ABCO)_2[Ru^{II}(bpy)(CN)_4]$: emission spectra under λ_{exc} = 400 nm (left); temperature dependence of the relative thermal sensitivity (Δ – emission lifetime; middle); SHG and TPA emission signals under 1040 nm laser irradiation (right).

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O-17

POLYCYANIDOMETALLATES AS EFFECTIVE TOOLS FOR MODULATING EUROPIUM(III)-TERBIUM(III)-BASED OPTICAL THERMOMETRY

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Functional photoluminescent materials arouse an immense scientific interest due to their broad application spectrum in optical storage and communication, chemical sensing, and optical thermometry. In this regard, polycyanidometallate-based materials incorporating lanthanide, Ln(III), complexes are promising candidates for advanced functional materials due to the versatility of d- and f-metal complexes utilizing highly customizable inorganic and organic ligands which enable the rational design and modulation of physicochemical properties of the material.[1-3] We have undertaken the challenge of employing Eu(III) and Tb(III) complexes, whose emission is sensitive to temperature changes, for the combination with poly-cyanidoplatinate(II,IV) ions into the materials showing the optical thermometric property that can be highly tunable through, e.g., the d-metal-ion-substitution or the excitation-wavelength-variation. Our studies resulted in a series of novel luminescent materials, including one-dimensional $\{[\mathrm{Eu}^{\mathrm{III}}_{0.6}\mathrm{Tb}^{\mathrm{III}}_{1.4}(\mathrm{H_2O})_4(\mathrm{terpyO_3})_2][\mathrm{M}^{\mathrm{II}}(\mathrm{CN})_4]_3\}\cdot 8\mathrm{H_2O}$ (M = Pd, Pt; $\mathrm{terpyO_3}$ = 2,2′:6′,2′′-terpyridine tri-N-oxide) coordination polymers, serving as the effective colorimetric, as well as emission-lifetime- and emission-intensity-ratio-based ratiometric luminescent thermometers, for which the optical properties are efficiently modulated by the Pd-to-Pt substitution (Figure 1).[4] Using this example and others, we will discuss the role of cyanido metal complexes in tuning Ln(III)-based ratiometric optical thermometers.

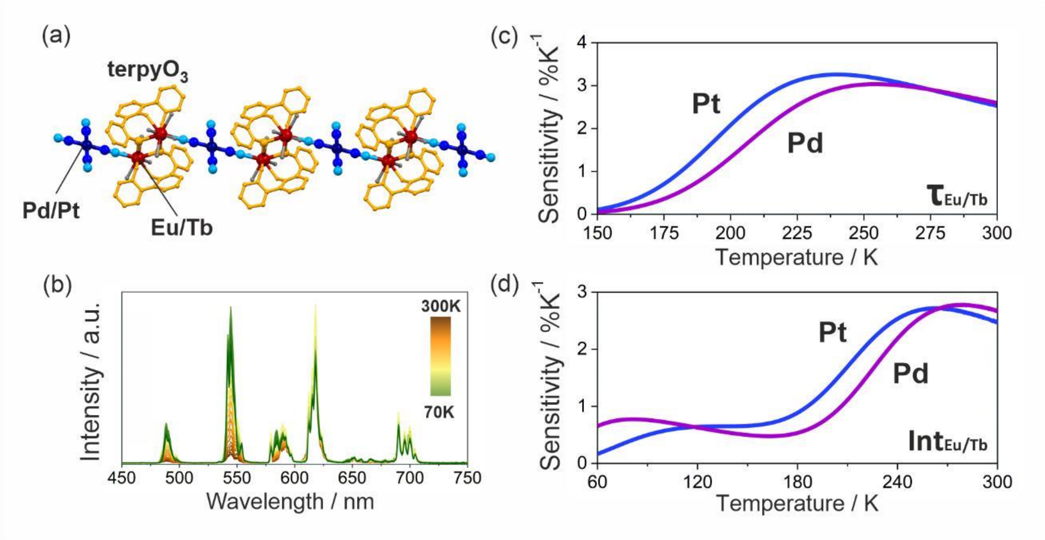

Figure 1. The structural view on the $\{\mathrm{Eu_{0.6}Tb_{1.4}(Pt/Pd)_2}\}$ coordination chains (a), the temperature dependence of the emission of the $\{\mathrm{Eu_{0.6}Tb_{1.4}Pd_2}\}$ derivative (b), and the relative thermal sensitivities for the 323 nm excitation for two different indicated thermometric parameters (c, d).

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O-18

CADMIUM(II)-IRIDIUM(III) COORDINATION CHAINS AS CHIRAL LUMINOPHORES FOR SENSING OF ORGANIC SOLVENTS

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Current trends in designing molecular materials lean towards multifunctionality based on an interplay between different physical properties, including luminescent, electrical, or solvent vapor sorption ones, in a single-phase material; such behavior makes them highly desired in the design of LEDs, chemical sensors, and optoelectronic devices.[1,2] A vital part of the research is dedicated to the related materials incorporating polycyanidometallates of transition metal ions, such as cyclometalated-cyanido iridium(III) complexes, which are further combined with other d-block metal complexes. This enables the possibility of employing chiral ligands, whose presence in the system introduces chirality in the coordination network, which is particularly interesting in terms of generating circularly polarized luminescence and SHG activity.[3,4]
In this context, we present chiral coordination chains of $\{[\mathrm{Cd^{II}}(S\text{-mpm})][\mathrm{Ir^{III}(ppy)_2(CN)_2}]_2\}$ (S-mpm = (S)-α-methyl-4-pyridinemethanol; ppy = 2-phenylpyridine) (**1**) with cyanido-bridged $\{\mathrm{Cd_2Ir_2}\}$ squares, exhibiting a *single-crystal-to-single-crystal* structural transformation upon solvent sorption. The accompanying changes in charge-transfer-based luminescence make them potentially applicable in the field of photoluminescent sensors of organic solvents (Figure 1).

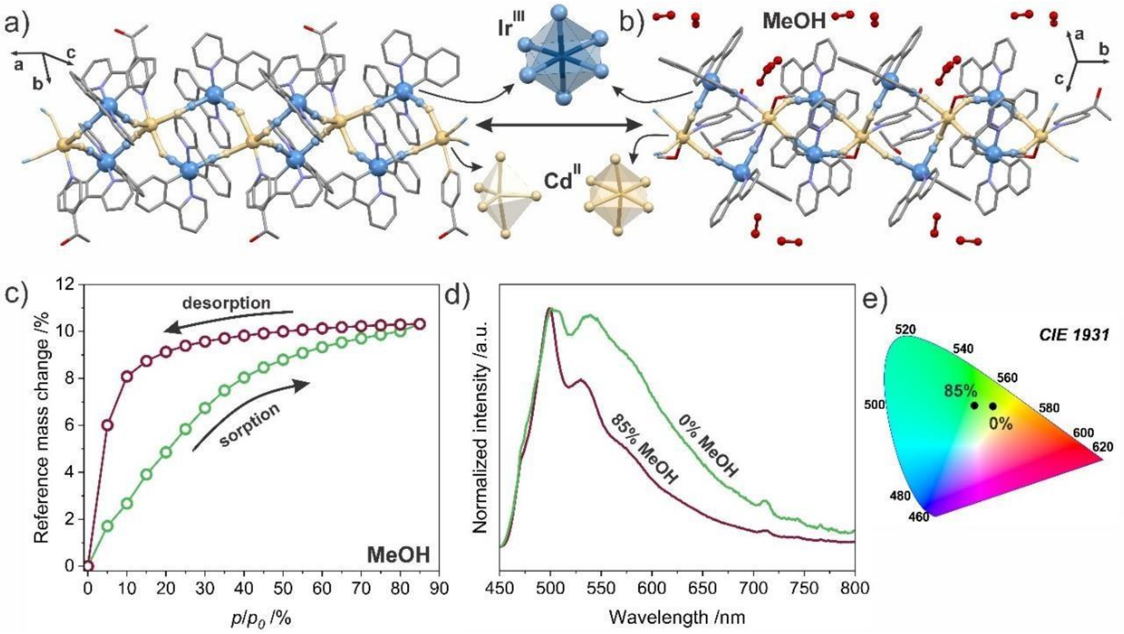

Figure 1. Representative structural fragment of **1** in 0% (a) and 85% (b) methanol partial pressure; methanol sorption curve of **1** (c); emission spectra of **1** at room temperature in indicated MeOH partial pressures (d, λ_{exc} = 420 nm) and corresponding CIE 1931 chromaticity diagram depicting the changes in luminescence color (e).

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O-19

EMISSIVE CERIUM(III)-PLATINUM(II) SINGLE-MOLECULE MAGNETS SENSITIVE TO SOLVENT VAPORS

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The recent decade has brought significant advancement in the field of coordination compounds based on the lanthanide(III) ions combined polycyanidometallates of transition metals, flashing out their remarkable photoluminescent properties, including multi-colored emission which can be sensitive to external stimuli such as solvent vapors, temperature, or pressure. This family of coordination compounds is also known for its strong magnetic anisotropy that leads to the Single-Molecule-Magnet (SMM) behavior. The conjunction of such diverse optical and physical properties makes them the perfect candidates for applications in various branches of technology, such as high-density data storage, chemical sensors, and optical thermometry.[1-4] In this regard, we present two coordination frameworks based on Ce^{III} complexes and $[Pt^{II}(CN)_4]^{2-}$ metalloligands, including 3-D coordination framework, $\{[Ce^{III}(MeOH)_2]_2[Pt^{II}(CN)_4]_3\}\cdot4MeCN$ (**1**), as well as coordination layers, $\{[Ce^{III}(H_2O)_6]_2[Pt^{II}(CN)_4]_3\}\cdot7H_2O$ (**2**), combining solvent-vapor-dependent SMM behavior with guest-molecule-variable multi-colored emission (Fig. 1). Their potential in luminescent sensing of chemicals is discussed.

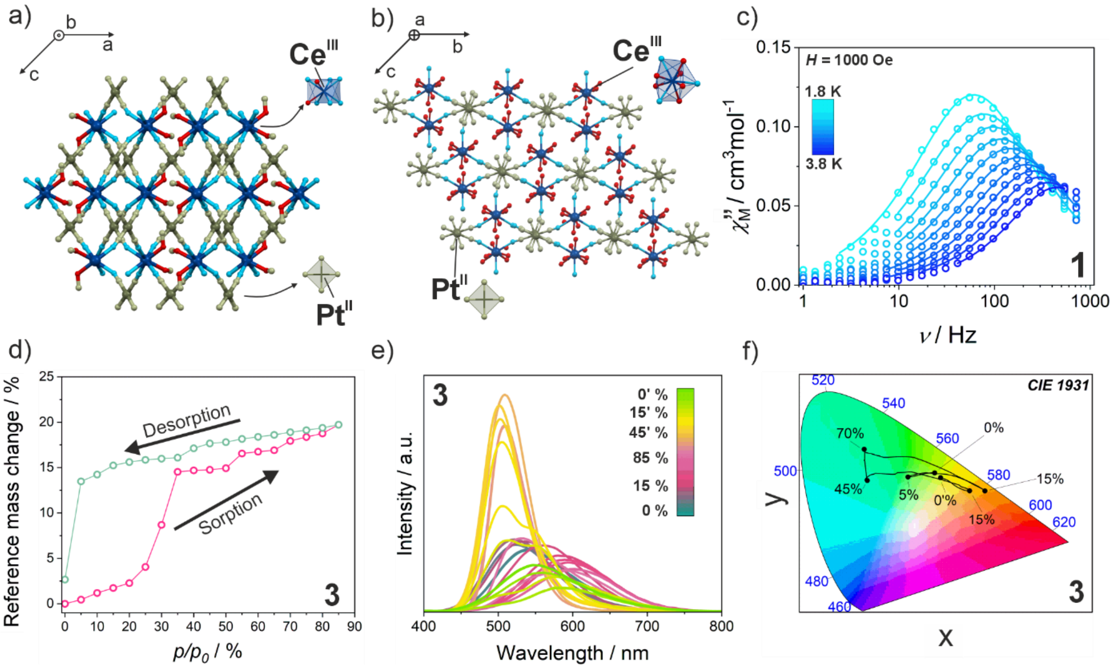

Fig 1. Representative structural fragments of **1** (a) and **2** (b); *ac* magnetic characteristics of **1** (c); water sorption isotherm of **2** (d); emission spectra of **2** in the 0-85% RH range (e), and corresponding changes in emission color visualized on the CIE 1931 chromaticity diagram (f).

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O-20

YAG:Dy co-doped with Tb for lifetime-based phosphor thermometry from room temperature to 1600 °C

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Phosphor thermometry is an optical measurement technique with high spatial resolution and accuracy, which has shown great potential for temperature measurement of hot-end components in aero-engines and gas turbines. YAG:Dy shows the highest upper temperature limit of 1700 °C compared to other phosphors[1, 2]. However, the temperature-sensitive range for YAG is less than 600 °C. In this study, we propose an alternative solution of using a second sensitizer (Tb^{3+}) in addition to the original activator (Dy^{3+}) in YAG, so that the measurement range can be greatly expanded by combining different temperature-sensitive ranges covered by two ions.

Accordingly, an fiber optic coupled measurement system was developed for lifetime-based temperature sensing on the luminescent behavior of YAG:Dy, Tb prepared by sol-gel method. As a good sensitizer, Dy^{3+} can enhance the green light emission (544nm) of Tb^{3+} by energy transfer when excited by 355 nm light source which is unable to effectively excite Tb^{3+} lonely. The lifetime of Tb^{3+} (544 nm emission) enables a wider measurement range from room temperature to 1450 °C. As the doping concentration of Tb^{3+} increases, both the lifetime of Tb^{3+} at room temperature and the upper limit of temperature measurement show a slight increase. Meanwhile, the lifetime of Dy^{3+} (458 nm emission) shows a temperature sensitivity between 1100 °C and 1600 °C. The combination of Dy^{3+} with Tb^{3+}, allows for the extension of the measurement range (room temperature to 1600 °C).

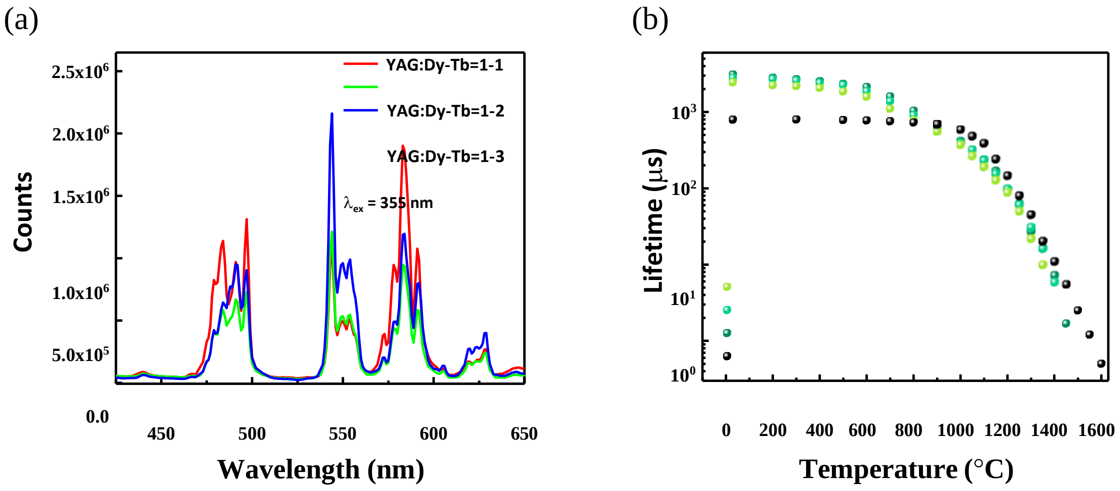

Figure 1. Emission spectrum (a) and lifetime-temperature curves (b) of YAG:Dy, Tb excited by 355 nm.

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O-21

A phase transformation–phosphorescence model of YSZ:Eu and its application in two-dimensional thermal history measurement

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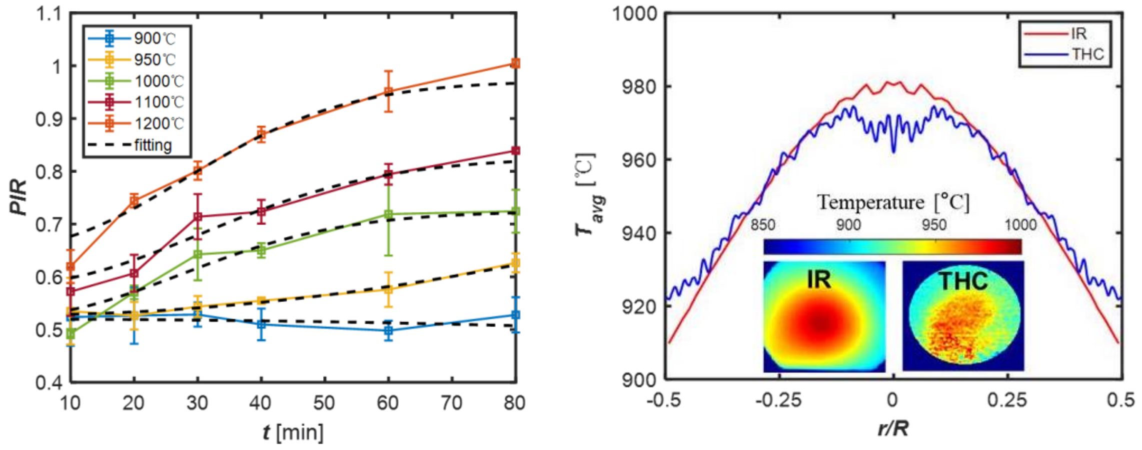
Phosphorescence thermal history sensors are off-line temperature measurement devices with promising applications in harsh environments. However, changes in phosphorescence after heating at various temperatures for different durations cannot be precisely quantified based on current theory. In this study, europium-doped yttria-stabilized zirconia (YSZ:Eu) was selected as a potential thermal history sensor and its structural and phosphorescence properties were characterized after heating at various temperatures. It was found that the tetragonal-to-cubic phase transformation of zirconia had a major effect on the phosphorescence intensity ratio (PIR) of YSZ:Eu.

Accordingly, a novel phase transformation–phosphorescence model was developed based on crystal field theory, Avrami equation and Judd–Ofelt theory, and was used to quantify phosphorescence changes induced by heating YSZ:Eu at various temperatures for different durations. Dual-parameter calibration results showed that PIR increased from 0.5 to 1.0 as the heating temperature and duration increased from 900 °C to 1200 °C and from 10 min to 80 min, respectively. The mean relative fitting error using novel model was 2.2 %.

Finally, thermal history measurement was demonstrated in a flame-impingement experiment which was conducted using a phosphor coated plate. Two-dimensional (2D) surface temperature distribution of the plate obtained by camera-based thermal history measurement was compared with that obtained using an infrared camera. The average temperature difference between two methods was around 5.9 °C. These findings could enhance theoretical understanding of thermal history sensing and will facilitate advancement from single-point to 2D thermal history measurement.



(a) (b)

Figure 1. (a) Dual-parameter calibration curves as a function of heating duration with fitting curves based on theoretical model, (b) Two-dimensional and circularly-averaged temperature distributions compared with the results generated by the infrared camera

O-22

LINEAR AND NON-LINEAR OPTICAL AND MAGNETO-OPTICAL PROPERTIES OF PURE AND MULTICOMPONENT TELLURITE GLASSES

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We report the thorough study of linear and non-linear optical, magneto-optical and structural properties of pure TeO_2 [1] and TeO_2–ZnO–BaO (TZB) [2,3] glasses with regard to different synthesis and material processing conditions. Prepared glasses were synthesized by melt-quenching and intermittent quenching technique from 900 °C in platinum or alumina crucible and characterized prior to and after optical polishing. The position of the long-wavelength/phonon absorption edge was investigated using various optical models and experimentally obtained data of refractive index and Verdet constants were used for the estimation of magneto-optical anomaly parameter for pure and TZB multicomponent tellurite glasses. During synthesis in alumina crucible, up to about 11 wt.% of Al_2O_3 incorporates into the pure TeO_2 glass (verified by EDS/XRF and Raman/FTIR spectroscopy) partially transforming the original pure TeO_2 glass backbone structure composed of [TeO_4] trigonal bipyramids to [TeO_{3+1}] and [TeO_3] structural units with the expected integration of Al into Te−O−Al bridges. The presence of Al_2O_3 results in lowered density, linear and non-linear refractive index and Verdet constant and in increased optical-band-gap energy and Abbe number compared to pure TeO_2 glass prepared in platinum crucible. Systematic decrease in linear refractive index by ≈ 0.04 compared to $n_{1550} = 2.178$ for a pure TeO_2 glass prepared in platinum crucible was also found to be caused by optical polishing process.

Studied TZB glasses exhibit large values of linear and non-linear refractive index, Verdet constant and optical-band-gap energy and were compared to those of pure TeO_2 glass. BaO substitution by ZnO leads (at constant TeO_2 content) to an increase in linear and non-linear refractive index as well as Verdet constant while the optical-band-gap decreases.

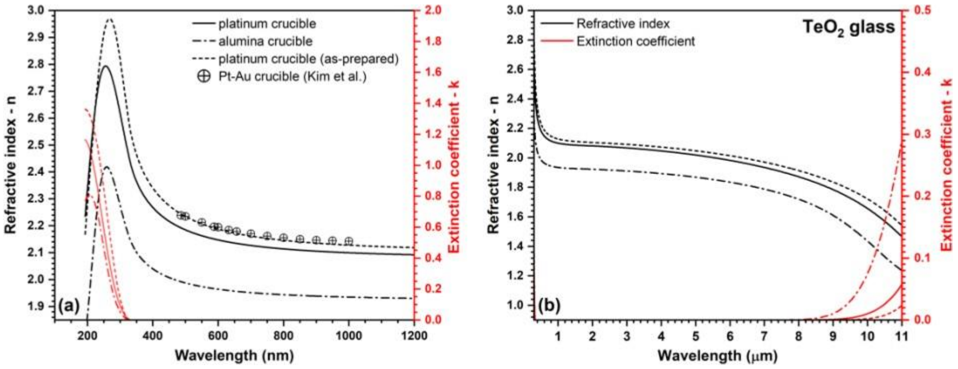

Fig.1. Spectral dispersion of refractive index and extinction coefficient of as-prepared and polished TeO_2 glass prepared in platinum or alumina crucible. Obtained values are compared to those in Ref. [4]

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O-23

COMBINING LUMINESCENCE WITH INDIUM-TIN OXIDE NANOPARTICLES AS HEATING ACTUATORS

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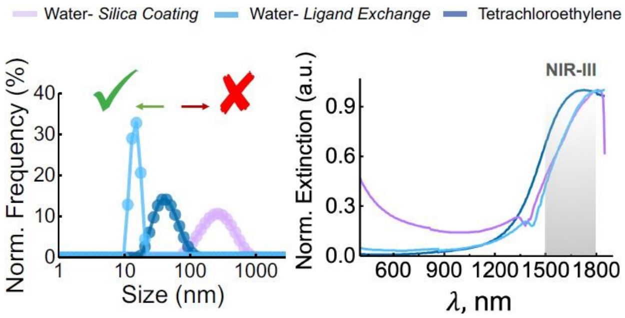
Certain optically triggered nanoparticles (NPs) greatly facilitate the light-into-heat conversion into a region of interest, thus serving for photoacoustic imaging (PAI) and photothermal therapy (PTT), as attractive in vivo biomedical applications which require local and controlled delivery of heat. More specifically, plasmonic NPs with their optical extinction engineered to lie within the third near-infrared window (NIR-III, 1500-1800 nm) allows higher penetration depth into tissues and less side- effects (e.g. heating of non-targeted regions) than those ones working in the NIR-II (1000-1350 nm). That is because of minimal absorption and scattering undergone by the excitation beam at NIR-III wavelengths when propagating through tissues.

This work addressed the lack of nanoparticles working exclusively in such NIR-III range by preparing indium oxide plasmonic NPs doped with tin (ITO), purposedly tuning their optical extinction to the 1600-1800nm range. Furthermore, these ITO NPs show a heat-conversion-efficiency (HCE) value above 80% under irradiation at 1700 nm. Remarkably, a potential theranostics system was straightforwardly mimicked by mixing the ITO NPs with luminescent Nd-doped NaGdF4 NPs, -nowadays a widely used workhorse for NIR-II *in vivo* imaging and temperature sensing. Spectra obtained after excitation of the nanofluid at 800 nm showed a minimum spectral distortion and very low reduction over Nd-doped NPs emission intensity. Hence, it constitutes a demonstration of the minimal interference from ITO absorption over the information-carrying emission, from those Nd-doped NPs acting as imaging agents/sensors and located close by. The spectral profile of ITO NPs´ optical extinction and their high HCE value make them ideal candidates not just for PAI and PTT, but as a novel tool to be combined with other (luminescent) NPs for an integrated theranostics platform.



Left: Dynamic Light Scattering (DLS) plot of ITO NPs in different solvents (made water-dispersible through two different methods). *Right*: Optical extinction of such ITO NPs.

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O-24

ACTIVE MICRORESONATORS WITH WHISPERING GALLERY MODES: MORPHOLOGICAL FEATURES AND POTENTIAL APPLICATIONS

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Active microcavities based on easily available components are promising composite structures for photonics device applications. Main areas for such structures include laser gain media, sensor components, and unclonable functions for creating unique protection labeling. In the present work, we fabricate and systematically study a series of active WGM resonators based on different sized polystyrene microspheres and heavy metal-free ternary $AgInS_2/ZnS$ quantum dots with broad and tunable photoluminescence bands coated on their surface as a gain medium. To fabricate a layer of $AgInS_2/ZnS$ QDs on the surface of polystyrene microspheres, the electrostatic layer-by-layer deposition method was employed. Due to the unique properties of $AgInS_2/ZnS$ QDs, the most common problems of such structures are solved and we created microresonators with high photostability, long fluorescence decay time and high fluorescence quantum yield.

This study highlights the influence of the gain medium/resonator base properties and the cavity morphology on the mode parameters of active microsphere-based WGM resonators. The variation in the mean size and emission wavelength of the quantum dots allowed us to establish a correlation between their characteristics and the WGM properties, including the resonance peaks intensity profile and the Q-factors. In the same time, the variation in the mean size of polymer microsphere allowed us to modify such characteristic as modes repetition rate, free spectral range. Statistical analysis of the data showed that even for the same pot microspheres there are significantly influence of size and shape to the characteristics of the modes, including the distribution of resonant wavelengths and the presence of splitting.

Experiments on additional coating to the surface of the microspheres, changing the external environment around microresonators, as well as modifying the temperature of the resonators and creating special patterns by such structures demonstrate the possibility of further applications in the fields such as sensors, light sources, optical filters, anti-counterfeit protection, etc.

This research was funded by the Russian Science Foundation (Agreement 23-72-10010),

O-25

Crystal Growth and Optical Properties of Ce-doped $(Lu, Tb)_3(Al, Ga)_5O_{12}$ Scintillators for X-ray Imaging

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[Introduction] Scintillators are essential for X-ray imaging in diverse applications such as nondestructive testing, medical diagnostics, and airport security control. Sensitivity is one of the crucial parameters in high-resolution X-ray imaging, determined by factors such as light output and density. Compounds with garnet structures show high potential for scintillation applications due to their excellent optical transparency, high density, and flexible cation substitution. Recently, garnet scintillators co-doped with Ce and Tb, such as Ce-doped $(Gd, Y, Tb)_3(Al, Ga)_5O_{12}$, have been investigated since the efficient energy transfer between Ce^{3+} and Tb^{3+} can improve the luminescence and scintillation properties [1]. In this study, the application of Ce and Tb co-doping to $Lu_3Al_5O_{12}$ (LuAG) single crystal was considered. Kamada et al. have previously reported the pivotal role of Ga in modifying both the bottom of conduction band and the $5d_1$ level of Ce^{3+}, resulting in more than a twofold increase in light yield compared to LuAG [2]. Building upon this insight, we explored the optical and radioluminescence properties of the Ce-doped $(Lu, Tb)_3(Al, Ga)_5O_{12}$ single crystal and investigate the specific influence of Ga within the host material on the energy transfer between Ce^{3+} and Tb^{3+}.

[Materials and Methods] As starting materials, CeO_2, Tb_4O_7, Lu_2O_3, Al_2O_3 and Ga_2O_3 powders with a purity of 99.99% were used and weighed in stoichiometric composition. $(Lu_{0.845}\ Tb_{0.15}\ Ce_{0.005})_3Al_2Ga_3O_{12}$ (LuGAG:Ce,Tb) crystal was grown by the micro-pulling-down (μ-PD) method [3]. Crystal was grown from an Ir crucible under the Ar+2%O_2 atmosphere and LuAG single crystal was used as seed.

[Results] We were succeeded in growing transparent LuGAG:Ce,Tb single crystal (Fig. 1). Under excitation into Ce^{3+} 4f-5d band at 426 nm, the typical emission spectra associated with the Ce^{3+} and Tb^{3+} were simultaneously observed in LuGAG:Ce,Tb and the Ce^{3+} emission band shifted towards the short wavelength compared to LuAG:Ce,Tb (Fig. 2). The results of more detailed measurements will be presented in the conference.

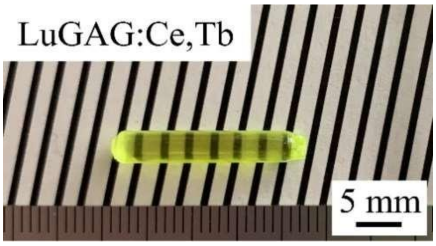

Fig. 1 Photograph of the grown LuGAG:Ce,Tb crystal.

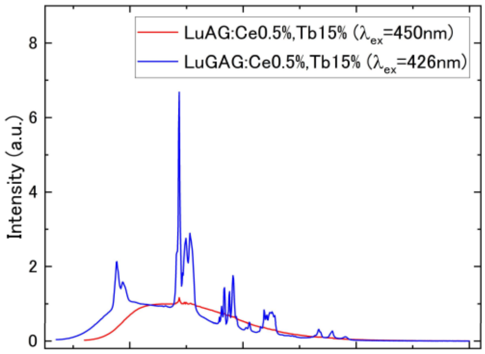

Fig. 2 Photoluminesece emission spectra.

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O-26

Scintillation properties of Zn_2SiO_4 nanoparticles in Na_2O-ZnO-SiO_2 glass system: Toward a distributed sensor of harmful radiation

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Crystalline scintillators, such as YAG:Ce, are widely applied today in many fields [1]. However, crystalline materials are generally unsuitable for the preparation of fiber-optic distributed radiation sensor due to the difficulty of drawing crystalline fiber [2]. On the other hand, silica-based glass is one of the most applied materials in fiber-optic technology, but the scintillation response of typical silicate glasses is rather low. The scintillation characteristics of the fiber can be improved by so-called nano-structuralizing of the fiber core by creating an inorganic nanocomposite of scintillating nanoparticles distributed inside the glass matrix [3]. The final luminescence properties of such nano-structuralized optical fiber are then given by the properties of the incorporated nanoparticles. Therefore, the successful preparation of inorganic nanocomposites consisting of radioluminescent nanoparticles distributed inside host glass matrix represent the challenging task for current material research.

In presented work we introduce the scintillation and optical study of the Na_2O-ZnO-SiO_2 glass system prepared using controlled crystallization of precursor glass by annealing in the 700 – 900 °C range. This system contains scintillating nanoparticles of various forms, such as Na_2ZnSiO_4, α-Zn_2SiO_4, Zn_2SiO_4. Their structural and morphological characteristics are investigated by the X-ray diffraction and transmission electron microscopy analysis. Their scintillation and optical properties are afterwards studied by the methods of time-resolved luminescence spectroscopy and by the setup for a fast scintillation decay measurement with time resolution below 100 ps. All studied samples exhibit the broad and efficient UV emission under the X-ray (40 kV, 15 mA) excitation which peaks at around 330 – 360 nm of spectral range. Furthermore, this emission reaches almost 600% of the intensity of the standard $Bi_4Ge_3O_{12}$ scintillation material. Corresponding fast scintillation decay time in the orders of few units of nanosecond of these scintillating nanoparticles in glass-ceramics matrix makes them worth of further investigation in the field of distributed radiation detectors.

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Acknowledgment

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O-27

Development of Tl:$Cs_3(Cu, Li)_2I_5$ Scintillator Crystals for Neutron and Gamma-ray Dual Detection

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Real-time dose rate monitoring system is required to remove the debris safely from the Fukushima Daiichi Nuclear Power Plant, and we have developed a dose monitor consisting of a scintillator, optical fiber and CCD spectrometer. Its scintillation photons are read outside the reactor under the lower dose rate condition than inside the reactor. The presence of neutrons emitting from ^{244}Cm as well as gamma rays in the reactor has been suggested [1], and detailed mapping of neutrons is also required. In addition, a scintillator is required to have high neutron sensitivity and long emission wavelength of over 500 nm, because of separation from noises with a dominant emission band of below 500 nm generating from the optical fiber itself under the high does-rate environment. On the other hand, conventional neutron scintillators have emission wavelengths of shorter than 450 nm. In this study, we focused on Tl-doped $Cs_3Cu_2I_5$ (Tl:CCI) scintillator [2] because of a high light output of more than 98,200 photons/MeV. 1% ^{6}Li-admixed $Cs_3Cu_2I_5$ (CCIL) has been reported at 96,000 photons/thermal neutron [3], and detection efficiency of neutron is expected to increase by increasing the amount of ^{6}Li doping.

We grew 5% and 10% ^{6}Li-admixed Tl:$Cs_3(Cu, Li)_2I_5$ (Tl:CCIL) crystals by the vertical Bridgman-Stockbarger method, because ^{6}Li has a large neutron capture cross-section. The phase of obtained crystals were investigated by the powder X-ray diffraction pattern (D8, DISCOVER Bruker). The photoluminescence properties of CCILs were measured with a spectrofluorometer (FP-8300, JASCO). In addition, to evaluated the light output excited by gamma-rays and thermal neutrons from a ^{137}Cs gamma-ray source and ^{252}Cf neutron source, the pulse height spectra were also measured with a photomultiplier tube (R7600U-200, Hamamatsu Photonics), multichannel analyzer (Pocket MCA8000D, AMPTEK). Here, fast neutrons emitting from a ^{252}Cf source were moderated to thermal neutrons using paraffin blocks.

We succeeded in growing Tl:$Cs_3(Cu, Li)_2I_5$ (Tl:CCIL) single crystals. The photoluminescence results of Tl:CCILs are shown in Fig.1. Tl:CCILs have an emission wavelength of 490 nm and 530 nm, which is longer than Tl:CCI's emission wavelength of 495 nm. The light output excited by thermal neutrons was estimated to be approximately nine times higher than that of Ce:Li-glass (GS-20) 6,000 photons/thermal neutron. In this presentation, we report detailed luminescence and scintillation properties of the grown Tl:CCILs.

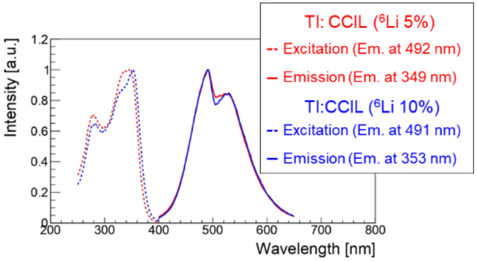

Fig.1 Photoluminescence spectra of Tl:CCILs

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O-28

SPECTRAL OPTIMISATION OF INTENSITY RATIO PHOSPHOR THERMOMETRY FOR $Mg_4FGeO_{5.5}$:Mn (MFG)

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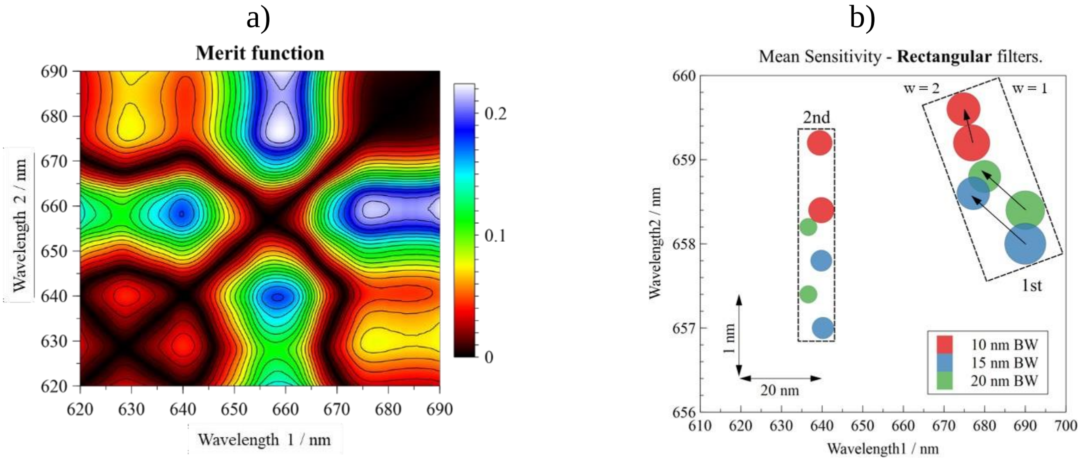
Introduction

We describe a process for identification of the optimum wavelength bands for intensity ratio (IR) phosphor thermometry using the thermographic phosphor MFG [1]. Luminescence spectra of an MFG/water brush-painted coating applied to a metal thermal validation target (traceable to ITS-90 [2]) are first captured over the temperature range from 20 °C to 620 °C, using a fibre-coupled grating spectrometer and 340 nm UV excitation LED. Bespoke Labview software is used to analyse the spectra by sweeping the two wavelength bands from 620 nm to 690 nm and extracting the luminescence signals, intensity ratios and relative sensitivities for each band pair. Three metrics are then determined: 1) total luminescence signals, 2) average sensitivities (%/°C) and 3) the merit function (product of the first two metrics), averaged over all temperatures. The analysis was performed for rectangular and Lorentzian filters of bandwidths and FWHM, respectively, of 10 nm, 15 nm and 20 nms. Band optimisation using the merit function gives weight to both the sensitivity and the luminescence magnitude, reducing the riskof finding bands that offer little luminescence.

Figure 1 shows output of the optimisation for rectangular bandpass filters. In a) the merit function for 10 nm BW filters is shown; two maxima are identified (1st – 660 nm/685 nm, 2nd – 635 nm/660 nm). In b) the mean sensitivity (circle size) and optimum centre wavelengths (x-y position) for the two maxima are shown; w = 1→2 corresponds to increasing the weighting of the total luminescence signals and moves the optimum wavelengths towards the centre.


a)

b)

Figure 1 MFG IR phosphor thermometry optimisation: a) merit function for rectangular filters (10 nm BW); b) mean sensitivity/optimum centre wavelengths for the strongest two peaks of the merit function.

Summary

Band optimisation analysis software has been developed to determine the best wavelengths for IR phosphor thermometry. For MFG, it was found that the traditional bands at 635 nm/660 nm are not optimum, with bands at 660 nm/685 nm offering higher sensitivity. The software can be used to analyse any luminescence spectra vs temperature series and will be invaluable for NPL's future development work in high and low temperature phosphor thermometry.

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O-29

THERMAL PROFILES OF ELECTRICALLY HEATED IN718 ALLOY SAMPLES USING IMAGING INTENSITY RATIO (IR) PHOSPHOR THERMOMETRY

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Introduction

Strain testing of metals at elevated temperatures can be undertaken using an electro-thermal-mechanical-testing machine (ETMT), where a coupon is heated electrically and subjected to a prescribed strain. Accurate knowledge of the coupon's temperature is critical to determine robust thermo-mechanical data for the metal. Here we describe the challenges of conventional non-contact thermometers and demonstrate how imaging IR phosphor thermometry can provide the required 2D temperature profile with low uncertainty. We describe the phosphor thermometer and coating ($Mg_4FGeO_{5.5}$:Mn [1] + binder), the calibration, and measurements on two Inconel-718 coupons (one tapered and one rectangular) with central coupon temperatures of up to 700 °C, as measured by a thin wire Type-R (control) thermocouple welded to the centre underside of the coupon. Comparison with finite element models is also presented.

Figure 1 a) shows the experimental set-up with the tapered Inconel-718 coupon installed in the ETMT machine under interrogation by the phosphor thermometer: Figure 1 b) shows the vertical temperature profiles measured with the phosphor thermometer and parabolic fits.

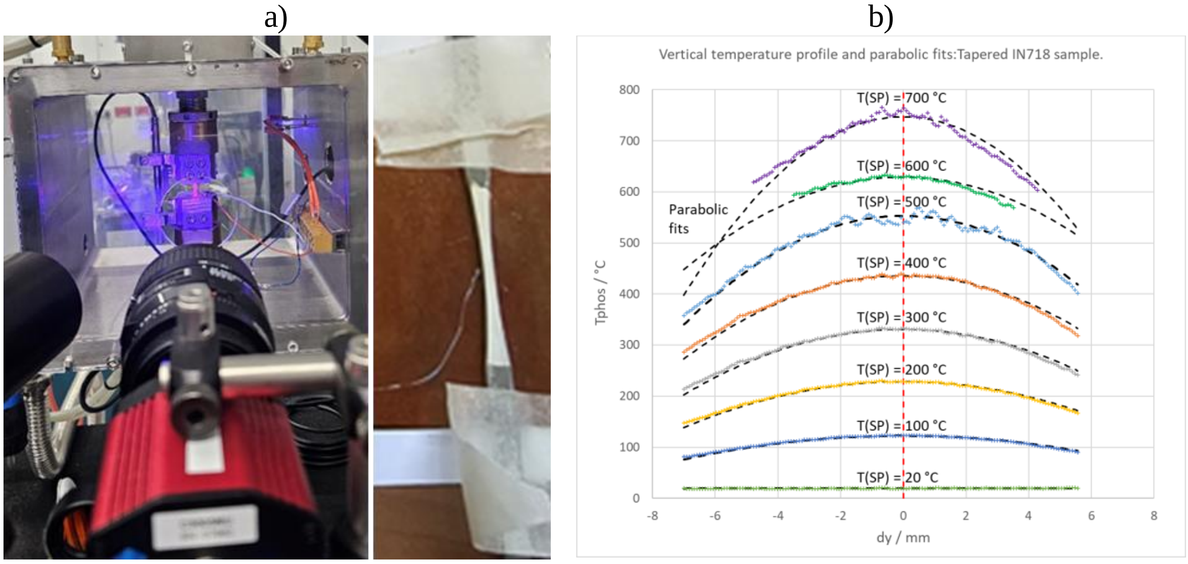

Figure 1 Imaging phosphor thermometry of an Inconel-718 coupon during heating with an ETMT machine: a) experimental set-up with the thermometer interrogating the coupon (LHS) and the phosphor coated coupon with a thin-wire thermocouple attached to the centre (RHS); b) vertical temperature profiles measured with the phosphor thermometer and parabolic fits (T(SP) is the setpoint temperature).

Summary

The vertical temperature profiles for tapered and rectangular Inconel-718 coupons were measured using imaging phosphor thermometry and were in excellent agreement with finite element models, with the sharpness of the parabola being greater for the tapered coupon. A systematic difference between the central temperatures measured by the phosphor and the control thermocouple was also observed. This difference is currently under investigation.

[1] Magnesium-fluorogermanate phosphor (Mg4FGeO5.5:Mn), Phosphor SV 067 N, OSRAM GmbH.

O-30

A real competitor to classic ruby: Photoluminescence properties of Cr^{3+}-activated AlB_4O_6N

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Ruby (α–Al_2O_3:Cr^{3+}) with its two narrow and bright *R* emission lines at 693.3 nm is probably one of the best studied photoluminescent materials. Besides its role as a model phosphor for theoretical tests, it was relevant as the first lasing material [1] and has become a *de facto* standard for optical pressure sensing [2]. Despite its high internal quantum yield, one major drawback is the presence of two *R* lines based on the trigonal distortion at the Al sites in corundum, which merge together at higher pressures than 50 GPa.

In this work, we want to present a Cr^{3+}-activated oxonitridoborate, AlB_4O_6N:Cr^{3+}, prepared in a multi-anvil press at 7 GPa/1673 K having strikingly similar optical properties to ruby. The compound crystallizes homeotypically to swedenborgite. The Al sites are well-isolated with almost perfect octahedral symmetry that results in a single bright *R* emission line at 683 nm [3]. Given the even stronger ligand field in AlB_4O_6N:Cr^{3+} together with its condensed structure, thermal quenching temperatures due to a crossover from the $^2E_g(^2G)$ to the $^4T_{2g}(^4F)$ state in the oxonitridoborate even surpass those of ruby. This behavior can be understood by means of the angular overlap model of ligand field theory [3] and is related to a very uncommon trigonal planar coordination of the O atoms in AlB_4O_6N. Another consequence of the uncommonly strong ligand field combined with the observation of a single *R* line is an expectedly higher dynamic working range as an optical manometer without the sacrifice of precision, thus making this compound a real competitor to ruby.

Besides its potential as an alternative optical pressure sensing standard, the strong field in AlB_4O_6N:Cr^{3+} also offers the possibility to use it as a bright and precise Boltzmann thermometer for the red spectral range [4]. In fact, coupling between the excited $^2T_{1g}(^2G)$ and $^2E_g(^2G)$ states separated by around 600 cm^{-1} allows to use it as a red-emitting luminescent thermometer with competitive performance to the primary, green-emitting standard β–$NaYF_4$:Er^{3+}, Yb^{3+} [5].

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O-31

SIMULTANEOUS ONLINE PHOSPHOR THERMOMETRY AND DIGITAL IMAGE CORRELATION (DIC) DURING METAL FORMABILITY TESTING

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Hot stamped car parts are vital for building more energy efficient and cleaner components. Material formability data at high temperatures is crucial for efficient manufacturing. These datasets, built from strain measurements, are obtained from high-temperature biaxial tests [1]. For this, precise thermal control and accurate temperature measurements are mandatory. Two phosphor thermometry instruments (PTIs) were implemented; an innovative imaging device and a fiber-based system, that provided full-field and pointwise measurements, respectively. $Mg_4GeO_{5.5}F:Mn$ coated aluminum cruciform specimens were tested, as they were mechanically stretched in a Gleeble machine (resistance heated deformation testing system). A 50:50 beamsplitter and two spectral filters centered at 660 nm and 635 nm, with 10 nm FWHM, were used for both[2]. A 365 nm fibre-based LED was the excitation source. A high-speed camera-based Digital Image Correlation (DIC) system was implemented to obtain simultaneous strain measurements. The imaging system, based on the TwinCam (Cairn Research), allowed two-cameras (Thorlabs DCC3260M) to share a single lens (Sigma 85 mm f#1.4), minimising distortion and optical misalignments.

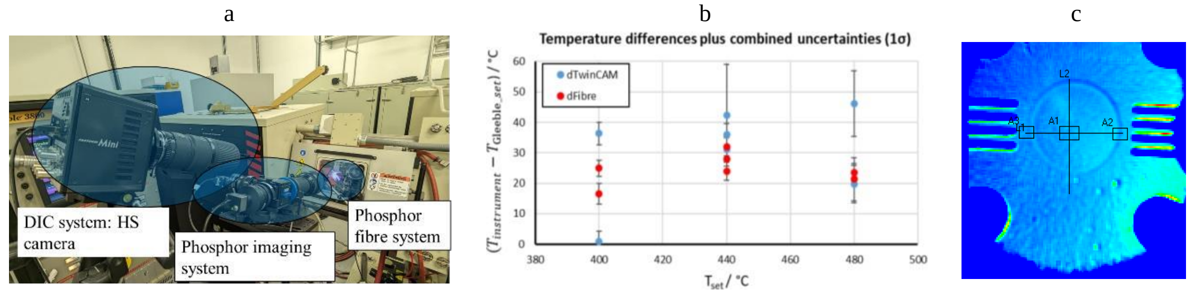

Figure 1 a) Experimental setup depicting all three systems used for DIC + thermography measurements; b) Average central temperature differences between the fibre and imaging systems relative to the Gleeble machine's thermocouple reference (T_{set}); c) Temperature field of the cruciform with areas and lines where the spatial temperatures were averaged for analysis (A1 is area used for sub-figure b)).

Calibration was performed between 20 °C to 550 °C. Set temperatures of 480 °C, 440 °C and 400 °C were tested for a total of 7 samples. The centre temperature of each cruciform was controlled using feedback from a TC soldered to their back face. Temperatures, in the samples' centre, were higher than those shown by the machine's TC, between 1 °C - 40 °C (imaging) and between 16 °C - 30 °C (fibre), see Figure 1 b). Combined uncertainties (1σ) of 1 °C - 16.7 °C (imaging) and 1 °C - 7.1 °C (fibre) were obtained. The higher temperatures measured by both PTIs (relative to the control thermocouple T_{set}) might be deviations from the Gleeble's own TC. The PTIs were able to accurately track the deformation although some temperature inhomogeneities (noted at room temperature), due to optical artifacts, need further investigation.

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O-32

DESIGN STRATEGIES FOR BLUE-TO-UV UPCONVERSION PHOSPHORS WITH PR^{3+}

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The growing environmental awareness of society and COVID-19 pandemic has increased the focus on efficient narrow-line emitting ultraviolet (UV) light emitters for disinfection or mild photocatalysis with nanocrystalline phosphors [1]. As UV LEDs with high external quantum efficiencies are still lacking [2], an alternative approach to such emitters is an exploitation of the technologically advanced blue InGaN LED and the concept of blue-to-UV upconversion (UC). Pr^{3+} ($4f^2$) has attracted attention for this concept in the last decade [3]. The electronic structure of Pr^{3+} allows to resonantly excite the ^3P_J ($J = 0, 1, 2$) levels with blue light (~ 450 nm), followed by absorption of a second blue photon thus populating the $4f^15d^1$ configuration located in the UV range. As the energy of $4f^15d^1$-based states strongly depends on the surrounding ligand field, the choice of the host compound is decisive for a resonant match of two blue photons with those states in the UV range [4]. However, the host compound does not only influence the energy of $4f^15d^1$-based states, but also has a strong impact on the excited state dynamics of the intermediate $^3P_0$ level related to the cutoff phonon energy. For a better understanding of the control of the blue-to-UV UC with Pr^{3+}, investigation of a variety of inorganic compounds is necessary to understand structural influences. Within this work, selected halidoelpasolites, oxyfluorides, garnets, silicates and borates are activated with Pr^{3+} to understand the relation between UC efficiency, energy and shift of the $4f^15d^1$ excited state within the configurational coordinate diagram, as well as the excited state dynamics. For that purpose, quantum yield measurements, steady-state, time-resolved, and temperature-dependent luminescence spectroscopy with different excitation sources and powers are combined.

A two-photon UC process can be observed in all selected Pr^{3+}-activated hosts. Increasing the cutoff vibrational energy of the host results in a decreasing decay time of the $^3P_0$ level due to a more efficient multiphonon relaxation into the lower-energetic $^1D_2$ level, which ultimately results in a lowered UC efficiency. Temperature-dependent time-resolved spectroscopy of the $4f^15d^1$-based states reveals a non-radiative crossover to lower-energetic $4f^2$ levels in some of the hosts and implies the relevance of a limited shift of the equilibrium geometry of the UV-located excited states. It turns out that several parameters must be carefully mutually matched within a host compound for effective blue-to-UV UC with Pr^{3+}.

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O-33

SYNCHRONOUS SWITCHING OF ELECTRICAL AND OPTICAL PROPERTIES IN ORGANIC-INORGANIC HYBRIDS

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Stimuli-responsive materials gain significant scientific attention in the pursuit of novel technologies as they display remarkable changes in physical properties upon even subtle changes in the surroundings.[1,2] They offer a fast response to such external stimuli as light, voltage, or temperature, which opens applications, e.g., in drug delivery, data storage, or lighting devices. Our goal was to construct novel luminescent systems which can be highly sensitive to external stimuli.[3] We selected tetracyanidonitridorhenate(V) complexes, $[\mathrm{Re^V(CN)_4(N)(L)}]^{2-}$ (L = aliphatic or aromatic organic ligand), that are strongly emissive due to their electronic transitions of either metal-to-ligand charge transfer (MLCT) or d-d mechanisms, and their optical properties are sensitive to chemical factors and temperature.[4] We combined them with polar *N*-methyldabconium ($\mathrm{Medabco^+}$) cations which resulted in novel organic-inorganic hybrids showing strong green photoluminescence. Thanks to the cations revealing non-innocent temperature-activated dynamic vibrations, these materials show an order-disorder phase transformation demonstrated in structural, electrical, and spectroscopic studies. Moreover, this phase transition results in the unique luminescence switching effect.[5]

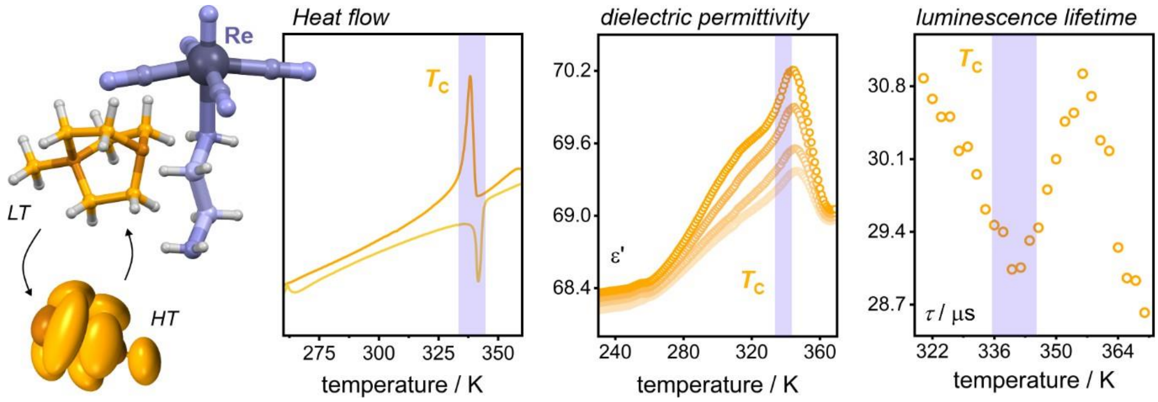

Fig. 1. The crystal structure of $\mathrm{(Medabco)_2[Re^V(CN)_4(nitrido)(en)]}$ hybrid (en = 1,2-diamino-ethane), together with differential scanning calorimetry (DSC) curve profile as well as the temperature-dependences dielectric permittivity (ε') and photoluminescence lifetime (τ).

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O-34

Persistent Phosphors for Outdoor Applications: Bridging the gap between models and real-world conditions

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Persistent phosphors hold immense potential for outdoor applications [1], but their performance varies greatly with environmental factors, such as temperature and solar irradiance. How close are we to the reliable and widespread application of glow-in-the-dark bike paths or outside safety signage?

In our previous attempt to answer this question, the test conditions were still not fully matching due to much shorter excitation times and the drastic reduction of the broad solar spectrum to a monochromatic near-UV light source [2]. These shortcomings are addressed by conducting a field test in a suburban area of Ghent, Belgium over the course of several weeks. Apart from the performance of a set of persistent phosphors, the (spectrally resolved) solar irradiance, and temperature at the phosphor level are also measured. Our open setup, with lux sensors underneath the phosphor patches, provides an unobstructed view and therefore also allows for evaluation of the visual impression.

Using this comprehensive data set, a simple, predictive model is built to estimate the light output under varying temperature and illumination profiles on longer than usual time scales (8 to 16h after sunset), crosschecked with the input from thermoluminescence measurements. Recent insights into measuring thermal quenching in the presence of trapping defects [3] help to refine this model, which then in turn allows to assess the application potential of the different persistent phosphors.

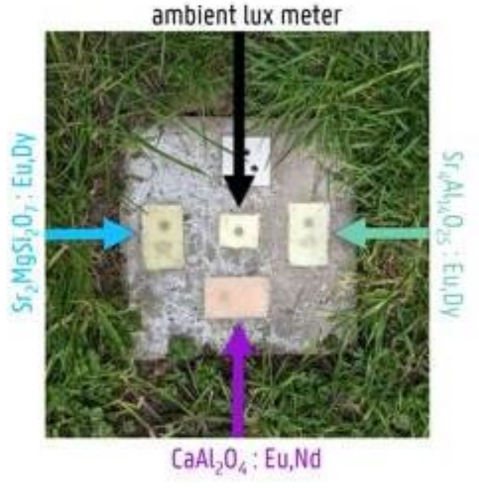

Figure: Photo of the prototype concrete tile with embedded lux and temperature sensors. The lux meters are situated beneath the phosphor patches.

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O-35

EFFECTS OF REFRACTIVE INDEX AND GRAIN SIZE ON SCINTILLATOR PROPERTIES OF THRMAL NEUTRON SCINTILLATOR

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Thermal neutron (n) scintillators are used in various fields such as non-destructive testing, resource exploration, medical care, and counterterrorism. In recent years, decommissioning as represented by the Fukushima Daiichi Nuclear Power Plant (F1) has attracted worldwide attention, and market is also expanding. In reactors decommissioning, scintillation detectors for thermal neutron detection is required to detect n-rays emitted only from fuel debris under very high-γ background. The selection of scintillator is important, and high neutron sensitivity, high light yield, fast decay, and enough n/γ discrimination performance are required. Up to now, we have focused on eutectic scintillators containing high concentration of ^{6}Li for thermal neutorn detection. Representative among those reported so far are Ce:LaCl$_3$/LiCl[1], Ce:LaBr$_3$/LiBr[2] and Tl:CsI/LiBr [3] , etc. These eutectics are composed of ^{6}Li-containing phase and scintillator phase having a crane size of several ~ several tens of μm. Eutectics tend to have inferior transmittance to single crystals, and the transmittance changes due to the difference in the refractive index of each crystal phase. In the eutectics n-rays are converted into α-rays and ^{3}H in the ^{6}Li-containing phase and convert the α rays and ^{3}H into light in the scintillator phase. Therefore, it is important to optimize the grain size in consideration of the path length of α rays and ^{3}H, which affects the scintillator performance. In this study, the relationship between the refractive index difference gap in the eutectics, sample thickness, and the attenuation of the light output was investigated. In addition, the relationship between growth rate, grain size, and energy spectrum was also investigated.

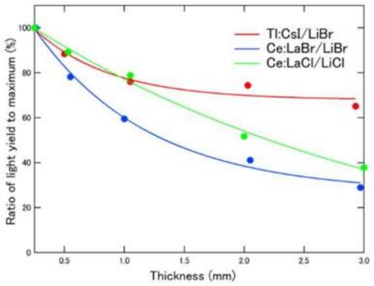

Fig.1 Ratio of light yield to maximum light yield at different thicknesses

Rod-shaped eutectics of Ce:LaCl$_3$/LiCl, Ce:LaBr$_3$/LiBr and Tl:CsI/LiBr with 4mmϕ x 20mmL were grown. Thereafter, wafer samples of different thicknesses were prepared for the light output measurement using ^{252}Cf neutron source. Fig.1 shows the relationship between thickness and light output. The refractive index gaps of LaCl$_3$/LiCl, LaBr$_3$/LiBr and CsI/LiBr are 0.379, 0.412 and 0.122, respectively, and the smaller the refractive index gap, , the less the deterioration of the light output due to the increase in sample thickness. Fig.2 shows the BEI of Tl:CsI/LiBr grown at various speeds. In addition to simulating the path length of the α rays and ^{3}H, the correlation between grain size and energy spectra was discussed using samples. Details of the above discussions will be presented.

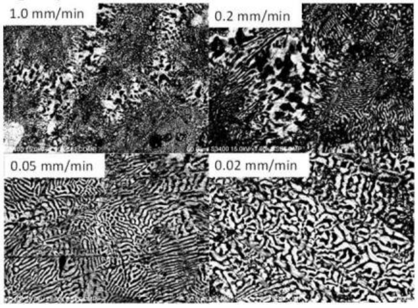

Fig.2 BEI of Tl:CsI/LiBr grown at various speeds.

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DISTANCE CONTROL OF NON-RADIATIVE TRANSITIONS TO DESIGN LUMINESCENT THERMOMETERS

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Luminescence thermometry has become attractive as a method for remote and non-invasive temperature sensing. Different readout methods can be used, depending on the observed optical signal and the employed emitter. A commonly used kind of thermometer uses the luminescence intensity ratio (LIR) of two thermally coupled excited states, which generally follows Boltzmann's law [1]. This method requires narrow emission bands and typically high quenching temperatures, which is usually well fulfilled by the trivalent lanthanoid ions, given their intraconfigurational $4f^n$-$4f^n$ transitions. While the optimum performance range of such thermometers is basically controlled by the exploited energy gap between the two coupled excited states, the dynamic working range of such a LIR-based Boltzmann thermometer is kinetically controlled by a competitive interplay between the non-radiative coupling of the two excited states and their radiative decay to probe luminescence [2]. A generally known strategy to control the non-radiative transition rate is the cut-off phonon energy of the host based on the energy-gap law [3], but recent studies have shown that it can be influenced by the lanthanoid-ligand distance and covalence of the lanthanoid-ligand bond [4]. In order to demonstrate the universality of this approach and thus, the control of the dynamic working range of luminescent thermometers by subtle changes in the host composition, suitable activators and their respective non-radiative $4f^n$-$4f^n$ transition (Pr^{3+} ($n = 2$, $^3P_1 \leftrightarrow {}^3P_0$), Eu^{3+} ($n = 6$, $^5D_0 \leftrightarrow {}^5D_1$) [4] and Tb^{3+} ($n = 8$, $^5D_4 \leftrightarrow {}^5D_3$)) were studied in the series of isostructural host compounds β-Na*RE*F_4 and Li*RE*$(PO_3)_4$ (*RE* = La, Gd, Y, Lu), respectively. In all cases, a universal increase of the kinetic onset temperature for Boltzmann thermometry with decreasing average lanthanoid-ligand bond length could be demonstrated, implying that the cutoff phonon energy is not the only possible parameter that can be exploited to control the dynamic working range of Boltzmann thermometers.

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O-37

Spectroscopic Properties of Nd^{3+} Doped Sr_2LaF_7 Nanoparticles

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Lanthanide-doped nanocrystals are extensively investigated systems due to their distinctive visible emission characteristics, which offer significant advantages over alternative materials. These advantages encompass exceptional thermomechanical properties, chemical stability, substantial Stokes shifts, sharp emission spectra, and long emission lifetimes. Among the various crystal hosts, alkali-earth-lanthanide nanophosphors (M_2LnF_7, where M represents Ca, Sr, Ba, and Ln^{3+} encompasses Y, La, Gd, Lu) have been proposed as good host materials for their remarkably elevated upconversion (UC) luminescence properties and the possibility to be grown in dimensions suitable for biomedical imaging applications.

Particularly noteworthy is the intense emission of Neodymium (Nd) ions across various infrared regions, notably at wavelengths around 900 nm, 1064 nm, and 1300 nm. These emissions stem from transitions between the $^4F_{3/2}$ and lower-lying $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ energy states, respectively, with many different applications.

In this work, we present a thorough investigation of the spectroscopic properties of Sr_2LaF_7 phosphors with different Nd^{3+} ions concentrations (x=1, 2, 3, and 5 mol%). The samples were synthesized using the hydrothermal method and structurally and morphologically characterized. Powder X-ray diffraction analysis confirmed that the materials crystallize in a cubic crystal structure while transmission electron microscopy shows nanoparticles with an average particle size of ~ 40 nm.

A study of the emission spectra as a function of the pump power, shows a slightly sublinear trend on all the Nd^{3+} ions concentrations, which indicates the presence of some loss energy transfer processes. Moreover, we studied the emission trend as a function of the concentration at a fixed pump power to find the optimum concentration for maximum emission intensity. We found an increase of the emission up to 3% Nd concentration and a decrease at higher concentrations.

We also studied the emission of the samples as a function of the sample temperature. We investigated the emission between -190 °C and 600 °C, with particular focus over the physiological range, i.e. 15-50 °C. Moreover, we will present the lifetime of the observed emission levels with insight into the possible energy transfer processes.

O-38

Imidazolium-based double perovskites containing Cr^{3+} ions for highly sensitive luminescent thermometry

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The constant development of technology requires the implementation of accurate and precise thermometers. Luminescent thermometry is a novel approach, in which the remote readout of the temperature is based on temperature-dependent luminescence of the sensor. Due to the remote measurement, the variety of the sensing ranges depending on the used material as well as the possibility of performing plunge measurements, this particular method may be a useful tool for many demanding industrial and scientific applications.

Among various materials, the group of double formate-based perovskites with the general formula $[A]_2M^IM^{III}(HCOO)_6$, where A represents an organic cation (e.g. EA^+), M^I and M^{III} stand for mono- (e.g. Na^+) and trivalent metal ions (Al^{3+}), respectively, exhibits particularly interesting multifunctional characteristics. Such compounds, called hybrid materials, create a three-dimensional framework, containing metal cations and anionic linkers. Organic cations, in turn, are localized inside the framework's voids. Hybrid perovskites may show a variety of interesting physical characteristics, e.g. dielectric and magnetic phenomena as well as temperature-dependent optical properties.[1,2]

The potential of hybrid perovskites as luminescent thermometers is particularly seen in materials containing Cr^{3+}, due to their luminescence properties, strongly dependent on the host material. The coexistence of two types of temperature-dependent emission: narrow spin-forbidden $^2E_g \rightarrow {}^4A_{2g}$ or broad spin-allowed $^4T_{2g} \rightarrow {}^4A_{2g}$ transitions, provides a sufficient condition for the thermometric model determination based on a ratiometric approach. By comparing the intensities of these two types of emission, it is possible to obtain a luminescence thermometer with high sensitivity and a wide range of usefulness.[1,4]

The presentation will be focused on the characteristics of a series of $[IMI]_2NaAl_{1-x}Cr_x(HCOO)_6$ ($x=0$, 0.01, 0.03, 0.05), which contains synthesis, structural characteristics, and luminescent properties. Particular attention will be paid to the structural and luminescent properties of representative materials used as highly sensitive luminescent thermometers.

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O-39

The novel, inorganic LED phosphor based on Ce^{3+} and Cr^{3+} doped silicates

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Inorganic phosphors doped with rare earth or transition metals become noticeable for their unique properties and possible applications. One of the most important is to use a phosphor for white light generation [1]. Since the discovery of blue InGaN LED chips in 1993 [2], the energy efficient white light sources based on this technology have been broadly studied and developed. Multiple factors can be taken into account during the preparation of new phosphor materials. They should be characterized by an excitation spectrum well matched to the excitation LED source, high quantum efficiency of emission, high thermal stability, and short photoluminescence lifetimes to minimize saturation at high excitation intensity. Moreover, the material should be simple to manufacture, nontoxic, and the precursors should be inexpensive and broadly available [1].

One of the frequently used class of compounds, which can cover those criteria are silicates. Their structure can vary depending on different subclasses. The silicate tetrahedra unit can create independent islands, chains, layers, or even three-dimensional frameworks as in the tectosilicates subclass. Due to the variety of structures, the ligand field strength can be different, and the emission of the optically active ions can be tuned and cover the whole visible light range [3].

In this work, a new silicate material doped with Ce^{3+} and Cr^{3+}, synthetized by a simple sol-gel method is presented. The optimization of the dopant concentration was performed. The material phase purity was controlled by powder XRD analysis. Furthermore, the spectroscopic properties such as absorption, excitation, emission spectra, and luminescence lifetime measurements were broadly investigated. In the achieved emission spectra under 375 nm excitation, two main bands were present. The first, spin-allowed, broad band with a maximum at around 460 nm can be attributed to the Ce^{3+} 5d → 4f transition. The second, spin-forbidden, narrow line with a maximum at around 687 nm corresponds to Cr^{3+} ions emission from ^2E excited level to the $^4A_2$ ground state. It was shown that Ce^{3+} ions occupy one position in the crystal unit. Therefore, the observed broad emission is a convolution of two bands coming from the transition from 5d to two energy sublevels: $^2F_{5/2}$ and $^2F_{7/2}$. The calculated energy difference is equal to 2196 cm^{-1}, which is close to the theoretical splitting between these two energy sublevels.

In conclusion, the received result, the high emission intensity together with the stability of the matrix makes this material promising as a phosphor for LED applications.

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O-40

HOW Pr^{3+}-DOPED LUMINESCENT THERMOMETERS SHINES - EXPLORING THEIR BRIGHT SIDES AND BOUNDARIES

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Luminescence thermometry has emerged as a versatile technique for temperature sensing in a variety of scientific and industrial applications. Among the various luminescent materials investigated for this purpose, Pr^{3+}-activated phosphors have garnered significant attention due to their unique spectroscopic properties, the possibility of integration into various systems, and their potential for precise temperature measurements, specifically when excited into their allowed 4f→5d broad-band absorption. Furthermore, the ability to tailor their luminescent properties through dopant concentration and host matrix composition presents opportunities for fine-tuning their performance to specific temperature measurement requirements.

However, like any technology, Pr-activated phosphors also have limitations that need to be considered. Several challenges and limitations must be addressed to realize the potential of Pr-activated phosphors for luminescence thermometry fully. Issues such as thermal quenching, spectral overlap with other emission bands, and potential degradation at high temperatures pose significant hurdles that require careful consideration and mitigation strategies. Furthermore, a comprehensive understanding of the underlying luminescence mechanisms and accurate calibration procedures is paramount to ensure the reliability and accuracy of temperature measurements.

The necessity for further research in this area is evident, as addressing these challenges will not only advance our fundamental understanding of luminescence processes in Pr^{3+}-activated phosphors but also enhance their practical utility in temperature-sensing applications. Success in overcoming these hurdles holds promise for the development of highly sensitive, accurate, and robust luminescence thermometry systems, with potential implications ranging from fundamental research in materials science to practical applications in various fields of technology.

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O-41

Understanding the Excited State Properties and the Luminescence Mechanisms of *ns*^{2} Type Ion Doped Phosphors: A First-Principles Study

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Luminescent materials doped with *ns*^{2}-type ions, such as Bi^{3+}, Sb^{3+} ions, exhibit several excited states that can provide optical transitions, including the optical transitions within the electronic configuration of *ns*^{2} ions, the valence band to *ns*^{2} ions charge transfer (CT) transitions, the metal-to-metal charge transfer (MMCT) transition between the *ns*^{2} ions and the conduction band, and the intervalence charge transition (IVCT) between the dopant pair. The luminescence properties of these materials are significantly influenced by the environment, making the *ns*^{2} ions excellent activators for phosphors. Our talk will present the first-principles studies that revealed the geometric and electronic structures of the ground and excited states of *ns*^{2} ions, constructed the configuration coordinate diagrams, and analyzed the dynamic processes of excitation, relaxation, and emission. We will also briefly present some work on *ns*^{2} ions doped phosphors studied by the combination of first-principles and experimental methods, demonstrating the importance of theoretical calculations for the design and performance improvement of novel luminescent materials.

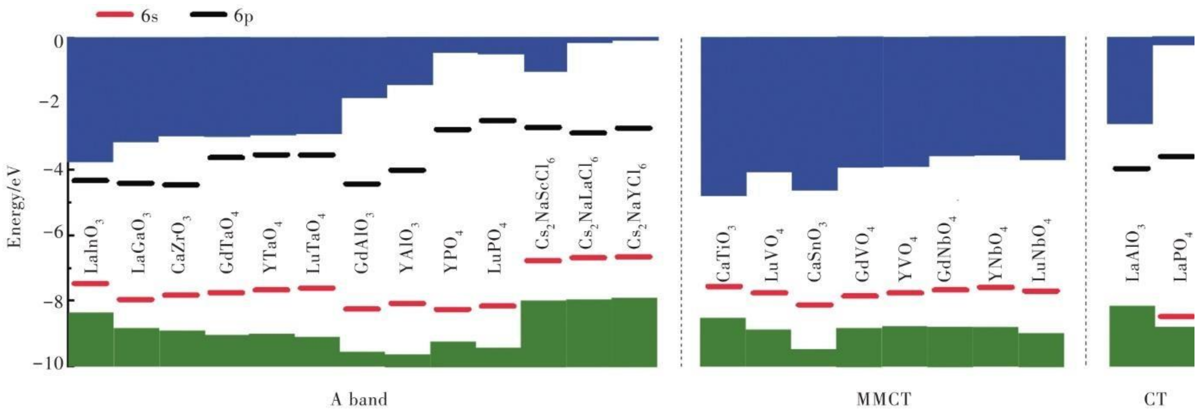

Figure 1. The charge transition level diagrams of Bi^{3+} doped systems that produce dominantly A band，MMCT or CT emission as confirmed by experiments. Wherein the VBMs are determined by their vacuum referred binding energies, 6s and 6p are the electron and hole trap states provided by Bi^{3+} in the hosts. The relative energies of 6s to VBM and CBM to 6p give the trap depths.

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O-42

CYANIDO METAL COMPLEXES FOR ADVANCED SOLIDS LINKING NON-LINEAR OPTICS WITH PHOTOLUMINESCENCE

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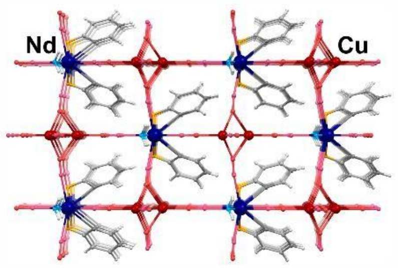
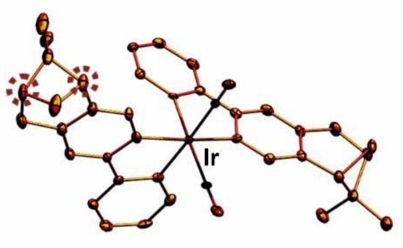
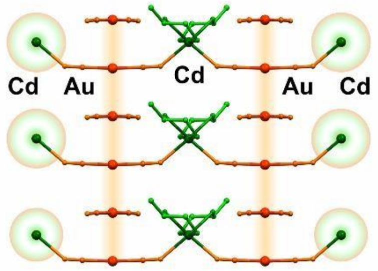
Among the primary aims of modern coordination chemistry lies the synthesis of novel functional materials for future applications in novel devices, employing their various magnetic, optical, dielectric or electronic, and mechanical features.[1] Owing to rational design based on the self-assembly of functional components, such materials bear the desired physical properties or their conjunction giving rise to multifunctional single-phase systems[2] The latter scenario, in recent years, was fruitfully employed for achieving stimuli-responsive systems, such as sensors, and studying cross effects stemming from solid-state interactions between the assembled molecular units.[3]

From the large group of optical phenomena found for coordination systems and MOFs, visible-light or NIR photoluminescence gained enormous attention due to its application potential and a variety of means to achieve it by using different chemical components. In such a context, the usage of cyanido metal complexes was found as a promising pathway resulting from the sensitizing capabilities towards f-block metal ions and their intrinsic optical properties. On the other hand, a different mechanism of non-linear light conversion, resulting from the crystal symmetry breaking, ie. second harmonic generation (SHG), could be employed for a number of cyanido-bridged systems, often coupled with the set of magnetic phenomena.[1] Therefore, our route to combine both above-mentioned effects within a single-phase material through cyanide chemistry is a natural pathway to achieve optical multifunctionality. Within this talk, we will present different strategies for functionalizing cyanide-based systems toward photoluminescence and SHG activity, including the construction of lanthanide(III)-copper(I) polar frameworks,[4] inducing chirality in novel emissive cyanido metal complexes,[5] and using aurophilic interactions for tunable luminescence and non-linear optical responses.







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O-43

Tb^{3+} DOPED BISMUTH GERMANATE GLASS SYSTEMS FOR GREEN LASER APPLICATIONS

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Glasses doped with rare earth ions are materials that have the potential to be used in many technological application areas because of their important features such as low cost, simple preparation process, and good optical performance. In this study, a new series of Tb^{3+} doped Bi_2O_3-GeO_2 (BGO) glasses have been synthesized by the traditional melt quenching method and their structural, thermal, optical, and luminescence properties have been investigated with various techniques. The density of glasses reaches up to 5.93 g/cm^3 which is highly required for scintillation application. The non-crystalline state of the fabricated glasses was verified by XRD measurements. The [BiO_3] and [GeO_4] structural units have been determined by Fourier transform infrared analysis. The absorption band at 500 nm is related to the optical transitions of Bi^{3+} ions. In addition, the optical band gaps, refractive indices, and Judd-Ofelt values were calculated to determine their radiative properties. Photoluminescence (PL) and PL decays have been evaluated. The emission spectra of the glasses demonstrate various bands at approximately 486, 541, 584 and 620 nm under 378 nm excitation. The most intense peak in the spectrum occurred at 541 nm as green emission. The Commission International de l'Eclairage color coordinates and correlated color temperature values of title glasses are consistent with the bright green emission obtained by the luminescence spectra. Also to investigate the scintillating potential of the materials X-ray excited luminescence spectra were obtained and compared with the commercial BGO crystal. The current findings of Tb^{3+} doped BGO glasses were discussed in terms of potential applications in green color display devices, solid-state green lasers and scintillators.

O-44

INFLUENCE OF ALKALINE EARTH FLUORIDES ON STRUCTURAL AND PHOTOLUMINESCENCE PROPERTIES OF OXYFLUORIDE GLASSES

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In this study, a new series of Dy^{3+} doped oxyfluoride borogermanate (B_2O_3-GeO_2-Al_2O_3- MF_2-DyF_3 (M=Ba^{2+}, Ca^{2+}, Sr^{2+}, BGAMDy) glass systems was fabricated via melt quenching method. Their physical, structural, optical, and luminescence properties were investigated using XRD, FT-IR, UV-Vis, PL emission and excitation spectra measurements. The XRD pattern has confirmed the material's amorphous nature. FT-IR analysis confirmed the existence of [BO_3], [BO_4] and [GeO_4] structural units. BGAMDy glasses present a high transmittance of about 90% within the visible range, implying their potential utility in wLED applications. The influence of alkaline earth fluorides on the luminescence properties of various excited levels of Dy^{3+} has been evaluated. The strongest yellow emission of Dy^{3+} ions ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) has been obtained for SrF_2 doped glass. Among the glasses slight changes have been observed for yellow-blue ratios, CIE chromaticity coordinates (x,y) and correlated color temperatures (CCT) depending on the type of alkaline earth fluorides. Pure white light emission was obtained for all the samples. The results endorsed the usability of the glasses in solid-state lighting device applications such as w-LEDs and lasers.

O-45

Designed optical environments to tailor the emission on nanophosphor thin films

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Rare earth (RE) emitters are key materials for efficient light generation due to their chemical and thermal stability combined with high photoluminescence quantum yield (PLQY). Their versatility makes them attractive for a wide range of applications.[] Herein, we show that the integration of RE nanocrystals or nanophosphors into designed optical environments allows fine control over the properties of the emitted light without changing their chemical composition or compromising their efficiency. In particular, we theoretically and experimentally study the influence of the optical environment on the radiative decay rate of RE transitions in luminescent nanoparticles forming a thin film, and provide a way to rationally tune the spontaneous decay rate and hence the PLQY in an ensemble of luminescent nanoparticles[1].Then, we demonstrate a versatile and scalable method to fabricate periodically corrugated nanophosphor surface patterns that exhibit strongly polarized and directional visible light emission. A combination of inkjet printing and soft lithography techniques is used to obtain arbitrarily shaped light-emitting motifs. Such pre-designed luminescent patterns, in which the polarization and angular characteristics of the emitted light are determined and finely tuned by the surface relief, can be used as anti-counterfeiting labels, as these two specific optical features provide additional means to identify any unauthorized or counterfeit copy of the protected item. The potential of this approach is exemplified by the processing of a self-standing photoluminescent quick response code whose emission is both polarized and directional. Physical insight into the mechanism behind the observed directionally outcoupled photoluminescence is provided by finite-difference time-domain calculations[2] Our results pave the way for large-scale processing of phosphor materials with tailored control of their properties, which is of great interest for the development of multifunctional light-emitting sources and smart luminescent coatings.

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OPTICAL PRESSURE SENSORS UTILIZING THE $^4T_{2g} \rightarrow {}^4A_{2g}$ ELECTRONIC TRANSITION OF Cr^{3+} IONS

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Ruby ($Al_2O_3:Cr^{3+}$) stands out as a leading example among luminescent pressure sensors, widely employed as the pressure indicator in diamond anvil cell [1]. It also represents a method of pressure determination relying on a calibration curve that correlates the spectral position of a narrow emission band with the applied pressure. Despite its extensive use, ruby presents significant limitations. Firstly, it exhibits a relatively low sensitivity in detecting pressure changes based on the shift of the emission band associated with the $^2E_g \rightarrow {}^4A_{2g}$ electronic transition of Cr^{3+} ions, approximately 0.365 nm/GPa. Additionally, ruby's spectroscopic properties are influenced also by temperature, rendering the determined pressure value unreliable. Hence, there is a need for a development of a novel approach to address these limitations and enhance the potential application of luminescent pressure sensors. An approach with promising potential, yet remains poorly explored, is the exploitation of emission associated with the $^4T_{2g} \rightarrow {}^4A_{2g}$ electronic transition of Cr^{3+} ions. The applicative potential is attributed to the strong dependence of the $^4T_2$ energy level on the strength of the crystal field, and consequently, on metal-oxygen distance ($Dq \sim R^{-5}$), which varies with applied pressure.

Therefore, this study presents an exploration of the potential for exploiting the $^4T_{2g} \rightarrow {}^4A_{2g}$ electronic transition of Cr^{3+} ions in pressure sensing. We conducted research on oxide materials doped with Cr^{3+} ions, among others $Li_3Sc_2(PO_4)_3$ and $LiScGeO_4$, which provideweak crystal fields affecting Cr^{3+} ions [2,3]. The studies revealed that by leveraging the most common approach based on the pressure-dependent spectral shift of the emission band,sensitivity is significantly enhanced. However, the ambiguity in determining the maximum of the broad emission band affects the precision of pressure readouts. Consequently, we introducedalternative approaches in pressure sensing, based on luminescence kinetics and a ratiometric approach utilizing the luminescence intensity ratio of spectral ranges within the broad emissionband of Cr^{3+} ions, which have not been explored in luminescent manometry before. This led toimproved sensitivity of luminescent manometers while ensuring precise and accurate pressurereadings independent of temperature fluctuations. Based on the conducted research, we demonstrated the invaluable role of utilizing the $^4T_{2g} \rightarrow {}^4A_{2g}$ electronic transition of Cr^{3+} ions, thereby paving the way for a new class of luminescent manometers with significant applicationpotential.

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O-47

Phase Stability and Electronic Structure of Tri-Halide Perovskites

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Organic-inorganic hybrid perovskites (OIHP) have been extensively studied since the discovery of its application in new type of the solar cell by Prof. Miyasaka in 2009 [1]. At the beginning of the studies for these materials, photoelectric conversion efficiency was at about 9 %, which has been increased more than 20 % as high as the conventional Si type of solar cells. In view of the fabrication cost of the solar cells using the OIHP, it is apparently much cheaper than the conventional ones and flexible types of solar cells can be realized using OIHP for photo absorption layer of the cell. However, big issue to overcome for the real use of OIHP in the solar cell system is durability for long-term use. Although $MAPbI_3$ is currently used, where MA = $CH_3NH_3^+$, in the solar cell fabrication, $MAPbI_3$ degrades into PbI_2 at high temperatures and/or by humidity. In addition, most of the molecular ions occupy A site of the perovskite structure in lead tri-halide perovskites. Recently, substitution of lead by other elements such as tin have been actively studied. In the current study, we have investigated phase stability and electronic structures of tin tri-halide perovskites, in which A site is occupied with inorganic ions such as Cs^+ and Rb^+ by using the first principles calculations. For the study of the phase stability at finite temperature, phonon densities of states were calculated with the aid of the phonopy package [2]. Resultant phase stability deduced from the calculated free energy and electronic structures will be shown on site.

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O-48

Interstitial Sodium-Stabilized Divalent Europium in Lu_2SiO_5 and Green Persistent Luminescence

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Eu^{2+}-activated inorganic phosphors are commercially used in optoelectronic fields due to their exceptional luminescence performance. However, it is challenging to realize Eu^{2+} luminescence in such hosts with only trivalent cations due to the absence of suitable lattice sites for Eu^{2+} occupancy. Herein, we develop a new design strategy involving Na ions doping to introduce defects in Lu_2SiO_5 to achieve Eu^{2+} luminescence, in which the excess positive charge resulting from Na occupying the interstitial sites facilitates the reduction of Eu^{3+} to Eu^{2+}. Lu_2SiO_5:Na, Eu display a broad-band green emission at ~500 nm, ascribed to the 5*d*–4*f* transition of Eu^{2+} at Lu1 and Lu2 sites. Furthermore, the phosphors exhibit green persistent luminescence for 10 hours after UV, sunlight, or white LED excitation owing to the Na_i defects, indicating promise for information encryption, fingerprint recognition, and optical anti-counterfeiting. The demonstration of defect-assisted Eu^{2+} luminescence initiates further exploration to design advanced inorganic phosphors for broad applications.

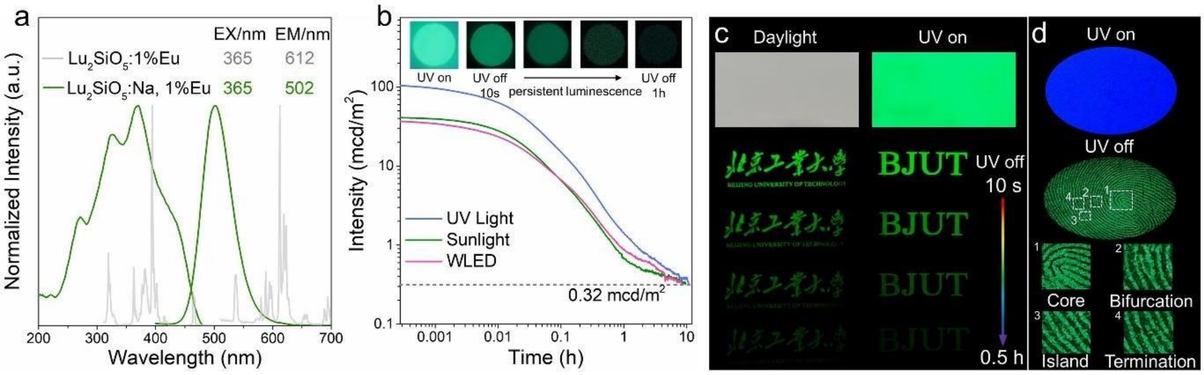

Figure 1. (a) The excitation and emission spectra of Lu_2SiO_5:1%Eu and Lu_2SiO_5:Na, 1%Eu at room temperature. (b) (a) PersL decay curves of Lu_2SiO_5:Na, 0.1%Eu after UV light (254 and 365 nm), sunlight, and WLED (bule chip + YAG) irradiation for 10 minutes, respectively. The insets show the afterglow photographs of Lu_2SiO_5:Na, 0.1%Eu after UV light irradiation for 10 min. (c) Photographs of information encryption patterns under daylight, UV light on and off. (d) Photograph of the treated fingerprint on a card with the blue background fluorescence under UV light on, and the photographs of the fingerprint with specific details after switching off UV light.

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O-49

Rationalizing persistent luminescence: Getting into the processes

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Persistent luminescence materials (PersL) are able to emit light long after the photoexcitation has ceased. This unusual ability finds applications in diverse fields such as nanomedicine, security or data storage.[1-2] Despite the wide gamut of applications and opportunities opened by PersL, the mechanisms behind it are not yet fully understood. This fact, prevents the design of new PersL materials that are capable of meeting the requirements of future applications such as high efficiency and brightness. In this context, having a complete picture of the different processes which determine PersL and how they are affected by parameters that can be tuned in the laboratory such us composition, doping and optical environment is key.[3-5] However, the more extended tools of PersL characterization are based on thermoluminescence (TL) and PersL decay measurements, which give limited information about critical magnitudes such as trapping efficiency. In this work, we propose an approach based on PersL modelling relying on rate equations and global fitting of experimental measurements.[6] We also serve from theoretical predictions to design new experiments that shed more light on key parameters determining PersL efficiency, showing for the first time a steady-state method which is able to directly characterize charge trapping, at the same time that it gives information about trap depth distribution and the type of PersL process which is occurring in a material. This novel method will result in deeper knowledge of PersL and will allow to compare PersL efficiency in different materials, providing a direct way to test how synthesis parameters affect PersL and hence, facilitating the development of new PersL materials.

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O-50

The role of size and composition in pressure-sensitivity of $CuInS_2$ QDs

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Mechanical forces are involved in several biological processes, such as wound healing or tumor progression.[1,2] Therefore, comprehension of the magnitude of these forces can provide us critical information for further diagnosis and treatment of diseases. For this purpose, nanoparticles with mechanical pressure-dependent luminescence are ideal probes for minimally invasive readout of forces at the (sub)cellular level. Semiconductor QDs have attracted attention in the *nanomanometry* field due to the dependence of their photoluminescence emission features on the applied pressure. One ideal candidate for pressure sensing on the nanoscale are copper indium sulfide (CIS) QDs, since they have a sizable band gap pressure coefficient (α), and are less toxic compared to other nanoprobes, such as Pb- and Cd-based ones. In this work, we studied the response of CIS QDs to external mechanical forces, and how their size and composition play a critical role in the force-sensitivity. When CIS QDs are subjected to pressure, the peak position showcases a blueshift, while when the pressure is released, the original peak position is recovered. This recovery highlights that CIS QDs are working in the elastic regime, opening the possibility to measure forces in dynamic systems at the (sub)cellular level. By optimizing the size and composition of these QDs, we can develop luminescence nanoprobes that can be suitable for measuring forces below ~20 nN in biological systems.

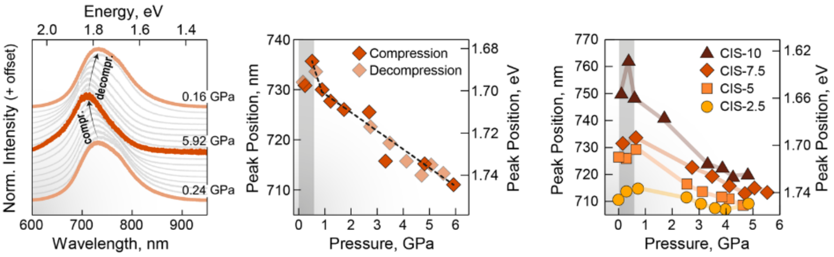

Figure 1. Photoluminescence spectra of CIS QDs subjected to a compression/decompression cycle and change in the peak position as function of the size while subjecting to a compression cycle.

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O-51

Growth and scintillation properties of Ce^{3+}, Pr^{3+}, and Mg^{2+} co-doped $Lu_3Al_5O_{12}$ single crystals

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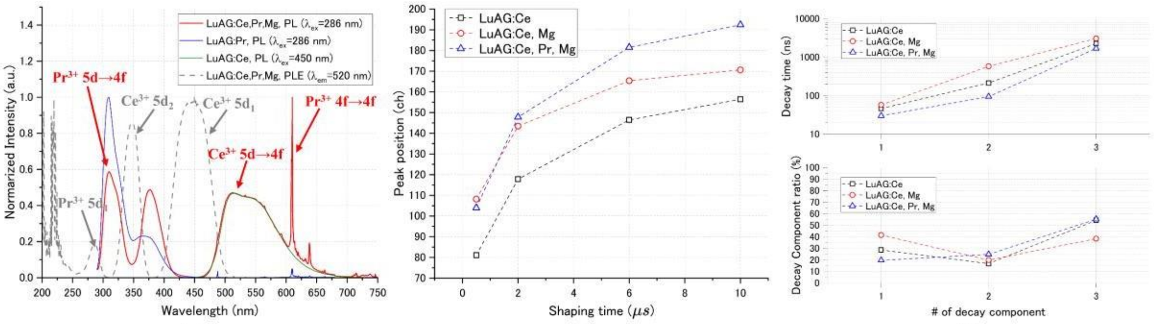
[Introduction] Scintillators convert high-energy photons or particles into visible or ultraviolet light, characterized by high density, rapid decay, and scintillation efficiency. $Lu_3Al_5O_{12}$ (LuAG), a garnet crystal, boasting high density (6.67 g/cm^3) and an effective atomic number (Zeff = 63). Investigations on Ce^{3+} and Pr^{3+} doped LuAG have been conducted [1], with particular interest in the 310 nm emission of Pr^{3+} aligning with Ce^{3+} absorption, prompting research on energy transfer mechanisms. Xiong et al. [2] synthesized LuAG co-doped with Ce^{3+} and Pr^{3+}, reporting a scintillation light yield of 34,000 photons/MeV. Kamada et al. [3] enhanced scintillation light yield and decay time by co-doping LuAG:Ce with 200 ppm Mg^{2+}. In this study, LuAG single crystals co-doped with Ce^{3+}, Pr^{3+}, and Mg^{2+} were grown via the micro-pulling-down (μ-PD) method, compared with LuAG:Ce and LuAG:Ce,Mg.

[Materials and methods] A stoichiometric blend of $MgCO_3$, CeO_2, Pr_2O_3, Lu_2O_3, α-Al_2O_3, and Gd_2O_3 served as the initial material. Utilizing the μ-PD method, single crystals of $(Lu_{0.995}, Ce_{0.005})_3Al_5O_{12}$ (=LuAG:Ce), $(Lu_{0.9948}, Ce_{0.005}, Mg_{0.0002})_3Al_5O_{12}$ (=LuAG:Ce, Mg), and $(Lu_{0.9928}, Ce_{0.005}, Pr_{0.002}, Mg_{0.0002})_3Al_5O_{12}$ (=LuAG:Ce, Pr, Mg) were grown.

[Results] The PLPLE spectra of LuAG:Ce, Pr, Mg display distinct peaks under Pr^{3+} excitation (λ_{ex}=286 nm): a broad peak at 310 nm (5d→4f transition of Pr^{3+}), a sharp peak spanning 470 nm to 750 nm (4f→4f transition of Pr^{3+}), and a broad peak at 520 nm (5d→4f transition of Ce^{3+}). The position of the 662 keV gamma-ray photoabsorption peak is shown in Fig.1(b) at various shaping time constants of the spectroscopy amplifier. Notably, when the shaping time constant exceeds 2μs, LuAG:Ce, Pr, Mg peak positions are higher than LuAG:Ce, Mg. Regarding scintillation decay (Fig.1(c)), LuAG:Ce,Pr,Mg showed the fastest for all components, yet the proportion of longer components outweighs the others, potentially accounting for the heightened photoabsorption peak at longer shaping time constants. This presentation will explore the correlation between activator quantity and luminescence properties.



(a) (b) (c)

Fig. 1 (a) PLPLE spectra of LuAG:Ce, Pr, Mg, (b) Photoabsorption peak position v.s. shaping time constant for grown crystals, (c) Scintillation decay time and their proportion.

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O-52

LANTHANIDE MOLECULAR CLUSTER-AGGREGATES AS THE NEXT GENERATION OF OPTICAL MATERIALS

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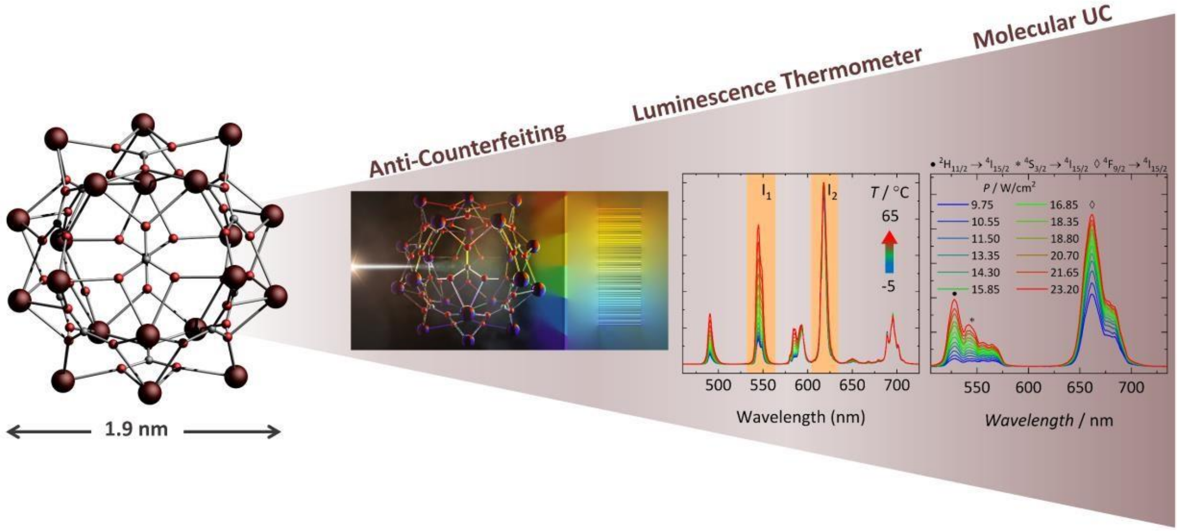
Molecular cluster-aggregate (MCAs) is an intriguing class of molecular compound with high nuclearity at the interface of molecular and nanoparticle worlds. Herein, we discuss the achievements of our group in the study of the optical properties of an icosanuclear lanthanide-based MCA, **{Ln$_{20}$}**.[1-3] Recent work by our group depicts some advantages of MCAs over nanoparticles and low-nuclearity molecules. Thanks to the molecular nature of these systems, a high uniformity in terms of size can be obtained, which is a great advantage over the size distribution of nanoparticles when aiming to control the optical properties at a single level. The high nuclearity allows a fine composition control, akin to nanoparticles, which enables a precise tunability of the optical properties. The present work aims to discuss the use and the impact that **{Ln$_{20}$}** MCA can have for obtaining highly efficient optical materials for luminescence thermometry[1] and anti-counterfeiting[2] applications. Also, some of our achievements in obtaining molecular upconversion[3,4] will be discussed.



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O-53

MAGNETO-OPTICAL THERMOMETRY WITH LANTHANIDE(III) COMPLEXES

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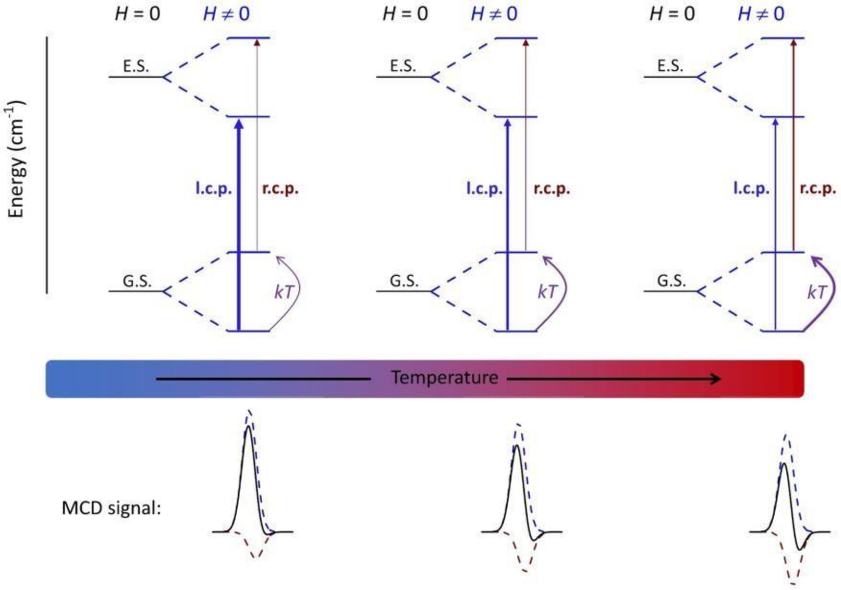
Over the past decade, luminescence thermometry has been demonstrated as a technique to remotely probe temperature, showing remarkable spatial resolution, high thermal sensitivity, and fast acquisition times. Several approaches have been demonstrated to target different probing strategies, such as band-shift, lifetime, energy-transfer-based ratiometric, and crystal-field sublevels thermometry, each approach having its own advantages/disadvantages.[1] Despite the success of luminescent thermometers, probing the temperature at very low temperatures (below 10 K) remains challenging. Most temperature-dependent processes that favor temperature-related spectral changes, such as energy-transfer, hot bands population, and quenching pathways, are inefficient at such low temperatures.

To tackle this issue, our group introduced magneto-optical thermometers based on magnetic-circular dichroism (MCD) technique.[2] The inherent temperature sensitivity of the MCD *C*-term, in conjunction with both positive and negative signals, enables highly sensitive magneto-optical temperature probing below 10 K.

Additionally, in this work, we aim to discuss the possibility of developing magneto-optical thermometers based on magnetic circularly polarized luminescence (MCPL), the emission counterpart of MCD. The advantage of using MCPL instead of MCD is that the first is an emission-based technique; therefore, the geometrical requirements are less strictly, removing the need to work in transmission mode.



Temperature effect on MCD transitions. Increasing the temperature results in a higher population of the upper Zeeman sublevel by a factor of *kT*.

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OPTICAL PROPERTIES OF INAS/GASB AND INAS/INASSB TYPE-II SUPERLATTICES FOR MID-INFRARED OPTOELECTRONICS APPLICATIONS

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Modern optical gas detection systems utilize the technique of tunable laser absorption spectroscopy for different applications in science, manufacture, or medicine. Superlattice structures composed of semiconductors from the 6.1 Å family enable type-II band alignments and have the potential to exceed state of the art figure of merits of widely used infrared detectors. In this study, InAs/GaSb [1] and InAs/InAsSb [2] type-II superlattices were grown using molecular beam epitaxy and characterized using Fourier-transform infrared spectroscopy and pump-probe transient absorption technique. Photoluminescence spectra were obtained for all samples in 10 to 300K temperature range and then complemented with photoreflectance measurements for characteristic temperatures to increase the sensitivity of the measurement for less optically active transitions. The obtained energies were compere to the calculated (by 8kp formalism) energies of confined electron and holes states. In addition, pump-probe measurements were performed to investigate the dynamics of carrier relaxation and recombination processes in proximity of transition energies observed in previous experiments. In comparison to InAs/GaSb in case of gallium free superlattice, the additional channel for carrier relaxation has been revealed. Presented findings could provide valid insights in the fundamental properties such as carrier lifetimes within InAs/GaSb and InAs/InAsSb SLs to further optimize and improve the working parameters of possible future applications in the field of infrared optoelectronics

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O-55

THE BEHAVIOR OF LA_2O_2S:Eu AS A FUNCTION OF EXCITATION DURATION

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The Emerging Measurements Company (EMCO) *LabKit* was developed to measure the time- and temperature-dependent emissions of phosphors. Collected data is displayed on an attached oscilloscope and can be saved for future analysis using a standard computer. It is unique in the field as being the only turn-key method currently available that can measure the prompt fluorescent decay and rise times over a temperature range of -10 to 80 °C. It allows researchers to quickly determine the fluorescent decay and rise times for most phosphors, improving the ability to analyze materials.

The *LabKit* allows users to vary several settings including LED Pulse Width, Pulse Repetition Rate, Peltier Cooler Current, and Photomultiplier Tube (PMT) Gain. A Peltier cooler in the *LabKit* can be used to control sample temperature. The sample holder doubles as a heat sink lending stability to the desired temperature setting. The EMCO *LabKit* uses a 373 nm light source diode from AMS OSRAM, which has a FWHM of 10 nm. A sample holder with accompanying Peltier cooler was positioned at 45˚ with respect to both the LED and filter chamber. A Hamamatsu H10721-110 PMT was used to detect emitted light from the sample. A Tektronix MDO3024 Oscilloscope was used to record the data. The built-in MATLAB® fitting app was used to fit the data.

At the second ICPT one of the authors presented work demonstrating that the emission of several phosphors is dependent on the excitation duration. This exciting discovery presents the possibility of being able to tailor phosphors' behavior to the need of an investigator. The present work expands upon that discovery by examining the emission of La_2O_2S:Eu over a range of excitation durations, from 0.870 - 74.00 µs. A small quantity of the well-known phosphor from Phosphor Technology, Limited was used for this research. A 400 nm cut-on filter was used in conjunction with a bandpass filter centered at 514.5 nm with a 10 nm FWHM to observe the 514 nm emission. Following the results presented in our other talk, the emissions were fit as a double exponential decay. The fitted parameters, total integrated light yield, and several quantities calculated from the fitted parameters were plotted as a function of excitation duration at each temperature from 10 – 55 °C. The calculated quantities include the average decay time, the branching ratios for the two decays, and the ratio of the shorter decay time to the longer decay time.

Even over this limited range of excitation durations, preliminary measurements yield exciting results. The average decay time, for example, appears to follow a power law as a function of excitation duration. The total integrated light yield exhibits the familiar behavior of a charging capacitor. The ratio of decay times appears to be a capacitive charge multiplied by a capacitive discharge as a function of excitation duration. The intensity of the shorter decay has also been fit as function of both excitation duration and temperature.

O-56

Synthesis, Stability and Application of All-inorganic Perovskite Metal Halide Luminescent Materials for Information Display and Detection

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The all-inorganic perovskite metal halide has wide application prospect in that field of wide color gamut LED display, information detection and the like. However, there are still many problems, such as non-green synthesis, poor water resistance, aggregation-induced luminescence quenching and urgent need to broaden the application field. Firstly, the design strategies of composite materials, including perovskite @ organic composite layer, perovskite @ inorganic composite layer, perovskite @ superhydrophobic composite layer and perovskite @ inorganic glass composite layer, are systematically proposed in this paper. Through the composite structure, the problems of poor water resistance and aggregation-induced luminescence quenching are solved in one step. Secondly, the high efficiency sensitization strategy was introduced, and a variety of rare earth doped double perovskite metal halide near-infrared luminescent materials with high luminescent efficiency were designed and obtained, and their potential applications in the fields of composition detection, anti-counterfeiting and night vision were explored; Finally, a liquid perovskite metal halide scintillator material with multicolor emission and high chemical stability is designed and obtained through a low-temperature synthesis and surface passivation strategy.

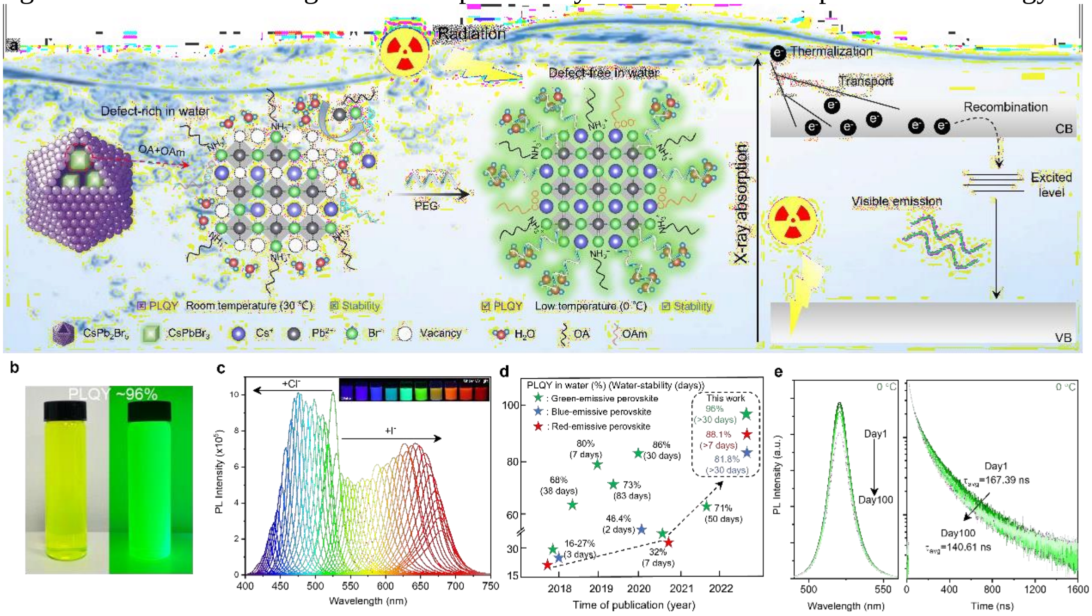

Figure 1 Synthesis route and Spectroscopic Properties of Aqueous Metal Halide Perovskite Liquid Scintillator

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O-57

2D SURFACE PHOSPHOR THERMOMETRY IN A SHALLOW BOILING WATER CHANNEL

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Boiling is an extremely endothermic phenomenon, particularly suited to cooling or other heat transfer applications such as energy production. However, its inherent complexity makes it difficult to describe quantitatively. In this study, we investigate the effects of boiling on surface thermal dynamics at atmospheric pressure in a water-cooled, electrically-heated channel with a rectangular section and a low height-to-width ratio. This particular geometry is far removed from the classic configurations found in the literature [1]. Thus, the documented empirical correlations are not applicable and a new experimental investigation is a necessary premise for the design of an industrial scale system. In particular, the measurement of temperature boundary conditions as a function of the state of the coolant flow is key to ensure the reliability of numerical simulations. As shown on the right-hand side of Figure 1, the boiling flow is strongly unsteady. This study aims at establishing a local and time-resolved description of the thermal processes at play.

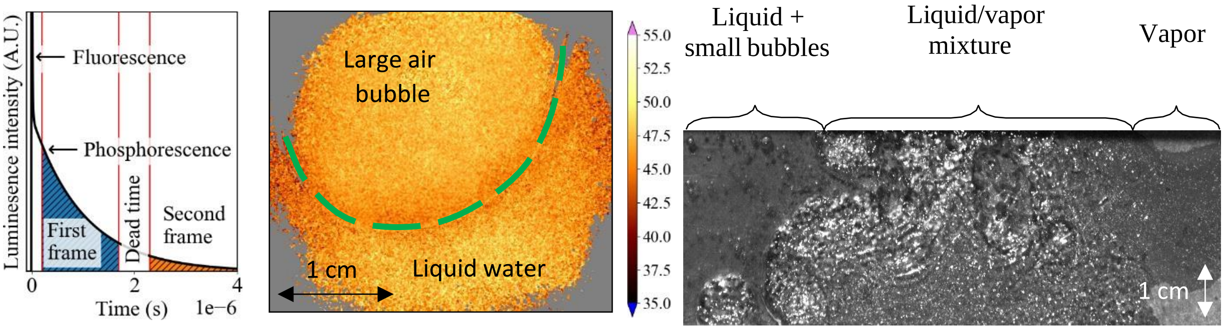

Figure 1- Left: Timing diagram for double-frame decay time phosphor thermometry (PT). Center: Surface temperature field (temperature in °C; grey = no data) obtained with PT through the transit of an air bubble in liquid water at thermal equilibrium. The interface position is highlighted with a green dashed line. Right: Direct visualization of the multiphase water flow in the cooling channel.

2D decay-time phosphor thermometry (PT - Figure 1, left and center) enables space- and time-resolved direct sensing of the wall temperature field. The surface is coated with a fast-decay $(Sc_{0.2},Y_{0.8})VO_4{:}Bi^{3+}$ phosphor, exhibiting a high sensitivity peaking at 4%/°C around 100 °C. The phosphor is excited at 4 Hz by a 355 nm laser pulse, and the luminescence decay is collected with a double-frame CCD camera. Owing to its self-referential nature, decay-time PTis only marginally affected by the presence of a bubble on the optical path. Moreover, the shortfirst image duration ($\geq$1.2 µs) of the sensor means the initial fast-decay luminescent phenomenaare not integrated (see Figure 1, left). This eliminates the associated uncertainty while retaining maximum sensitivity and range. As seen on Figure 1 (center), far from the interfaces the measurement is identical through the liquid and the bubble. There is a slight perturbation in the vicinity of the interface, due to the pronounced curvature of the gas air interface in this region, which may necessitate the development of masking algorithms.

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O-58

TOPOCHEMISTRY TO THE RESCUE FOR GENERATING NEW HOST MATRICES FOR LUMINESCENT MATERIALS: A STUDY OF oA-La_2O_2S (Ln= Ce, Eu, Pr)

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Recently, a metastable form of La_2O_2S oxysulfide (referred to as oA-La_2O_2S) was synthesized by topochemical deintercalation of sulfur atoms from the $La_2O_2S_2$ precursor [1-3]. This new material is a polymorph of the well-known and thermodynamically stable La_2O_2S compound (referred to as hP-La_2O_2S), distinguished by having two distinct lanthanum environments instead of one. For the past 50 years, hP-La_2O_2S has been used as a host lattice for various luminescence applications. Consequently, Ce, Pr, and Eu-doped oA-La_2O_2S phases were naturally prepared and optically characterized [4]. The primary contributions to the luminescence spectra are in the green, green and red, and red regions of the visible spectrum for Ce, Pr, and Eu-doped oA-La_2O_2S, respectively and significantly differ from emissions observed in Ce, Pr, and Eu-doped hP-La_2O_2S (violet, green, and orange, respectively). Based on this example, the interest of topochemistry as soft chemical route to prepare new phosphors and/or new host lattices for lanthanide will be discussed.

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O-59

TiO_2-based interfacial charge transfer complex with dihydroquercetin: Optical properties and reactivity of photogenerated species

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The TiO_2-based interfacial charge transfer (ICT) complex with dihydroquercetin was prepared by the condensation reaction of hydroxyl groups from inorganic and organic parts of the hybrid and displays light absorption in the visible spectral range. The density functional theory (DFT) calculations on a cluster model that mimics the ICT complex agree with spectroscopic measurements. The reactive paramagnetic species generated in the dispersed unmodified TiO_2 powder and surface-modified TiO_2 powder with taxifolin upon excitation with ultraviolet and visible light were identified by indirect electron paramagnetic resonance (EPR) spectroscopy techniques. The spin trapping and spin scavenging revealed the differences between the behavior of the unmodified and surface-modified TiO_2 powders with taxifolin before and upon excitation. On one side, the TiO_2-based ICT complex with taxifolin efficiently scavenges reactive oxygen species by the taxifolin's hydroxyl groups and, on the other side, the promotion of electrons from the ground state of taxifolin to the conduction band of TiO_2 takes place under visible light excitation.

O-60

POSSIBILITIES OF TUNING OF Mn^{4+} AND Cr^{3+} LUMINESCE IN Ga_2O_3 BY ALLOYING WITH Al_2O_3 AND In_2O_3

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The work focuses on the possibilities of tuning the luminescence properties of Mn^{4+} and Cr^{3+} ions in gallium oxide (Ga_2O_3) by alloying with Al_2O_3 and In_2O_3.

To address this we carried out a comprehensive study on $(Al_{1-x}Ga_x)_2O_3$:Mn^{4+} (x = 0; 0.05; 0.10; 0.15; 0.2; 0.25; 0.5; 0.75; 1.0), $(Ga_{1-x}Al_x)_2O_3$:Cr^{3+} (y = 0; 0.1; 0.2) and $(Ga_{1-x}In_x)_2O_3$:Cr^{3+} (x = 0.05; 0.1; 0.15; 0.2; 0.3; 0.4; 0.5) phosphors [1, 2]. Our investigation delved into various aspects, including photoluminescence (PL), PL excitation (PLE), diffuse reflection (DR) spectra and PL decay kinetics of the materials over a broad temperature range from 4 to 350 K. Additionally, we studied persistent luminescence (PersL) and thermally stimulated luminescence (TSL) after UV excitation within the temperature range from 77 to 600 K for the Cr^{3+}-doped materials. The phase composition and crystal structure of the materials were examined using the X-ray powder diffraction technique.

Our findings reveal the potential for fine-tuning the performance of the studied materials as NIR persistent phosphors and non-contact luminescence thermometers through the alterations of the chemical composition of the Ga_2O_3-based host material. Performed low-temperature and time-resolved PL studies shed light on the nature of the Cr^{3+} and Mn^{4+} centers present in the alloys. The luminescence results are discussed in correlation with the crystal structure data for the studied materials providing deeper insight into behavior of these materials.

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O-61

THE RELATION BETWEEN CRYSTALLINITY AND LUMINESCENT PROPERTIES IN LUTETIUM PHOSPHATE NANOPARTICLES

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Rare-earth doped nanoparticles are promising materials for various applications due to the bright luminescence in the wide range from UV to IR [1]. Frequently these applications require nanoparticles in a form of stable colloids, hence imposing certain limitations on synthetic path. The majority of the methods of synthesis of dispersible nanoparticles are based on "soft chemistry" approach, in other words preparation routes avoiding extreme conditions and first of all high temperature, that leads to aggregation and re-crystallization processes. The "soft chemistry" methods allow to obtain morphologically uniform and non-agglomerated nanoparticles, but the other side of the coin is the low degree of crystallinity of synthesized nanomaterials related to diffusion limitations at low formation temperatures. As a result, strong quenching of luminescence is usually observed in as-prepared nanomaterials and the crucial step on the way to any practical application of luminescent nanoparticles is to eradicate this shortcoming.

In present work we performed the synthesis of $LuPO_4:Pr^{3+}$ nanoparticles – a promising material for radiotherapy enhancement [2,3] – using the solvothermal synthesis in dimethyl sulfoxide-water media. The role of synthetic conditions on morphology and luminescent properties is discussed. Comparison of data of XRD analysis, electron microscopy, Raman andluminescence spectroscopy of as-prepared and thermally treated nanoparticles allowed us to reveal the influence of local disorder and nanoparticles size on the intensity and kinetics of the luminescence. We've shown that while long range order is characteristic for both as-prepared and annealed nanoparticles, strong local disorder is responsible for drastic alteration in luminescent characteristics before and after the annealing of nanoparticles. Another important aspect is the mean size of the particles and the degree of their agglomeration. We've proposed that the low-angle boundaries forming between the nanoparticles during calcination to the large extent offset the differences between nano- and bulk material.

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O-62

Investigation of Sc_2O_3 Single Crystal for Luminescence Thermometry

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【Introduction】 Temperature is one of the physical parameters that have a great influence on chemical reactions, and accurate temperature measurement is very important in various fields. For temperature measurement, contact and non-contact temperature measurement methods such as thermocouples and radiation thermometers have been widely used. However, these temperature measurement methods have difficulty in measuring temperatures under high frequencies, high electromagnetic fields, and in environments where access is difficult, thus the development of novel thermometers that can be used in harsh environments is required. In order to measure temperatures in such harsh environments, the luminescence thermometry has been attracting attention. One of the temperature measurement methods of the luminescence thermometry is fluorescence intensity ratio (FIR) method, which uses the temperature dependence of luminescence characteristics from different excitation levels [1]. In this study, we focused on Sc_2O_3, which has a high melting point (2,430°C) and thermal conductivity (17 W/mK), and grew single crystal doped with rare earth ion as luminescent center.

【Materials and Methods】 $(Dy_{0.01}\ Sc_{0.99})_2O_3$ single crystal was grown by micro-pulling-down method [2]. Since the melting point of Sc_2O_3 is very high, we used W as the crucible materials. The die of 5 mm in diameter was used, and to suppress oxidation of the W crucible, deoxygenated stabilized ZrO_2 was used as an insulator and crystal growth was performed under a reducing atmosphere [3]. The grown crystal was annealed in an air atmosphere, and after cutting and mirror polishing, optical properties were evaluated.

【 Results 】 The grown $(Dy_{0.01}\ Sc_{0.99})_2O_3$ single crystal is shown in Fig. 1. Although the as grown crystal had black coloration, after annealing at 1200°C for 12 hours under an air atmosphere, transparent crystal was obtained. This suggests that the coloration was caused by absorption due to oxygen defects. Figure 2 shows the photoluminescence emission spectrum for excitation wavelength at 355 nm. The emission spectrum shows typical sharp emission peaks attributed to the Dy^{3+} 4f-4f transitions. Details of the crystal growth and the optical characteristics will be presented.

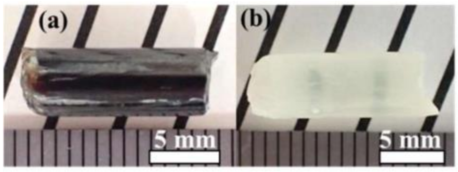

Figure 1 (a) The grown $(Dy_{0.01}\ Sc_{0.99})_2O_3$ single crystal (as grown), (b) The crystal after anneal in air atmosphere.

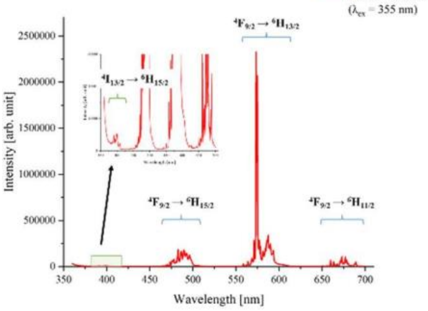

Figure 2 Photoluminescence emission spectrum (excitation wavelength: 355

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O-63

Temperature dependence of luminescence characteristics for (Y, Lu, Sc)$_2$O$_3$ single crystal

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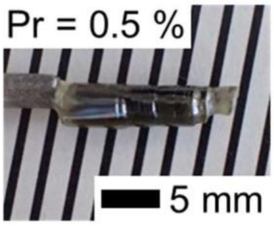
1. Introduction Luminescence thermometry is very promising and perspective temperature measuring method due to its fast response and applicability in various environments such as high electromagnetic fields and catalysis [1]. The temperature measurement method that uses the ratio of fluorescence intensity at two wavelengths with different excitation states is called the fluorescence intensity ratio (FIR) method, while the method using the fluorescence lifetime is called the fluorescence lifetime (FL) method. Lanthanoid ions have attracted considerable attention and have been widely studied in luminescence thermometry. Recently, Pr^{3+}-doped $Y_3(Al, Ga)_5O_{12}$ has been reported to have high sensitivity and a wide temperature range [2]. In this study, we focused on Pr^{3+} and investigated a novel luminescence thermometry using “mixed” sesquioxide as a host material, which is expected to have higher thermal conductivity.

2. Materials and Methods As starting materials, we used Lu_2O_3, Sc_2O_3, Y_2O_3 and Pr_2O_3 powders. After weighing these powders with a composition of $(Pr_{0.005}\,Y_{0.245}\,Lu_{0.250}\,Sc_{0.500})_2O_3$, they were wet mixed in an agate mortar and ethanol. The crystal growth was performed by micro-pulling-down (μ-PD) method using a W crucible and a metal W rod as a seed crystal [3]. The pulling down rate and growth atmosphere were 0.05 mm/min and Ar + 2% H_2 gas, respectively. After the crystal growth, annealing was carried out at 1200°C for 12 h in air. The grown crystal was cut and polished to 1 mm thickness. We evaluated the crystal structure, optical properties, and temperature dependence of the luminescence intensity.



3. Results The crystal grown by the μ-PD method are shown in Figure 1. We succeeded in growing transparent $(Pr_{0.005}\,Y_{0.245}\,Lu_{0.250}\,Sc_{0.500})_2O_3$ crystal using W crucible, but the coloration was observed. Figure 2 shows the radioluminescence (RL) spectrum of the crystal. From the result of the RL, the sharp peaks between 600 nm to 800 nm due to 4f–4f transitions of Pr^{3+} were observed. Details of the temperature dependence of luminescence characteristics will be presented.

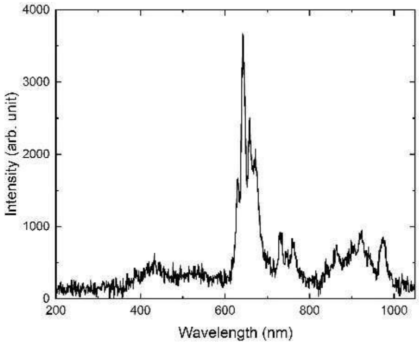


Fig. 2 Radioluminescence spectrum of the grown crystal at room temperature as grown.

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O-64

Dual-phosphor thermometry to probe the flame particle interaction in a model packed bed

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In this study, phosphor thermometry is applied to study the heat transfer between a flame and the cylindrical particles of a packed bed. Such reactor types are common in industry and the flame-wall heat transfer is of great interest as it impacts particle transformation as well as the flame itself. The model packed bed investigated here consists of a regular array of cylinders. A premixed flame is stabilised in the interstice between the cylinders. Flame luminosity is observed using a telecentric lens. 2D lifetime phosphor thermometry is performed simultaneously to obtain highly resolved 2D temperature measurements on the surface of the three cylinders confining the flame. A narrow strip of phosphor is coated on the circumference of the cylinder, midway along its length. The luminescence of phosphor coating is collected by a high-speed camera equipped with filters to isolate the phosphor luminescence from flame luminosity and black body radiation. A dual-phosphor approach is adopted to augment the temperature measurement resolution, as the cylinders are expected to be at different temperatures. The top cylinder is located downstream of the flame and hence at a higher temperature level than the bottom cylinders, which are cooled by surrounding air. In this approach, GAP:Cr^{3+} is coated on the top cylinder, and YAG:Cr^{3+} is coated on the bottom right and left cylinders. The temperature response of the decay time of the two phosphors is shown in Fig. 1a. The camera frame rate is set to 200 kHz, allowing to measure decay times as short as 10 µs. This corresponds to a maximum temperature of about 650 °C for YAG:Cr^{3+} and about 950 °C for GAP:Cr^{3+}. Calibration of the luminescence lifetime of YAG:Cr^{3+} and GAP:Cr^{3+} against temperature is shown in Fig. 1a. Changing the host from YAG to GAP enables measurements at a distinctively higher temperature over a given range of decay time. The results of simultaneous surface temperature measurements and chemiluminescence imaging are shown in Fig. 1b and c. The arcs with color gradient in Fig. 1b represent the detected cylinder edges, and the color gradient on them indicates the distribution of the surface temperature. The red arc between the cylinder edges represents the flame front. For a more detailed visualization of the temperature profile on the left cylinder, it is plotted against the azimuthal angle θ in Fig. 1c, with red vertical line pointing out the angle at which the flame quenches. As shown the peak temperature is near the flame quenching point. The top cylinder is 300 °C hotter than the bottom one. This data can be used to validate CFD simulations as the accurate modelling of the interaction of a flame with hot walls is evidently challenging.

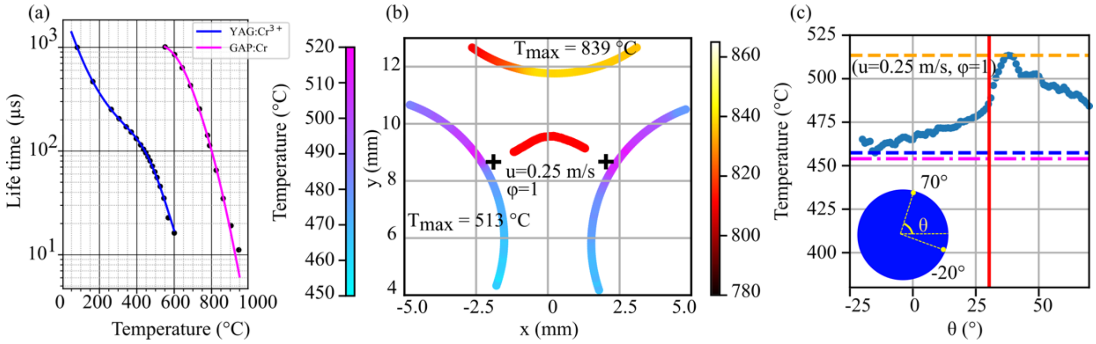

Figure 1- Temperature response of YAG: Cr^{3+} and GAP: Cr^{3+} (a), surface temperature distribution on all three cylinders, the red line delineates the reaction zone and the crosses indicate the flame sidewall quenching point (b), Azimuthal temperature distribution.

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O-65

FIRST ACTIVE AFTERHEATER USED IN LASER-DIODE FLOATING ZONE METHOD

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The furnaces with laser heating are the most advanced instruments for single crystal growth by the floating zone method (FZM) [1]. The newly developed furnaces with multiple lasers based on modern laser diodes offer a sharply demarcated hot zone with an almost flat horizontal thermal gradient. [2,3]

Crucible-free laser-diode floating zone method is particularly interesting in terms of preparation of high melting point oxide-based optical materials from garnet family, such as YAG based laser materials or multicomponent garnet scintillators. Well defined hot zone with laser heating enables reaching temperatures above 2000°C. The absence of crucible allows the use of oxygen rich atmosphere, which is advantageous for preparation of scintillators as an oxygen-poor growth atmosphere leads to oxygen vacancies. These act as shallow traps [4], thus contributing to longer scintillation response [5].

The usage of the floating zone method for the growth of the oxide-based scintillation and laser materials was limited because of the high mechanical strain resulting from the thermal gradient primarily in the vertical direction. The strain causes large cracks inside the single crystals. It is a well-known problem, particularly in the case of Nd:YAG [6].

We were able to develop, install and successfully use the active resistance heated afterheater in our Laser-Diode Floating Zone Furnace from Crystal Systems Corporation and we were able to dramatically improve the quality of single crystals of laser material Nd:YAG [7], scintillation materials GSAG [8] and GGAG.

We will describe in detail the construction of the afterheater, the measured vertical temperature profile in the furnace and the properties of the prepared single crystals of Nd:YAG, GSAG and GGAG. Afterheaters with similar construction could improve the quality of single-crystals in similar furnaces across the world at low cost.

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O-66

CORRELATIONS OF LOCAL SYMMETRY WITH STARK SPLITTING OF ENERGY LEVELS IN LANTHANIDES DOPED Y_2O_3 SESQUIOXIDE

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Analysis of the correlations of structure and optical properties of materials could provide an understanding of how dopants and local symmetry of host materials influence the Stark splitting of energy levels.

The earlier research provides some data but there are still limited published results of such correlations [1]. In our previous work, we used high-resolution (HR) luminescence spectroscopy and Er^{3+} dopant as probes in CaF_2 and BaF_2 crystals to show the impact of local site symmetry on the Stark splitting of energy levels [2].

In this work, we performed a similar analysis of several Ln^{3+} ions (Er^{3+}, Pr^{3+}, Eu^{3+}, and Nd^{3+}) separately doped in Y_2O_3 sesquioxide. The obtained HR photoluminescence data confirmed the published data related to the splitting of Ln^{3+} energy levels [3, 4]. This allowed to visualize the Stark splitting of energy levels difference for different Ln^{3+} ions and their correlations with local symmetry. The proposed approach could provide a clearer visualization of the presence of a second different phase or mixed phases in the host material.

The future work will take into consideration the use of structure-based Machine Learning (ML) prediction instruments for the Materials science area. Thus proposed correlations could serve as useful feeding data for ML descriptors for further optical properties predictions.

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O-67

CHARGE TRANSFER STATES IN LANTHANIDE COMPLEXES CONTAINING EFFECTIVE LIGHT HARVESTING π-BONDED ANTENNA LIGANDS

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A new approach to the design of highly luminescent lanthanide complexes has been developed based on a π-bonded type ligand, namely phenylsubstituted cyclopentadienyl [1]. Cyclopentadienyl (Cp) ligands are the most popular in the organolanthanide chemistry but a few reports on photophysical properties of the lanthanide complexes with Cp derivatives are known so far. All designed terbium complexes containing two, three and tetra-phenyl substituted Cp ligands exhibit relatively high quantum yields of the photoluminescence (up to 65%). The estimated values of radiative rate k_{rad} of the terbium ion vary in the range of 0.23-0.69 ms while the intrinsic quantum yield reaches 100 % in some cases.

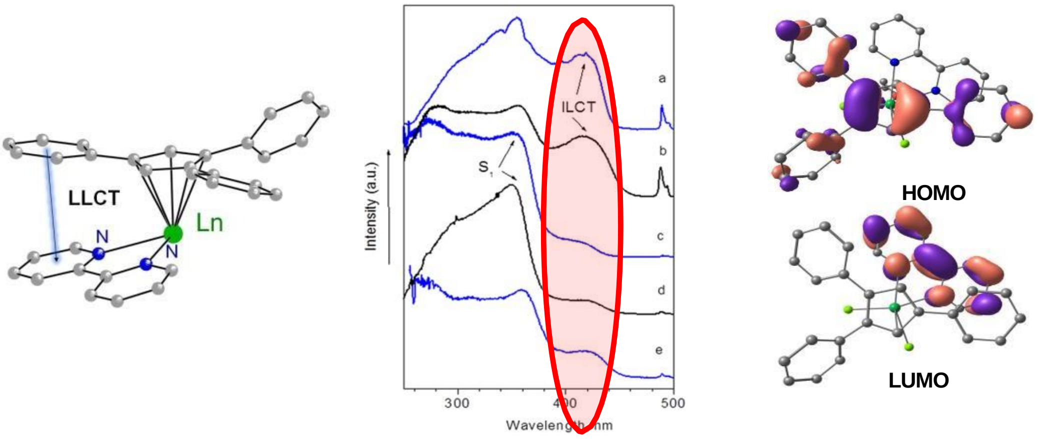

Figure 1. General view of complex $Cp^{Ph3}TbCl_2(bpy)(THF)$ (left), excitation spectra and visualization of the HOMO and the LUMO (right)

The analysis of the optical and structural data shows that the introduction of phenyl groups into the Cp ring leads to the inevitable appearance of an intraligand charge transfer (ILCT) state as an intrinsic property of the π-bonded antenna Cp ligand [2]. On other side we hypothesized and proved theoretically and experimentally the existence of ligand - ligand charge transfer (LLCT) state in these complexes and discussed the involvement of this state in the energy transfer process. New aspects for the design of the lanthanide complexes containing π-type ligands with desired luminescence properties were proposed.

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O-68

Development of Garnet-type Scintillation Crystal with Infrared Emission Band for the Dose-Rate Sensor with Optical Fiber

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To remove the debris in the Fukushima Daiichi Nuclear Power Plant as the decommissioning step, real-time dose monitors under the high dose-rate condition are required. We have proposed a dose monitor consisting of a scintillator, optical fiber and CCD spectrometer, and scintillation photons are read with the CCD under the lower dose condition as shown in Fig.1 [1]. Since the scintillator is coupled with an over-20-m long optical fiber, (a) the long emission wavelength (longer than 650 nm) and (b) high light output are needed for the scintillator to suppress the photon loss through the fiber, and to discriminate the noise in the below 550-nm region originating from the scintillation photons and/or Cherenkov photons in the optical fiber itself, here we describe this noise as "blue noise". In this study, we focused on Cr-doped $Y_3Al_5O_{12}$ (YAG) scintillator, which is known as an oxide scintillator glowing red, and such garnet has no hygroscopic nature..

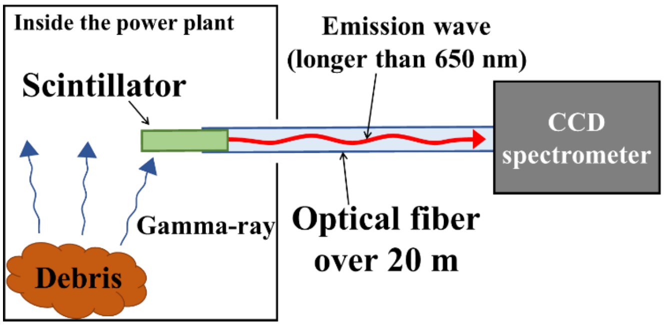
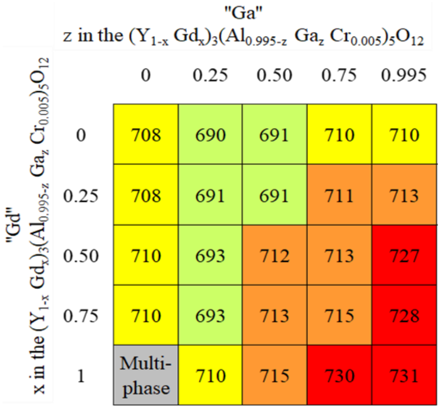


Fig. 1 Schematic view of the radiation dose monitoring system

We prepared sintered powder pellets of $(Y_{1-x}Gd_x)_3(Al_{0.995-z}\,Ga_z\,Cr_{0.005})_5O_{12}$ (x = 0, 0.25, 0.50, 0.75, 1, z = 0, 0.25, 0.50, 0.75, 0.995) were prepared as pellets by powder sintering method to pre-evaluate their luminescence properties. Finally, we determined compositions with emission wavelength of over 650 nm or much longer, and Figure 1 show the results of emission wavelength for these samples.



	0	0.25	0.50	0.75	0.995
0	708	690	691	710	710
0.25	708	691	691	711	713
0.50	710	693	712	713	727
0.75	710	693	713	715	728
1	Multi-phase	710	715	730	731

Fig. 2 Maximum peak of emission wavelength [nm] and composition of $(Y_{1-x}Gd_x)_3(Al_{0.995-z}\,Ga_z\,Cr_{0.005})_5O_{12}$

After this selection, $Gd_3(Ga_{0.995}\,Cr_{0.005})_5O_{12}$ (Cr:GGG) was found to be suitable for our application, so that a Cr:GGG single crystal was grown the micro-pulling-down method. Compared to the emission wavelength of Cr:YAG, that of Cr:GGG was red-shifted; the emission wavelengths were 707 and 731 nm for Cr:YAG and Cr:GGG, respectively.

Moreover, we evaluated the emission intensity with 20-m long optical fiber under the high-dose-rate condition up to 1 kGv/h using ~70-Tb ^{60}Co source at Kyoto University. The result shows we succeeded in wide dose-rate dynamic rage detector (a dozen mGy/h to a few kGy/h). We report details of these results in the conference.

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Highly Efficient Deep Red-Emitting Mn^{4+} Phosphors for Enhanced Plant Growth and Advanced Optical Thermometry

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The present research focuses on the development of a highly efficient deep red-emitting Mn^{4+} phosphor [1], synthesized through a traditional solid-state reaction followed by ball milling, tailored for both temperature sensing and artificial plant growth applications. Structural analysis using Rietveld refinement of X-ray diffraction (XRD) data confirms the orthorhombic phase with a *Pbam* space group in the synthesized sample. High-resolution transmission electron microscopy (HRTEM) reveals the presence of small-sized particles lacking distinct shape or uniform size distribution.

Photoluminescence emission spectra demonstrate sharp peaks around 659 nm and 631 nm when excited by UV light at 317 nm and blue light at 417 nm, respectively. These emissions are attributed to the $^2E_g \rightarrow {}^4A_{2g}$ and $^2T_{1g} \rightarrow {}^4A_{2g}$ transitions of Mn^{4+} ions [2]. The red color purity of nearly 100% is confirmed from the color calculator software using the CIE coordinates under both UV and blue excitations. Additionally, calculations of absorption efficiency and internal and external quantum efficiencies under 417 nm blue excitation underscore the material's suitability for indoor plant growth applications [3].

A prototype red LED was created by coating the synthesized red-emitting phosphor powders onto a 410 nm blue LED chip. The electroluminescence spectra from this prototype overlap with the absorption spectra of key organic pigments in plants, making it ideal for promoting plant growth [4]. Moreover, a detailed assessment of the thermometric properties for fluorescence intensity ratio (FIR)- and lifetime-based thermometry reveals an impressive absolute sensitivity of 0.00326 K^{-1} at 373 K, coupled with excellent reproducibility and temperature resolution [5]. Due to its small particle size and high luminescent efficiency, this Mn^{4+} phosphor shows significant potential for integration into various devices that require high-performance, non-contact optical thermometry.

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O-70

LANTHANIDE-BASED LUMINESCENT THERMOMETER: FROM FUNDAMENTALS TO THE PROTOTYPE

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About 30% of all the measurements conducted by the humankind refer to thermometry. Among the most important temperature ranges is the one of 25…200 ^{o}C, which is mainly important for the industry. The requirement raised by the industry often include a very strict demand of the intrinsic safety and fire safety, which generally contradicts to the use of the convenient thermometers, i.e. those based on the thermocouples. This is particularly dangerous in the oil and gas production, atomic stations, etc.

The use of the convenient thermometers, which require electricity in the area of measurements, is also hampered near to the sources of powerful electromagnetic radiation, for example, transformers, etc. All these numerous applications require the development of the thermometer where the measurement and information transmission do not require an electricity source in the immediate vicinity.

Luminescent thermometry can serve a perfect solution to this: while it still required electricity to power up the excitation source and signal processing, those can be significantly remote from the measurement region, if the information transfer is provided by the optical fiber. It is also one of the most accurate methods of temperature measurement, which allows for continuous real-time measurements and even mapping.

One of the most important applications of luminescent thermometry is the measurement of high temperatures, to which atomic stations and oil and gas production refer. As luminescent thermometers at high temperatures, inorganic lanthanide-based materials are usually used due to their high stability, combined with the narrowband emission at the constant wavelengths. However, very low intensity of their luminescence hampers their practical application, while the thermal stability of brightly luminescent coordination compounds is usually insufficient.

We proposed using heterometallic lanthanide metal-organic frameworks (MOFs), which are often stable to temperatures of 400-600 °C and exhibit very intense luminescence. Fundamental studies of these systems, including mathematical description, has allowed us to obtain composite materials capable of operating up to 400 ^{o}C in both the visible and NIR ranges. As a result, the first prototype of a luminescent thermometer was obtained [1].

This work was supported by RSF (20-73-10053).

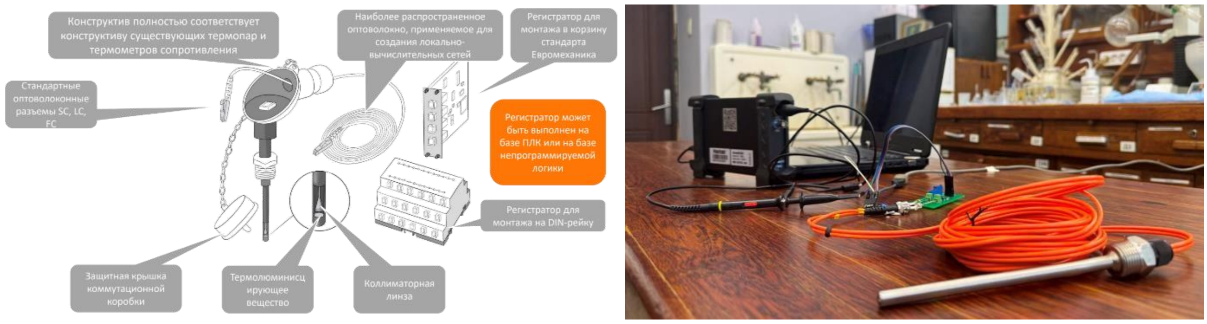

Figure 1. The scheme (left) and photo (right) of the first prototype of an industrial luminescent thermometer.

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O-71

MONTE CARLO CALCULATIONS FOR THE EXCITATION. A CONSEQUENCE FOR TL/OSL PHENOMENA AND THE DOSE RATE EFFECT

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Thermoluminescence (TL) and optically stimulated luminescence (OSL) phenomena are widely used in the field of dosimetry of ionizing radiation as well as luminescence dating of archeological and geological samples. Theoretical models of TL and OSL are based on the concept of trap levels within the energy gap which are related to defects of the solid state crystal lattice. Mathematical and numerical modelling consists usually of three steps: excitation, slow relaxation and stimulation (thermal or optical).

The last stage, which is most important for TL and OSL was calculated in the framework of localized, delocalized [1] and semi-localized [2] recombination mechanism between trapped charge carriers. These models give different predictions for the resulting TL/OSL curves that are generally consistent with experimental data for various materials. However, the excitation mechanism was always assumed to be delocalized, even in a solid consisting of localized trap-recombination center (T-RC) pairs [3]. The mechanism of excitation has important consequences for various TL/OSL properties, including the dose response characteristics. One of these consequences is the prediction of the dose rate effect (DRE). However, there are no unambiguous experimental evidence to confirm this effect.

In real solids, excitation by ionizing radiation is spatially limited by diffusion length of ionized charge carriers. Therefore, all (or almost all) trapping processes occur very close to the ionizing event. The paper presents the model and some preliminary results of Monte Carlo calculations performed for a solid with random distribution of defects. The calculations were performed using a crystal lattice with periodic boundary conditions to minimize the influence of surface. The consequences for the DRE effect are also discussed. The results confirm the generally insignificant effect of radiation dose rate on the TL/OSL response, which was observed experimentally.

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O-72

INFLUENCE OF THE FACET OF ZNO ON THE CESIUM LEAD BROMIDE ATTACHING ABILITIES IN A HETEROSTRUCTURE

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ZnO nanoparticles have demonstrated strong excitonic luminescence, with a decay time of around 400–500 ps [1]. Additionally, $CsPbBr_3$ (CPB) nanoparticles exhibit significant excitonic luminescence at a rate of around 300 ps [2]. The photoluminescence intensity of a $CsPbBr_3$/ZnO core/shell heterostructure was remarkably enhanced (17 times) [3]. This could have possible use in the scintillating detector of the Time-of-flight (TOF) positron emission tomography (PET). Moreover, both ZnO and CPB are promising materials for the solar cells thus implementing solar energy transformation and storage. Combined, they exhibited light harvesting and carrier transfer enhancement [4].

In the majority of cases, point defects of various origins are the elements impacting the photophysics of luminous materials. These can be of complex origin, especially at the boundary of a heterostructure. Therefore, the strategy is to separately investigate the ZnO substrate as well as CPB nanoparticles first in order to comprehend their impact on the CPB/ZnO heterostructure as a whole [5]. Secondly, the heterostructure itself will appear the subject of investigation in order to understand the peculiarities of the CPB attachment to the ZnO surface, especially, considering boundary and charge as well as energy transfer. It should be noted that the impact of either the Zn- or O-face along the <0001> axis or the Zn and O mixture along the <1010> (or comparable) axis of ZnO in this case is unknown. In particular, photo-, radioluminescence, thermally stimulated luminescence, electron paramagnetic resonance, X-ray diffraction and X-ray fluorescence as well as scanning electron microscopy, and atomic force microscopy methods will be applied to disclose the influence of the ZnO facet on the CPB/ZnO composite properties.

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O-73

Temperature dependence of the optical spectra in Cs_2SnCl_6 activated by Sb^{3+} and Bi^{3+}

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Perovskites are functional materials that can be useful for various applications, for example, at the same time such as a detector at specific temperature differences [1], or as a thermometer that can work in a cytostatic mode [2]. Especially, Cs_2SbCl_6 doped with either Bi^{3+} or Sb^{3+} seems an interesting material to study due to its high quantum efficiency and the possibility use in manufacturing LEDs [3]. It does not contain any non-environmentally poisonous Pb. So far, no test results are available which verified the intensity of the titled materials under low temperature conditions. For this purpose, the PL and PLE spectra of Cs_2SbCl_6 powder doped with either 10% Sb^{3+} or 5% Bi^{3+} were studied in wide temperature range. The results showed that the peaks produced with an excitation of 370 nm for Fig.1 a), respectively 355 nm for Fig.1 b) shifts to towards shorter wavelength by about 20 nm for the material doped with Sb^{3+} and about 25 nm for the material doped with Bi^{3+}, respectively, between 4.2 K and 300 K. An interesting phenomenon for both of them is the achievement of the maximum intensity around 20-40 K range for the Bi^{3+} material, and 40-80 K for the Sb^{3+}. A similar effect however is happening with the PLE spectra for the sample doped with Sb^{3+}, showing a shift to longer wavelengths with increase in temperature, from a peak of 355 nm to 365 nm with a stronger effect of quenching after 80 K. The origin of this effect will be discussed.

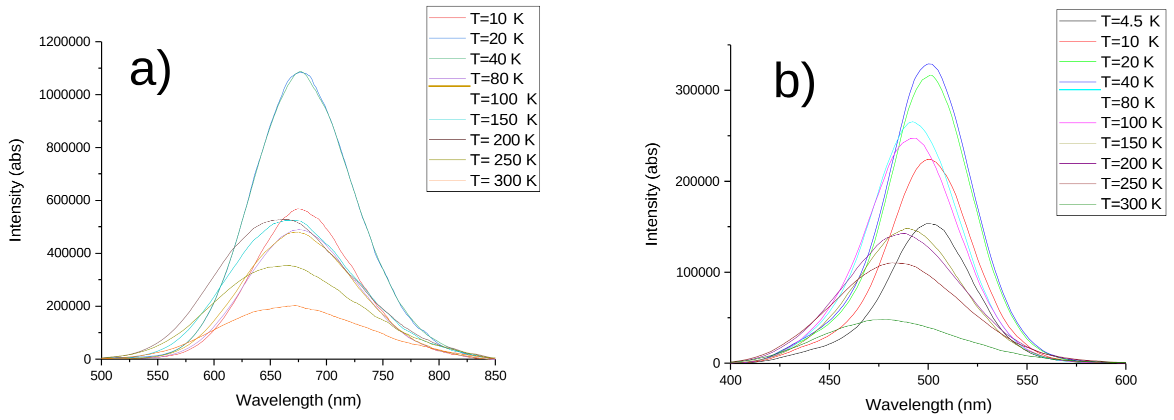

Figure 1. PL spectra under different temperature for Cs_2SbCl_6 doped with Sb^{3+}a) and Bi^{3+}b)

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O-74

Near-infrared photo- and radioluminescence of rare-earth-doped glass-ceramics based on Zn_2SiO_4

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Rare-earth (RE) ions such as Yb^{3+}, Er^{3+} or Ho^{3+}, exhibit well-known emission in the near-infrared (NIR) range, specifically around 1.0, 1.5 and 2.0 μm, resp. Silicate-based materials are frequently used as a host matrix for RE ions in laser, amplifier, or scintillator devices thanks to excellent material properties, such as thermal, mechanical or chemical stability. However, pure silica represents a rather poor environment for RE ions due to high phonon energy and low solubility of RE ions, which leads to non-radiative decay via multiphonon relaxation or concentration quenching. The preparation of glass-ceramics, with low-phonon energy nanocrystals embedded in amorphous silicate matrix, is a perspective way to enhance the luminescence of RE ions [1].

The zinc-silicate glass-ceramics based on ZnO or Zn_2SiO_4 nanocrystals receive growing attention thanks to their low phonon energy, which enables enhanced luminescence [2, 3]. In the past, ZnO especially received considerable attention thanks to the possibility of energy transfer of UV-VIS radiation to RE ions. However, Zn_2SiO_4 (willemite) nanocrystals are also interesting owing to strong radioluminescence properties, where high-energy radiation, such as X-rays, excite emission in UV-VIS region. The co-doping of RE ions into Zn_2SiO_4 based material therefore opens the way towards NIR emission pumping by high-energy radiation, potentially perspective in various applications, such as fiber-optic dosimetry sensors [4].

In this contribution, we prepared a set of zinc-silicate glass-ceramics co-doped with RE ions. The glass precursors were prepared by melt-quenching and the crystallization was induced by heat treatment. The influence of composition and RE content on the crystallization was observed, and the willingness of RE ions to incorporate in zinc-based phases, such as ZnO or Zn_2SiO_4 was evaluated. The luminescence properties of the materials were evaluated, both the photoluminescence of RE ions, and the radioluminescence related to Zn_2SiO_4. The possibility of radioluminescence in NIR region, facilitated by energy transfer from Zn_2SiO_4 to RE ions, was analyzed and discussed.

Acknowledgment:
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First-principles calculation of electronic structure of Li+ co-doped Eu3+-doped ZnO for photodynamic therapy (PDT) application

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Photodynamic therapy or PDT is one promising modality for deep cancer therapy. In fact, the excited adequate scintillator by X-ray radiation can itself excite a photosensitizer to generate reactive oxygen species (ROS), most importantly singlet oxygen (1O2), to damage tumour cells. It has well established that this application cert some properties of scintillators are required such as non-toxicity, high yield of scintillation, nanosized scale and spherical shape. Among ZnO semiconductor scintillator is a promising optical material which is attracting growing interest for PDT application. ZnO non-toxic and stable due to its certain chemical and thermal properties, and specific bandgap energy (3.37 eV), also high binding energy equal to 60 MeV and other advantages [1]. For this purpose, ZnO was activated by some rare earth ion such as Eu3+ and co-doped by Li+ ion to increase its luminescence properties. Using the pseudo-potential plane-wave based on the density functional theory (DFT), the electronic structures and optical properties of ZnO, and co-doped ZnO Li+ and Eu3+ were studied. This work aims to understand the Li+ ion role in luminescence of ZnO: Eu3+ by Using VASP code (Vienna Ab-initio Simulation Packages) [2-4]. Based on the experimental results obtained PL spectra (emission and excitation) at room temperature of the samples: pure ZnO and ZnO–co-doped (Eu3+, Li+) nanoparticles for various Li concentrations, we calculated the band gap and band structure proprieties. New function was used to be in good agreement with our experimental results such as HSE to properly describe the Bandgap, as well as GGA+U to locate strongly correlated energy levels [5]. In this work we discussed the results obtained by the simulation, thus compared them with our experimental data.

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O-76

FROM FUNDAMENTAL INSIGHT TO PROPERTY CONTROL IN $Tb_2Y_xAl_5O_{12}$:Ce (x= 1 AND 0.1) GARNETS VIA NONSTOICHIOMETRIC ENGINEERING: IMPACTS ON STRUCTURE, DEFECTS, , PHOTOCONVERSION, LUMINESCENCE AND SCINTILLATION PROPERTIES

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This study comprehensively investigated the impact of nonstoichiometry on the microstructure, defect density, luminescence, and scintillation characteristics of Ce^{3+}-doped $Tb_2Y_xAl_5O_{12}$ crystals (x = 0.1 and 1.0). Nonstoichiometric $Tb_2Y_{0.1}Al_5O_{12}$ and stoichiometric $Tb_2Y_1Al_5O_{12}$ crystals were grown via the micro-pulling down method. The non-equiatomic concentration of Tb atoms in the nonstoichiometric composition led to the formation of perovskite inclusions within the dominant garnet phase, forming a sub-eutectic composite structure [1]. Raman spectroscopy confirmed the garnet phase dominance and identified spatially heterogeneous domains and Al_2O_3-like clusters in the stoichiometric samples. Furthermore, it suggested the emergence of a perovskite phase in nonstoichiometric samples, indicating complex composite structures. Photoluminescence studies showed that nonstoichiometry disrupted the crystal lattice, enhancing the thermal stability of Ce^{3+} emissions up to 415 K in the nonstoichiometric sample, compared to 375 K in the stoichiometric sample. The nonstoichiometric crystal exhibited up to 15% higher luminous efficiency and a 34% greater scintillation light yield than its stoichiometric counterpart. The nonstoichiometric crystal exhibited a higher concentration of shallow trapping centers and a lower concentration of deep defect states, while the opposite trend was observed in the stoichiometric crystal [1]. Electron paramagnetic resonance (EPR) data revealed significant exchange ion interactions within the garnet lattice, highlighting efficient $Ce^{3+} \leftrightarrow Tb^{3+}$ energy transfer processes [2].

Acknowledgment:

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O-77

CR^{3+}-DOPED NEAR-INFRARED EMITTING PHOSPHORS FOR PLANT-FACTORY LIGHTING APPLICATIONS

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Broadband near-infrared (NIR) emitting phosphors have attracted considerable attention in food, bioimaging, night vision, and plant lighting. However, NIR phosphors targeting the absorption of far-red/phytochrome (P_{FR}) have rarely been reported. We note that gallium garnets are more suitable for satisfying the photomorphogenesis needs of plants. Accordingly, we have designed a Cr^{3+}-doped $Gd_{2.4}Lu_{0.6}Ga_4AlO_{12}$ NIR phosphor from original $Gd_3Ga_5O_{12}$:Cr^{3+} by substituting the large Gd^{3+} and Ga^{3+} ions with small Lu^{3+} and Al^{3+} ions to regulate relative energies and sequence of the two lowest excited states ^2E_g and $^4T_{2g}$. The optimal $Gd_{2.4}Lu_{0.6}Ga_{3.87}AlO_{12}$:0.13Cr^{3+} sample exhibits greater spectral overlap with the absorption of P_{FR}, originated from the raised peak emissions and the blue-shift of emission band. Meanwhile, the luminescence is greatly enhanced by 2 times when the flux of H_3BO_3 was added during the synthesis. Thanks to the excellent EQE and low thermal quenching behavior, a NIR pc-LED was fabricated by integrating the $Gd_{2.4}Lu_{0.6}Ga_{3.87}AlO_{12}$:0.13Cr^{3+},3 wt%$H_3BO_3$ on a blue chip-on-board chip, which has a high output power of 505.99 mW and photoelectric efficiency of 11.24% at 300 mA. To further evaluate the potential of this device for plant growth, pea seedlings (*Pisum sativum* L.) as the model was investigated. The difference is achieved the 79.84% and 67.72% in dry and fresh weight under different treatments. This study provides a reference to regulate the spectral profile of Cr^{3+}-doped NIR phosphors and sheds light on the practical application of Cr^{3+}-doped NIR phosphors in the field of plant lighting.

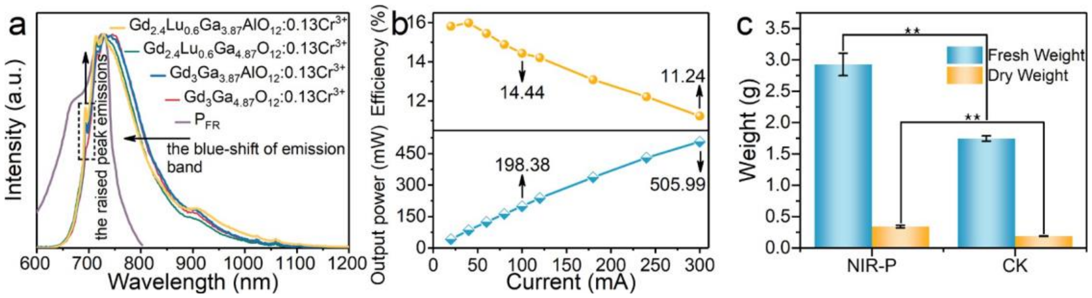

Figure 1. (a) The normalized PL spectra of different samples and the absorption spectrum of P_{FR}. (b) NIR output power and photoelectric conversion efficiency under different driving currents. (c) Fresh and dry weight in two treatments; N = 6. Average ± standard error (SE). Asterisks indicate significant differences at $p < 0.05$ (*), $p < 0.01$ (**), $p < 0.001$ (***).

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O-78

OPTICAL PROPERTIES OF HYBRID "POLIMER - OXIDE - CARBON NANOTUBES" COMPOSITES

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Polymers are widely used in industry and technology due to their easy production, light weight, and ductile nature as well. Polymer micro/nanocomposites (PNC) are of wide applications also due to their specific characteristics if compared to metal and ceramic composites. However, they possess some disadvantages such as low modulus and strength compared to metals and ceramics. That is why, the fillers (fibres, whiskers, particles) adding into polymer matrix open a way to enchance properties of polymers. A number of the PNC filled with inorganic nanoparticles (NPs) had already been developed for various, particularly optical applications.

Brief summary on morphology, structure and optical properties of the PNC which contain inorganic luminescent oxides NPs making the composites attractive for modern optical devices is provided in the work.

The features of the optical (luminescent) characteristics of the filled with oxide phosphors of various spectral compositions and decays PNCs have been also studied by us. $K_2Eu(PO_4)(WO_4)$ (orange-red emission, fast decay), $K_3Tb(PO_4)$ (green-yellow emission, slow decay), and $SrAl_2O_4$:Eu,Dy (green emission, long-lasting decay) NPs have been used as fillers. Their characteristics were compared with the ones for the specified phosphors in their "free" powder state.

Carbon nanotubes (CNT) were taken as the second filler of the composites under study. The CNT modify morphology, structure, mechanical, and electrical characteristics of composites, thus providing them with new properties.

Correlations of the optical properties with morphology, spatial, electronic and vibrational structure of composites were identified and analyzed. The interactions between matrix and filler and their ability to determine the difference between optical properties of the noted hybrid composites and optical properties of separed matrix and fillers have been analyzed.

The ways of possible application of the noted composites are discussed.

P-1

BSA BIOSENSING PLATFORM WITH LIQUID CRYSTALS ANCHORED ON PHYSICALLY MODIFIED PVA SUBSTRATE

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Polyvinyl alcohol (PVA) is a biocompatible polymer having many biomedical applications including as liquid crystal (LC)-based biosensors. A LC biosensing platform consists of LCs, alignment layers (ALs), and receptors. The working principle is that the interaction between receptors and target biomolecules disrupt the orderly alignment of LC molecules leading to a transition in the LCs optical appearance, easily observed under a polarized optical microscope (POM). The homogenous arrangement of LC molecules follows the alignment imposed by the surface pattern of AL consequently it plays an important role in the performance of a biosensors.

In this paper we report a simple approach for the detection of bovine serum albumin (BSA) using a LC biosensing platform. The LCs are supported on the surface of a modified substrate obtained from PVA irradiated solution and mechanically modified allowing the LCs to be homogenously aligned. Our previous studies reveal that the largest optical anisotropy andimproved adhesion and alignment of LCs was observed for films obtained from UV (for 10 and15 minutes) and MW (for 60 and 90 seconds) irradiated PVA aqueous solution which were subjected to rubbing, stretching, and scratching processes.

The proposed BSA biosensing platform consists in an optical cell obtained by assembling two identical PVA substrates, at a certain distance from each other (5-6μm). The inside of the cell was filled with heated LCs ($V = 5\ \mu L$) and was cooled down to room temperature. The target molecules were immobilized on the physical modified PVA substrate by depositing 4 drops ($V \approx 5\ \mu L$) of BSA solution, in the form of a 2X2 matrix. The films wereincubated at $T = 35$ ℃ and the surface was analyzed by AFM, ATR-FTIR, and contact angle measurements to confirm the presence of the biomolecules. After that optical cells were assembled with BSA immobilized and an etalon cell without BSA. Two nematic LCs, E7 and 5CB, were used to detect BSA as a model protein.

The performance of BSA biosensing platform was tested, for different BSA concentrations and incubation time, observing and recording the images obtained with Polarized Optical Microscope (POM). The disruption of homogenous alignment of LCs in the presence of BSA resulted in a dark-to-bright transition observed under POM. The obtained results were analyzed quantitatively through image analysis using the ImageJ software. The limit of detection (LOD) for the proposed biosensing platform was estimated and correlated with the techniques used to modify the PVA substrates.

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LIQUID CRYSTALS ALIGNMENT ON MECHANICALLY MODIFIEDSUBSTRATE OBTAINED FROM IRRADIATED PVA SOLUTIONS.

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New approach, based on physical methods, to modify the PVA thin films to control the Liquid Crystals (LCs) orientation is proposed. The concept is that using UV and microwave (MW) irradiation of PVA solutions followed by mechanically modification of the obtained film surface the adhesion, anisotropy, and alignment of LCs will be enhanced. Our previous studies reveal that PVA thin foils with improved anisotropy, without deteriorated physical and chemical properties are obtained when the PVA aqueous solutions were MW [1] or UV irradiated. Fine or deeper grooves/striations appeared along the stretching direction [2], the films become unidirectionally anisotropic [3] and the adhesion and alignment of LCs are improved. For this study, the films obtained from UV (for 60 and 90 seconds) and MW (for 10 and 15 minutes) irradiated PVA solutions were modified by different new strategies including: rubbing, stretching, and scratching with sandpaper. The mechanical modification of PVA films was realized through 3 different approaches: 1. Rubbing followed by stretching; 2. Rubbing followed by stretching and then parallel scratching of surface with sandpaper; 3. Rubbing followed by parallel scratching of surface and stretching. The rubbing was performed prior fully drying of samples in one single direction and one single turn with a rigid tooth network like a hair comb [3]. The surface of the polymer films was scratched with low roughness sandpaper. A single turn scratching was performed with a speed of 3 mm/s , keeping a constant contact with the surface of polymer. The rubbing and scratching procedures were done at room temperature and the stretching process was made at a 42-45 ^{0}C. The stretching degree was expressed as the ratio of the semi axes of an ellipse in which a circle drawn on the polymer foil degenerates. This new rubbing method, combined with scratching with sandpaper and stretching of PVA films, constitutes a novel and original preparation procedure of alignment layers (Als) for LCs.

The results were evidenced by using ATR-FTIR spectra analysis, contact angle measurements, optical microscopy images, and induced optical birefringence measurements using polarization ellipse method [4]. The adhesion and cohesion interactions between the modified surface of PVA and LCs was evaluated using contact angle technique. Polarized optical microscopy was used to evidence the orientation of LC at the surface of modified PVA films. Parameters as exposure time, stretching degree and roughness of the sandpaper were discussed regarding the used approach to achieve optimal orientation of nematic molecules at the surface of PVA for LC biosensor applications.

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P-3

INDUCED BIREFRINGENCE OF THIN FOILS OBTAINED FROM UV IRRADIATED POLY (VINYL ALCOHOL) SOLUTIONS

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In this paper, poly (vinyl alcohol) (PVA) (hydrolysed 99%, with average Mw = 22,000) foils, with comparable thickness (0.15-0.20 mm), were obtained by using 10 wt. % PVA aqueous solutions exposed to UV radiations for 10, 15, 20 and 30 minutes by means of a UV lamp ML-888 type with 4 pieces of 9W UV bulbs, with λ=365nm, at 7 cm, in the presence of air, at room temperature.

The main goal of this research is to evidence the effects on the induced optical birefringence of PVA foils obtained from irradiated PVA solutions, since it is known that the changes in chemical and physical properties of polymers induced by radiations can influence the asymmetry of their molecular structures in which the birefringence of polymers derives from [1]. The effects of ultraviolet (UV) irradiation were evidenced by using ATR-FTIR spectra analysis, contact angle measurements, scanning electron microscopy (SEM) images, and induced optical birefringence using polarization ellipse method [2]. It was found that the wavenumber of the absorption band of OH stretching shifts when the PVA solutions were exposed to radiations. According to Nagura et. al. this phenomenon may possibly arise due to structural changes occurring in the crystalline region of the PVA foils [3].

Supplementary tests were performed to induce molecular ordering in foils obtained from UV irradiated PVA solutions. The samples were cut in the form of standard tensile test specimen to generate a uniform stress–strain relationship in the sample [4] and were modified by new mixed approaches: stretching, rubbing before drying, rubbing before drying followed by parallel stretching [5]. The level of chain alignment in the samples was quantified by birefringence measurements. The produced anisotropy was correlated with the sample morphology examined via optical microscopy under crossed polarizers. It was found that the generated birefringence was larger for the mechanically deformed polyvinyl alcohol foils obtained from 10 and 15 minutes UV irradiated PVA solution.

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P-4

OPTICAL PROPERTIES AND CHEMICAL COMPOSITION OF HEMPOIL

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The hemp plant (*Cannabis sativa)* is cultivated and used to make cold-pressed oil from its seeds. Because of its rich chemical composition (minerals, vitamins, amino acids, fatty acids, phytosterols, and other bioactive components), hemp oil suits treating skin infections and inflammatory conditions and stimulates early healing and tissue regeneration.

The present work aims to investigate the fatty acid composition and optical properties of hemp oil used as a base oil for pharmaceutical applications. Gas-chromatographic methods, fluorescence spectroscopy, spectroscopy in the visible range, and calorimetry were applied to realize the set goals.

Unsaturated fatty acids predominate in the sample, while the saturated ones are only 9.67%. Of the unsaturated fatty acids, oleic acid predominates at 24.02%. Of the polyunsaturated fatty acids, linolenic acid predominates at 53.25%. Sterols and vitamin E are 1.75% and 0.5%, respectively.

In the excitation-emission matrix, there are 2 regions of maximum fluorescence signal. In the interval 350 nm - 450 nm, an emission maximum of around 680 nm is observed, related to the chlorophyll content. The second interval is near 480-550 nm, and the maximum radiation is around 700 nm, associated with other chlorophyll pigments.

The colorimetric characteristics were determined in the C colorimetric system. According to the adsorption spectrum, it was found that the dominant wavelength is 580 nm.

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P-5

SPECTRAL STUDIES OF B_2O_3 - ZnO – SrO – CaO GLASSES DOPED WITH Dy^{3+} IONS FOR WHITE LIGHT EMISSION APPLICATIONS

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Borate glasses are recognized for their distinctive properties, such as thermal stability, ease of obtaining at low temperatures, high transparency within the visible spectrum, and strong chemical durability. These attributes make them highly suitable for a variety of optical applications. When doped with rare earth ions like dysprosium (Dy^{3+}), borate glasses reveal remarkable optical and luminescent characteristics [1,2]. Dysprosium ions emit light over a wide visible spectrum, from blue to yellow, making glasses doped with these ions valuable in displays and lighting systems like lasers and LEDs. This research seeks to deepen understanding of how Dy^{3+}-doped borate glasses can be used in optoelectronic systems.

In this study, zinc-borate glasses doped with Dy^{3+} ions were synthesized using the melt-quenching method to investigate how the concentration of these ions affects the optical absorption, photoluminescence excitation, and emission spectra. Moreover, the dielectric properties of Dy^{3+} doped glasses, such as dielectric constant, dielectric loss, and conductivity, were studied at different frequencies.

Absorption analysis identified typical absorption transitions characteristic of Dy^{3+} ions in the prepared glass samples. The excitation spectra were obtained by monitoring emissions at 486 and 580 nm within the 270–440 nm range. Most intense peaks corresponding to $^6H_{15/2} \rightarrow {}^6P_{3/2}$, $^6P_{7/2}$, $^4P_{5/2}$, $^4I_{13/2}$, and $^4G_{11/2}$ transitions in Dy^{3+} ions were observed at wavelengths of 324 nm, 350 nm, 364 nm, 386 nm, and 426 nm respectively. The borate glass samples showed optimal luminescence when excited at 350 nm, particularly for glasses doped with 1.0 mol% Dy_2O_3.

The concentration of Dy^{3+} ions plays a significant role in the optical properties of borate glass. Modifying the concentration of these ions and the composition of glass, it becomes possible to manipulate the ratio of yellow to blue emissions, allowing for fine control over the emitted light spectrum, including the production of white light. The sensitivity of yellow radiation to changes in the surrounding environment of Dy^{3+} ions additionally provides an avenue for tailoring luminescent properties. The CIE coordinates demonstrate that the emission of all investigated glasses is in the white light region.

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P-6

Spectra control of europium-doped calcium silicate through topochemical reduction strategy for white LED application

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In this work, europium-doped calcium silicate (abbreviated as C_2S:Eu) was prepared by a topochemical reduction strategy with aluminum as a solid-state reducing agent at the calcination temperature from 300 °C to 1000 °C. The emission intensity ratio of Eu^{2+}/Eu^{3+} started to increase at 400 °C, indicating the occurrence of the reduction of Eu^{3+}. Such prepared samples showed stronger emission intensity from Eu^{2+} centers than the ones prepared by traditional CO reduction. Especially, the Al-reduced $C_2S:Eu^{2+}$ calcinated at 1000 °C exhibited PL intensity as 300% high as the CO-reduced $C_2S:Eu^{2+}$ prepared at the same temperature. This phenomenon is further explained from the standpoint of the different reduction reaction kinetics of solid state Al and vapor phase CO at the same temperature. This result suggested that this strategy can be used as an effective tool for the spectra control of the rare earth doped luminescent systems, thus opening up new avenues to develop novel optical materials for the white light emitting diodes applications.

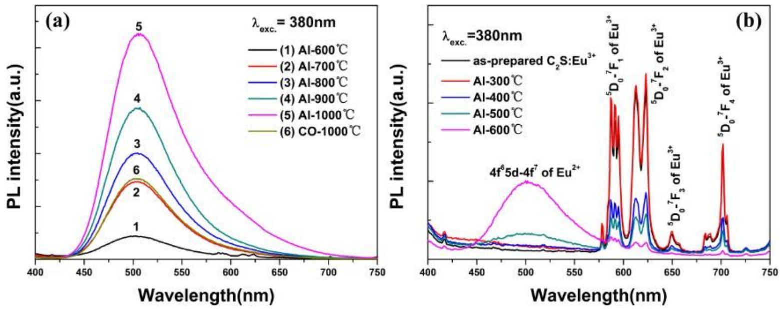

Figure 1: PL spectra of Al-reduced $Ca_2SiO_4:Eu^{2+/3+}$ with various calcination temperatures and the PL spectra of CO-reduced $C_2S:Eu^{2+}$ calcined at 1000 °C: (a) 600-1000 °C. (b) 300-600 °C

P-7

AN APPROACH TO THE DETERMINATION OF THE NUMBER OF EXPONENTIAL DECAYS PRESENT IN A DECAY CURVE

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The Emerging Measurements Company (EMCO) *LabKit* was developed to measure the time- and temperature-dependent emissions of phosphors. Collected data is displayed on an attached oscilloscope and can be saved for future analysis using a standard computer. It is unique in the field as being the only turn-key method currently available that can measure the prompt fluorescent decay and rise times over a temperature range of -10 to 80 °C. It allows researchers to quickly determine the fluorescent decay and rise times for most phosphors, improving the ability to analyze materials.

The *LabKit* allows users to vary several settings including LED Pulse Width, Pulse Repetition Rate, Peltier Cooler Current, and Photomultiplier Tube (PMT) Gain. A Peltier cooler in the *LabKit* can be used to control sample temperature. The sample holder doubles as a heat sink lending stability to the desired temperature setting. The EMCO *LabKit* uses a 373 nm light source diode from AMS OSRAM, which has a FWHM of 10 nm. A sample holder with accompanying Peltier cooler was positioned at 45° with respect to both the LED and filter chamber. A Hamamatsu H10721-110 PMT was used to detect emitted light from the sample. A Tektronix MDO3024 Oscilloscope was used to record the data. A custom MATLAB® code was used to fit the data.

At the second ICPT the authors presented work demonstrating that a double exponential decay emission had been properly fitted. This was done using the phosphors EuD_4TEA (which exhibited a double exponential decay) and EuD_3NO_3TEA (which exhibited a single exponential decay). For a long time, researchers have attempted to simplify the work of analyzing multi- exponential decays by treating them as single decays. This was because the non-linearity of the multi-exponential fitting equation made it possible to obtain different results for the same data. Now that an approach has been discovered that can properly resolve multiple decays, a new question is raised: how many exponential terms are present in a given curve?

A qualitative approach has been developed to discriminate against bad fits; that is, it rules out bad fits rather than ruling in good fits. A variety of plots have been made for the fitted results of the La_2O_2S:Eu emission as a function of temperature. This was done for single, double, triple, and quadruple exponential decays. Each plot is evaluated independently. If it is clearly evident that a plot is indicative of a bad fit, then that fit receives a demerit. On the other hand, if the plot appears to be representative of a good fit, or even if the plot is representative of a questionably good fit, it does not receive a demerit. The fit with the least number of demerits is accepted as the best fit for the data.

A small quantity of the phosphor from Phosphor Technology, Limited was used for this research. A 400 nm cut-on filter was used in conjunction with a bandpass filter centered at 514.5 nm with a 10 nm FWHM to observe the 514 nm emission. Application of the discrimination approach leads to the conclusion that over the temperature range of 10 - 55 °C the 514 nm emission of La_2O_2S:Eu is best fit by a double exponential decay.

P-8

Strontium Aluminate and Garnets Persistent Luminescent Single Crystals

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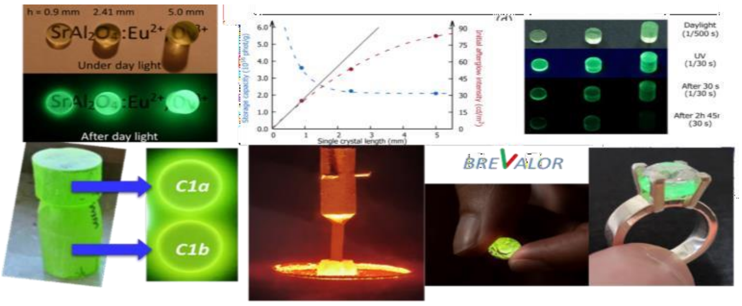
In persistent luminescent materials, energy can be stored under irradiation by controlled traps/defects[1,2]. This energy is released at ambient temperature for several hours by light emission once the excitation has been stopped. The work is focused on the following points: Development of persistent transparent single crystals in the family of strontium aluminates and garnets. Investigation of their optical features and comprehensive investigation of their persistentluminescence properties. All materials have been elaborated as single crystals by the Czochralskiprocess. Our objective is at first, to shed light onto the mechanism of the afterglow taking advantage of the lack of surface defects in comparison with powder samples. Minimally scattering $SrAl_2O_4$:Eu,Dy single crystals (as opposed to powder phosphors), allow to profit from a so-called volume effect[3,4], resulting in significantly increased emission intensity. Additionally,they allow to identify the reabsorption of the afterglow emission by trapped charges as an important loss mechanism, leading to a non-linear scaling of the emission intensity with the crystal size[5]. The results on the SAO:Eu,Dy are presented on the above part of the figure.

Ce^{3+} and Cr^{3+} doped garnets of general formula $Y_{3-x}Gd_xAl_2Ga_3O_{12}$ (YAGG:Ce,Cr) are defined as afterglow materials where the Ce^{3+} acts as emitting centers and the Cr^{3+} as an electron trap. The study of single crystals reveals that the balance between Al/Ga is difficult to control makingsometime a storage phosphors and materials with shallow traps. A precise control and study of the composition, including defects modeling, is reported[7]. In Figure (lower part, left), we can observe few samples of the YAGG:Ce,Cr characterized within this work.
Exploiting the volume effect in transparent or semi-transparent samples or surface structured materials will provide a promising avenue to enhance the overall emission intensity of afterglow/persistent luminescence materials. BREVALOR Sarl. is proposing new applications.



Crystals of SAO:Dy,Eu and YAGG:Ce,Cr and recent features [5,6]

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P-9

Tm:CALGO : Spectroscopy and laser results at 2.3 µm

ICOM 2024

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Mid-infrared lasers emitting around 2.3 µm are important for various applications such as detecting gases and pollutants in the atmosphere, studying combustion, and non-invasive glucose measurements. One way to produce such emission is through the use of thulium ions in the $^3H_4 \rightarrow {}^3H_5$ electronic transition. These ions can be efficiently pumped using commercial AlGaAs diode lasers emitting at ~0.8 µm. Additionally, an upconversion pumping scheme at ~1 µm has been demonstrated, which utilizes a non-resonant ground-state absorption and a resonant excited-state absorption to enhance efficiency through a photon avalanche effect [1]. We have successfully demonstrated the operation of a laser utilizing a disordered Tm:CaGdAlO$_4$ crystal on the $^3H_4 \rightarrow {}^3H_5$ transition at 2.3 µm. Using direct pumping at 0.79 µm, we were able to generate 264 mW of output in the range of 2301-2325 nm with a slope efficiency of 16.2% and 31.3% when compared to the incident and absorbed pump power respectively, and it had a linear polarization (σ).

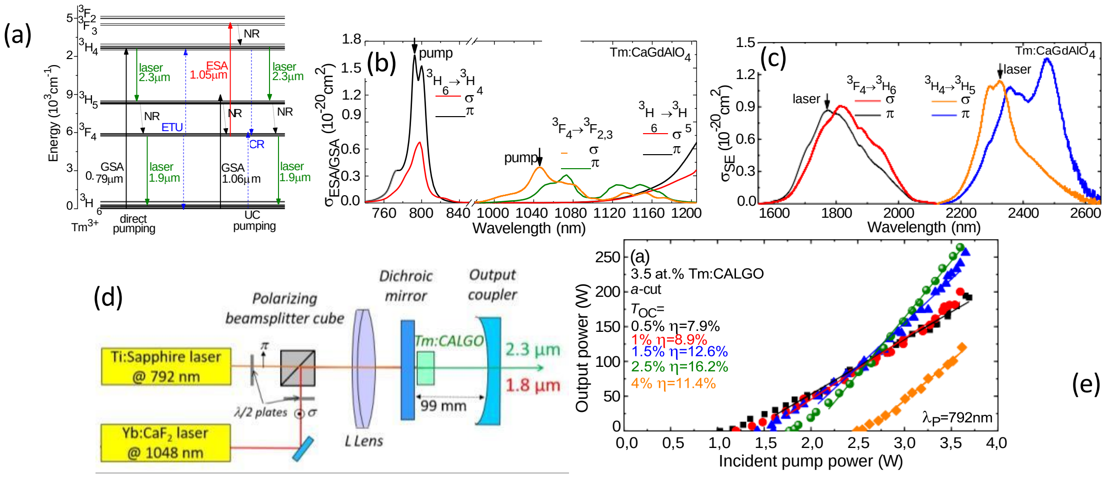

Fig. (a) Thulium level (b) Some GSA and ESA cross section (c) Cross section for laser emission (d) Experimental setup (e) Output power at 2.3 µm vs. Incident pump power at 0.8 µm

We have experimentally explored two methods to overcome the bottleneck effect of the metastable $^3F_4$ Tm^{3+} state: (i) cascade lasing on the $^3H_4 \rightarrow {}^3H_5$ and $^3F_4 \rightarrow {}^3H_6$ transitions and (ii) dual-wavelength pumping at 0.79 and 1.05 µm, which combines the direct and upconversion pumping schemes [2]. Both approaches have led to an increase in power scaling for the mid-infrared Tm-laser. Tm^{3+} ions in CaGdAlO$_4$ exhibit broad emission around 2.3 µm and 2.5 µm (with bandwidths of 128 nm and 100 nm respectively), making this crystal a promising candidate for *ultrafast pulse generation* and *tunability* in the mid-infrared. These researches are made under the SPLENDID2 ANR Project.

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P-10

LOCALIZED VIBRATIONS IN PHOTOLUMINESCENCE SPECTRA of IRON-DOPED ZNO

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Zinc oxide has been the focus of much research as this compound is used in various fields including optoelectronics due to its unique properties [1]. These properties are known to be sensitive to the presence of structural defects. For example, doping ZnO with transition metal ions typically results in localized vibrations that have been observed in photoluminescence spectra of ZnO:Fe at a temperature T = 4.5 K [2]. The process of defect formation must be taken into account when designing devices. However, the effect 3d transition metals on ZnO properties has not been fully studied.

In present work, we studied the structural and vibrational properties of the wurtzite phase of ZnO with Fe ions in various charged states using density functional theory and potential-based methods [3]. First principles calculations are performed to determine the atomic configurations around the defects, and the results are compared with those obtained using the static lattice method in the shell model. Both calculation approaches give the same character of lattice relaxation around the Fe impurity center, which can occupy cation lattice sites in the isoelectronic charge state Fe^{2+} and the single-positive charge state Fe^{3+}.

Using a recursive method, phonon local symmetrized densities of states projected onto the displacement of the nearest atoms surrounding the defects under study are calculated. The frequencies of localized vibrations of various types of symmetry induced by Fe impurities were also determined. The results of our calculations make it possible to interpret the structure of the phonon side band accompanying the zero-phonon line of the Fe^{3+} intracenter transition and to evaluate the influence of Fe^{3+} ions on the formation of vibrational satellites of the zero-phonon line.

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P-11

LUMINESCENSE OF NANOPARTICLES AND QUANTUM DOTSIN Zn-IMPLANTED SILICA LAYERS

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The ion implantation is an effective way to modify the optical and electronic properties of functional materials for various fields of practical application. Using ion implantation, it is possible to obtain phosphors in the form of solid-state matrices with optically active nanophase inclusions [1]. In this case, the size of nanoparticles, the state of interfaces, the nature of defects and electronic excitations, which ultimately determine the mechanisms and efficiency of photoluminescence (PL), become important. In this work, to study the role of Zn ions in the creation of luminescent centers and nanoparticles in SiO_2, synchrotron radiation was used in a spectral region, covering the fundamental absorption edge of silica up to 11 eV. As a result of ion irradiation of silica glasses and films followed by thermal annealing, optically active Zn_2SiO_4 nanoparticles and Si QDs quantum dots are formed in the surface layers of silica. The combination of spectroscopic methods made it possible to reliably establish the patterns of formation of excited states and radiative relaxation of nanoparticles and quantum dots.

Optical and X-ray photoelectron spectroscopy in combination with diffraction analysis indicate the presence of modifications of α- and β-willemite nanoparticles in silica matrices [2]. Glow associated with point defects in α- Zn_2SiO_4 and β-Zn_2SiO_4 nanoparticles is also observed. The electronic states of point defects are localized in sizes significantly smaller than the size of Zn_2SiO_4 nanocrystals, and the position of the PL bands is similar to the position of the bulk material. Temperature quenching of PL (different laws for the α-phase and β-phase) and broadening of emission lines are sensitive to the PL mechanism and reflect the influence of the amorphous silica matrix. Various mechanisms for excitation of luminescence of silicon quantum dots Si QDs formed in Zn-implanted silica have been identified. A distinctive featureof the emission of silicon nanodots is the manifestation of the quantum confinement effect.

Based on optical absorption and photoluminescence data, the ion-induced evolution of the defect structure of glasses and films was traced. According to experimental and calculated data,the staged interaction of primary oxygen-deficient defects leads to the formation of stable Si QDs with sizes of 1.5-3.5 nm and emission at 1.6-1.8 eV, excited by incoherent light. Based on spectroscopic and *ab initio* calculations, schemes of defect and excitonic PL mechanisms for nanoparticles/quantum dots and local centers in silica glasses and films are proposed. A significant influence of the structural disorder of the SiO_2 matrix is observed during the implementation of the excitonic mechanism for luminescence of the Si QDs [3]. It has been shown that by changing the mode of ion-beam exposure, it is possible to specifically control the optical properties and modify the type of active centers and nanophase inclusions in a wide-gap dielectric matrix.

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P-12

THE ROLE OF THE LIGHT LITHIUM ION IN THE FORMATION OF HIGH-TEMPERATURE PEAKS OF THERMALLY STIMULATED LUMINESCENCE IN NaCl CRYSTALS

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In ionic crystals (IC), low-temperature (4.2K→300K) peaks of thermally stimulated luminescence (TSL) have traditionally been investigated to interpret the recombination luminescence of radiation-induced defects, which occur during the delocalization process with an increase in sample temperature. Meanwhile, high-temperature (300K→800K) TSL peaks in IC have garnered scant attention, leaving a gap in comprehensive understanding regarding their nature and formation mechanisms in IC.

The widespread application of ionic crystals (IC) in dosimetric spectroscopy has brought to the forefront research into the nature and mechanisms of high-temperature (300K→800K) TSL peaks, which serve as indicators for detecting ionizing radiations using dosimetric thermoluminescent detectors.

In this context, the nature of high-temperature TSL peaks in X-irradiated NaCl single crystals was investigated over a broad temperature range of 300-800K (until the crystals were completely bleached of radiation defects) using the Harshaw 3500 thermoluminescent dosimetric system (Thermo Fisher Scientific, USA). The investigation covered both zone- refined crystals and those doped with lithium ions at concentrations ranging up to 400 ppm.

High-temperature TSL peaks were registered in two temperature ranges: at 360÷400K and 495÷620 K, conventionally designated as Type I and Type II TSL peaks, respectively. In NaCl-Li crystals, there is a light output increase of Type II TSL peaks (535÷570K), correlating positively with increasing lithium concentration. At concentrations of 400 ppm, the intensity growth reaches three orders of magnitude higher ($10^5 \rightarrow 10^8$) than in pure NaCl crystals and an order of magnitude higher than in TLD-100 thermoluminescent dosimeters.

A specialized heating device was developed with parameters similar to Harshaw model 3500. Incorporated into the measurement path of a luminescence setup, it facilitates scanning of spectra in the TSL peaks of crystals within the temperature range of 300K→800K for the first time. Experiments established that the spectra of high-temperature TSL peaks in NaCl-Li crystals exhibit maxima at 3.48 eV, coinciding with the spectra of X-ray luminescence (XL) and tunneling luminescence (TL).

On this premise, it is hypothesized that the dissociation of complex halogen formations at high temperatures (300-800K) produces a stream of unrelaxed holes and electrons (analogous to X-ray excitation). These particles subsequently recombine in the field of the light lithium ion, creating a potential well for their assembly with maximum luminescence output [1, 2].

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Up-Conversion Luminescence from Ca_2SnO_4:Er

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Up-conversion (UC) luminescence is a phenomenon that lower energy photons are converted to higher energy ones. Owing to the wide applications, especially for the combined use with solar cells [1], UC phosphors have been actively investigated. However, the current UC phosphors have not enough luminescence intensity for the device applications. In addition, durability for the long-term use is also a big issue to apply UC phosphors in the devices. Most of the efficient UC phosphors with high durability have been realized using oxide matrices doped with rare-earth ions, such as Y_2O_3:Er,Yb [2] and $CaWO_4$:Er [3]. In addition, it was examined co-dopings of additional rare-earth ions and an addition of alkaline metals, e.g., $CaTiO_3$: Er [4], to increase UC luminescence intensity.

In this study, we have investigated up-conversion luminescence behavior of Ca_2SnO_4:Er and the influence of additional dopings of rare-earth and/or alkaline metal ions. All the samples were prepared by a conventional solid state reaction method. The crystal structures and the phase of the fabricated specimens were examined by the powder X-ray diffraction method. The elemental analysis was carried out by X-ray fluorescence, and the energy levels and electronic structure were examined by the diffuse reflectance spectra by using UV-vis spectrometer equipped with integration sphere. UC luminescence measurements were performed at room temperature by 980 nm laser irradiation. In addition to such experimental analysis, the first principles calculations within a density functional theory were also carried out to investigate the local environment of the doped rare-earth ions and their electronic structures.

The UC luminescence spectrum of Ca_2SnO_4:Er is shown in Fig. 1. Change in UC luminescence behavior by additional co-dopings will be discussed on site.

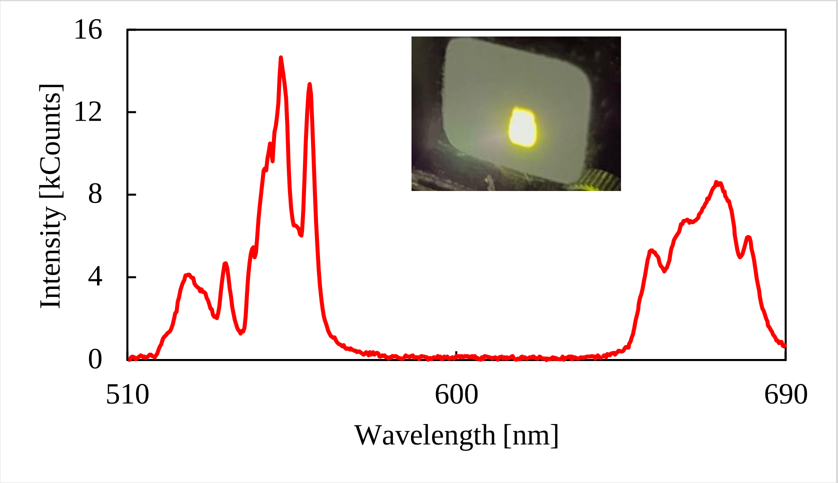

Fig.1 Observed up-conversion luminescence spectrum of Ca_2SnO_4:Er excited by 980 nm.

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Effect of rare earth co-doping on UC luminescence intensity in $CaSnO_3$:Er

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Up-conversion(UC) phosphors, which can convert light with longer wavelength to that with shorter one, have been extensively investigated owing to their potential applications in industrial and medical uses [1]. Although there are wide variety of the UC phosphors, oxide UC materials co-doped with rare earth elements, such as $CaSnO_3$:Er, Yb[2] and $CaMoO_4$:Er, Yb[3], have been studied as efficient UC phosphors with high durability at ambient condition. In order to enhance UC luminescence intensity, it was reported that additional co-doping of rare-earth ions works well. In this study, the effects of additional co-dopings of rare-earth elements, such as Tm, Yb, and Lu, into $CaSnO_3$:Er on the UC luminescence intensity were investigated.

All the samples were prepared using a solid state reaction method. Crystal structure analysis and phase identification were performed using X-ray diffraction measurements, and electronic structures were examined using UV-vis diffuse reflectance spectra. In addition, the valence states and the local environment of the doped rare-earth ions were evaluated using X-ray Absorption Fine Structure (XAFS) measurement. The UC luminescence measurements were carried out by 980 nm laser irradiation at room temperature.

Observed UC luminescence spectra of $CaSnO_3$:Er, $CaSnO_3$:Er,Yb and $CaSnO_3$:Er,Lu are shown in Figure 1, in which significant enhancements by additional co-dopings of Yb and Lucan be seen.

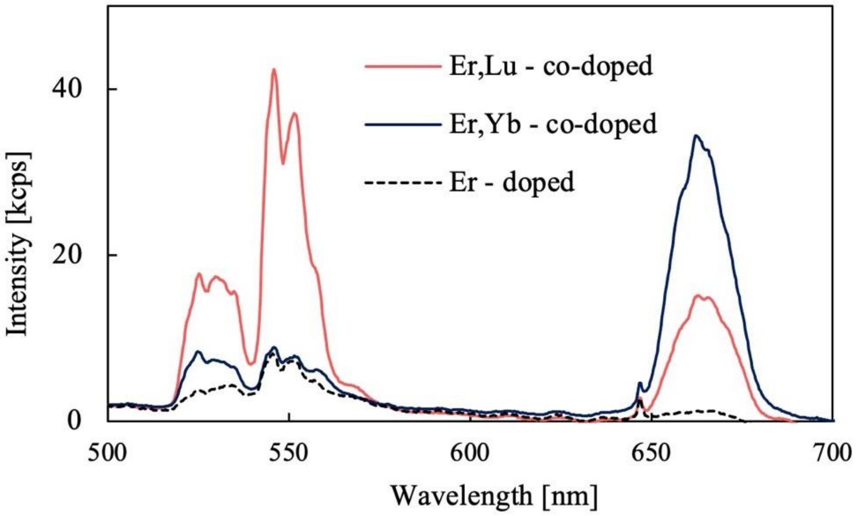

Fig1. Observed up-conversion luminescence spectra of $CaSnO_3$:Er, $CaSnO_3$:Er,Yb and $CaSnO_3$:Er,Lu.

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P-15

KINETIC MODELING OF CHARGE TRANSFER FOLLOWING PHOTONBLEACHING OF IRRADIATED LiF:Mg,Ti

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The normalized thermoluminescence (TL) dose response (f(D) of composite peak 5 in the glow curve LiF:Mg,Ti is linear (f(D) =1) from the lowest doses measurable of a few µGy to 1 Gy but then turns supralinear with f(D) increasing to ~ 2 at a dose of 30 Gy following Co-60 irradiation. The supralinearity is dependent on particle energy with f(D=30 Gy) decreasing to ~ 1.3 following irradiation by 20 kVp X-rays. The supralinearity and especially its dependence on particle energy can introduce significant difficulty in the application of this dosimeter, especially in clinical radiation therapy where an accuracy of 5% (1 SD) is required. Previously we have demonstrated that the linear dose response of composite peak 5 can be extended from 1 Gy to 30 Gy using 3.65 eV photon bleaching post-irradiation. With surface fluence of 1.2 -3.6 10^{18} ph cm^{-2} . No further effect on the dose response was observed at higher photon fluences extending to 1.4 x 10^{19} ph cm^{-2}. The energy of 3.65 eV was chosen so that the photon interaction would occur , as exclusively as possible, with the electrons in the TC associated with the 3.8 eV OA band. The overlap of the LED emission spectrum with the adjacent 4.3 eV OA band is minimal. The 3.8 eV OA band has been associated with the TC/LC configuration which has captured an electron and hole whereas the 4.3 OA band is correlated with the e-only TC/LC. Photon excitation at 3.65 eV liberates the electron from the e-h TC/LC leaving a hole which gives rise to a clearly observable increase in the intensity of glow peak 4. At 10 Gy and 20 Gy a fluence of 10^{18} ph.cm^{-2} reduces f(D) to unity; at 30 Gy, a fluence of 1.2 x 10^{19} ph cm^{-2} is required. There is a rapid decrease in f(D=10 Gy, 20 Gy) up to a fluence of 2 x 10^{18} ph.cm^{-2} which is followed by no further effect as the photon fluence is increased to 1.4 x 10^{19} ph.cm^{-2}. For D =30 Gy, the decrease in f(D) continues to 10^{19} ph.cm^{-2}. Investigation of this behaviour is the subject of this investigation. A kinetic model is described herein in the framework of conduction band/valence band solid state theory incorporating spatially correlated TCs and LCs. The model successfully simulates the bleaching action of the 3.65 eV photons producing the increased range of dose linearity as caused by the depletion of the occupied TCs and to a lesser degree charge transfer via the conduction band between the various configurations of the TC/LC system associated with composite peak 5.

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FINE STRUCTURE OF ABSORPTION AND EXCITATION SPECTRA OF 4f-5d TRANSITIONS IN MeF_2:Ln, Yb^{3+} CRYSTALS (Me = Ca, Sr, Ba; Ln = Dy^{3+}, Er^{3+})

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The absorption (excitation) spectra of 4f-5d interconfigurational transitions of trivalent lanthanide ions at low temperatures have a fine structure, which is more pronounced in low-energy bands. In the vacuum ultraviolet region, the fine structure has not been studied, largely due to the lack of intense excitation channels with high resolution. Only in Yb^{3+} doped CaF_2 the well-resolved lines attributed to 4f-5d transitions were found [1]. Currently, this opportunity has appeared due to the photoluminescence station FINESTLUMI, FinEstBeAMS with an undulator on the 1.5 GeV storage ring of the MAX IV synchrotron (Lund, Sweden) [2].

This paper presents the results of measuring the absorption and excitation spectra of 4f-5d transitions in CaF_2, SrF_2, BaF_2 crystals doped with Yb^{3+} and Dy^{3+} or Er^{3+}. A fine structure was discovered in the absorption and excitation spectra, which corresponds to 4f-5d transitions in the Dy^{3+}, Er^{3+}, Yb^{3+} lanthanide ions. At the same time, no fine structure was observed in crystals activated with Tm^{3+} or Ho^{3+}.

Based on experimental data, the position of the split $4f^{n-1}5d^1$ states of Dy^{3+}, Er^{3+}, and Yb^{3+} in CaF_2, SrF_2, and BaF_2 crystals relative to vacuum is shown.

The reason for the small linewidth in the excitation and absorption spectra of 4f-5d transitions remains unclear, but it is probably associated with the possible strong screening of the 5d states of Dy^{3+}, Er^{3+} and Yb^{3+} [3] by higher-energy filled 5p, 6s levels.

The authors thank Kirill Chernenko for his assistance in conducting the experiments.

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P-17

Growth, scintillation properties, and pulse shape discrimination capability of (Ca, Mg)I_2 scintillator

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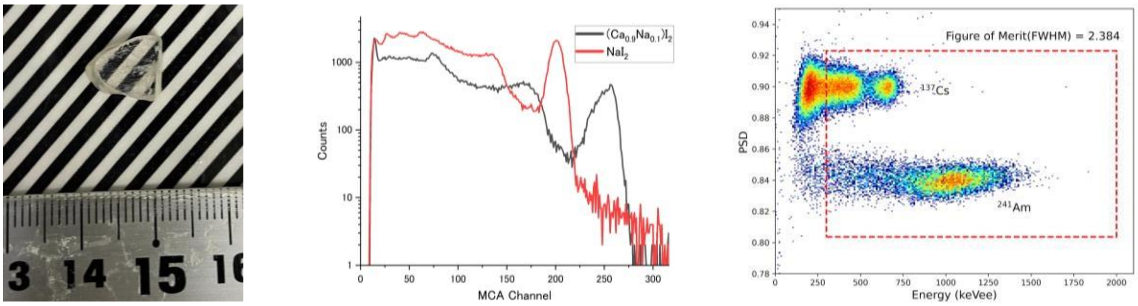
[Introduction] CaI_2 has been developed in recent years for use in the search for the study of neutrinoless double beta decay due to its high light yield of 107000 photons/MeV and good pulse shape discrimination (PSD) for alpha and gamma radiation.[1] However, CaI_2 single crystals have been reported to be difficult to process due to their high hygroscopic and cleavage natures. CaI_2 has a layered structure parallel to the a-b plane and the layers are separated from each other in the c-axis direction.[2] In this study, we aimed to suppress cleavage and optimize both processing and scintillation properties by substituting Ca with Mg, which possesses a smaller ionic radius, and by reducing the layer spacing in CaI_2.

[Materials and Method] 99.995% pure CaI_2, 99.995% pure MgI_2, were conbined in composition ratio of $(Ca_{0.9}Mg_{0.1})I_2$. The crystal growth was conducted by the Vertical-Bridgman method. Scintillation and PSD properties were evaluated.

[Results] Fig. 1(a) presents the as-grown and post-processed images of the $(Ca_{0.9}Mg_{0.1})I_2$ single crystal. The cleavage properties were significantly reduced compared to CaI_2. Fig. 1(b) depicts the energy spectrum of ^{137}Cs γ-ray source, revealing a light yield of 57,000 photons/MeV for $(Ca_{0.9}Mg_{0.1})I_2$ sample. PSD plot for $(Ca_{0.9}Mg_{0.1})I_2$ is illustrated in Fig. 1(c), with the calculated FOM (FWHM) being 2.502 in the energy range of 0.3 - 2.0 MeVee. Detailed results on crystal growth and scintillation properties across different composition ratios will be presented.



(a) (b) (c)

Fig.1 (a) Photographs of Bridgman-grown crystal, (b) Energy spectra of $(Ca_{0.9}Mg_{0.1})I_2$ and NaI_2, (c)PSD plot for $(Ca_{0.9}Mg_{0.1})I_2$ concerning energy variation with ^{137}Cs and ^{241}Am

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P-18

Real-Time Monitoring of CdTe Quantum Dots Growth

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Luminescent materials have been explored across a variety of applications due to their versatility. Quantum Dots (QDs) are a type of luminescent nanomaterial that possesses unique optical characteristics due to the quantum confinement effect. QDs are high-efficiency semiconductors with dimensions ranging from 2 to 10 nm, featuring a high surface-volume ratio and spectral tunability 1,2. The optical properties of QDs are directly correlated with their size, thus real-time monitoring of their growth during synthesis enables the development of QDs with specific size and luminescence characteristics. In this study, a novel approach was employed to monitor the luminescence of CdTe QDs in aqueous solution up to 90 °C, through in situ luminescence analysis 1,3. This technique allowed for a detailed examination of the evolution of light emission from the QDs during their growth (Fig. 1a). In comparison to in situ absorbance analysis, in situ luminescence measurements in reflection geometry are particularly advantageous as they are not affected by the increase in concentration of the colloidal suspension. Three reactions were monitored at temperatures of 70, 80, and 90 °C, resulting in QDs with maximum emission wavelengths centered at 550, 600, and 655 nm, respectively, and average sizes of 2, 3, and 4 nm (Fig. 1b). The reaction time was set at 3 hours, resulting in a total of 90 spectra for each analysis. In situ monitoring proved effective in allowing the adjustment of QDs emission color for desired applications, even for very small differences in particle size.

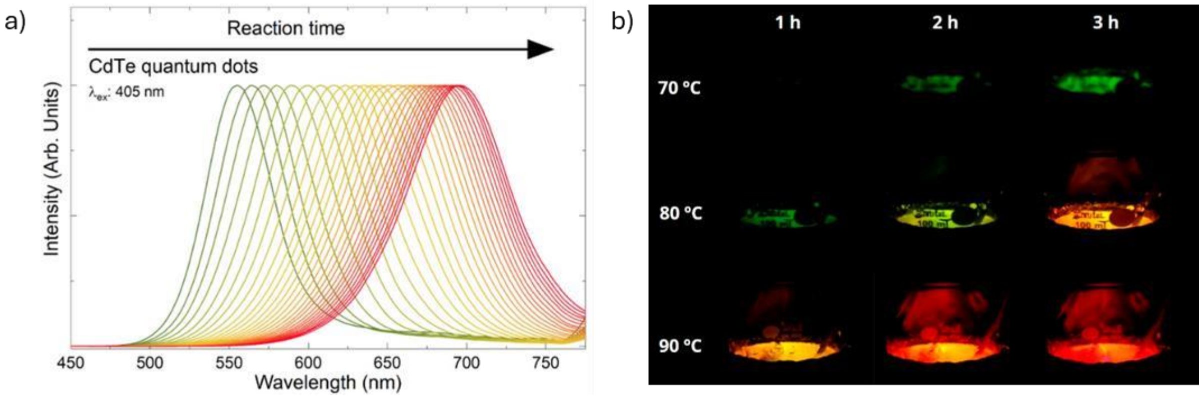

Figure 1. a) Luminescence spectra from in situ monitoring and b) emission color of CdTe QDs at temperatures of 70, 80, and 90 °C every 60 minutes over a period of 3 h

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P-19

Enhancing c-Si Solar Cell Efficiency in the UV Region: Using Eut^{+} as aDown-Shifting Layer

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Two polymers of [Eu(3DPIQC)$_3$] (where DPIQC = 3-(diphenyl phosphoryl)-1-isoquinolinecarboxylate), luminescent europium complexes with antenna ligands, were carefully embedded within a polyvinyl butyral (PVB) matrix [1,2]. The resulting material was used to create films that serve as luminescent down-shifting layers (LDSLs) for crystalline silicon (c-Si) solar cells. These films were characterized using photoluminescence spectroscopy, atomic force microscopy (AFM), UV-Vis spectroscopy, and fluorescence microscopy.

AFM analysis revealed that the films had low surface roughness, while fluorescence microscopy showed that the Eu complex embedded in PVB assumed a spheroidal configuration, which is particularly beneficial for optical applications. The LDSLs were used as energy converters in c-Si solar cells to enhance the utilization of high-energy photons, thereby improving overall efficiency.

Photovoltaic parameters measured before and after the deposition of the LDSLs on the c-Si cells confirmed a positive effect on cell efficiency. External quantum efficiency (EQE) curves indicated an enhancement in the performance of the photovoltaic cells in the UV region of the spectrum for some coated devices. Additionally, electrochemical impedance spectroscopy (EIS) was conducted to analyze the effect of the Eu complexes on the charge transfer process within the devices.

Acknowledgments: The authors acknowledge Grant FONDECYT 1220159, ANID-Chile and Proyect ANID/FONDAP 1523A0006 “Solar Research Center” SERC-Chile.

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P-20

A NOVEL APPROACH OF MICROCONTROLLER-BASED TRANSVERSE MAGNETO-OPTICAL KERR EFFECT MEASUREMENT SYSTEM

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The Transverse Magneto-Optical Kerr Effect (TMOKE) technique is the quickest and easiest optical experimental method for characterizing magnetic materials with reflecting surfaces[1- 4]. Compared to conventional TMOKE methods[1-4], a novel approach to the low-cost with a microcontroller-based system has been developed. As shown in Figure 1, the Kerr effect in this geometry can be calculated as the difference in the intensities of the polarized beams before and after reflection. The polarized beam emitted from a microcontroller-driven diode laser source was split into two beams. The first beam was directed into the optical reference detector and the second beam was diverted to the sample placed in the magnetic field. Afterwards, the first beam and the beam reflecting from the sample surface were then measured using optical detectors. The detectors are converted the light intensity into the frequency values. Then, the Kerr intensity was computed from the difference of the frequencies via the ESP32 microcontroller[5]. To obtain different magnetic field values, a modified closed-loop Proportional-Integral-Derivative (PID)[6] control technique was applied to drive electromagnets via the microcontroller. These processes were repeated as the Kerr signals versus the magnetic field of ±500 Oe at 10 Oe intervals to create a hysteresis loop. In this novel approach, the microcontroller was utilized to measure the physical quantities and control the system components. Thus, it is considered that a quite low-cost system for optically magnetic characterization was developed in comparison to conventional TMOKE methods.

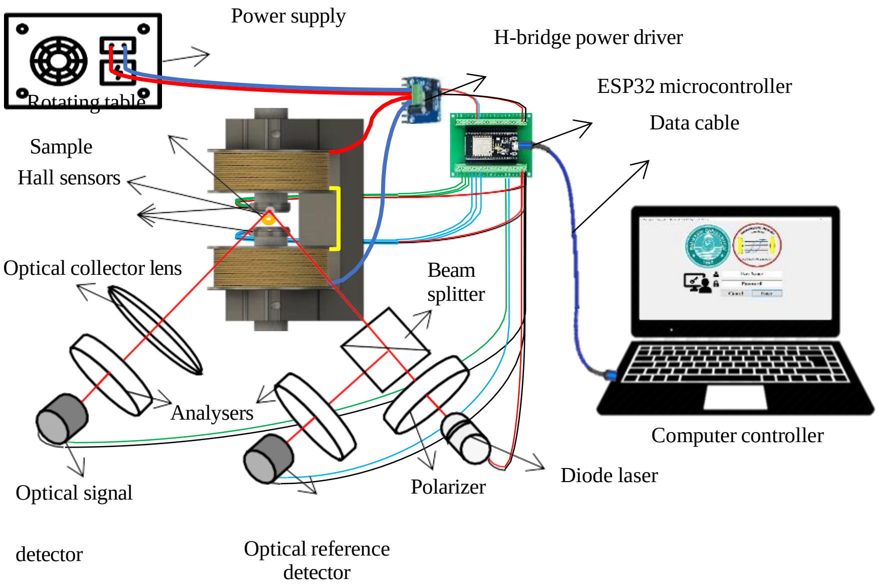

Figure 1. Schematic illustration of the TMOKE measurement system-based microcontroller

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P-21

GERMANATE OLIVINES: FABRICATION AND LUMINESCENCE MEASUREMENTS IN THE VISIBLE AND NEAR-INFRARED RANGES

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Germanate olivines are promising inorganic compounds due to their microwave dielectric properties [1]. Further studies shown that germanate olivines doped with transition metal ions are excellent candidates for inorganic phosphors. Germanate ceramics $Li_2MgGeO_4:Mn^{2+}$ belonging to olivine family are known as a green long persistent phosphors [2]. Rare earth doped germanate ceramics have been rarely investigated. Our previous results suggests that $Li_2MgGeO_4:Ln^{3+}$ (Ln = Pr and Tm) are interesting from the optical point of view [3]. In this study, we present results for undoped and rare earth doped germanate ceramics Li_2MgGeO_4. Rare earths are limited to erbium and holmium ions. Structure and properties of germanate ceramics were examined using various experimental techniques. In particular, luminescence properties of Li_2MgGeO_4 and $Li_2MgGeO_4:Ln^{3+}$ (Ln = Er, Ho) in the visible and near-infrared spectral ranges are presented and discussed in details. The luminescent results demonstrate that the narrow emission bands characteristic for electronic transitions of rare earth ions are well overlapped with broad band of ceramic host, which is assigned to F-type centers. Moreover, germanate olivines with erbium ions show enhanced and long-lived near-infrared luminescence due to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition at 1530 nm. It can be concluded that germanate ceramics Li_2MgGeO_4 doped with rare earth ions can be applied as inorganic phosphors emitting visible light and near-infrared radiation.

Acknowledgment: This research was funded by National Science Centre (Poland), grant number 2019/35/B/ST5/01924.

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P-22

LUMINESCENCE IN Yb^{3+}-DOPED TITANATE-GERMANATE GLASS

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Yb^{3+}-doped glasses have attracted a great interest due to their suitability for laser and optical amplifier applications [1-4]. Systematic investigations well demonstrated that near-infrared luminescence corresponding to $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions depends significantly on glass matrices containing various network-formers and network-modifiers [5-7]. In particular, luminescence properties of rare earth ions are enhanced greatly in the presence of TiO_2. Our previous studies suggest that Tm^{3+}-doped titanate-germanate glass is promising for infrared photonics [8]. In this work, we demonstrate that the spectral linewidth for the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ions at 1030 nm is influenced by quantitative relationship between two main glass components GeO_2 and TiO_2. Furthermore, near-infrared luminescence band related to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} is enhanced significantly in the presence of TiO_2. The presented research may be important in terms of potential luminescence applications in the near-infrared spectral range. Hence, our results concerning on near-infrared luminescence properties of Yb^{3+}-doped titanate-germanate glasses varying with TiO_2 concentration will be presented and discussed in details.

Acknowledgment: This research was funded by National Science Centre (Poland), grant number 2018/31/B/ST8/00166.

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Impact of Manganese Co-doping on the Luminescent and Mechanoluminescent Properties of $SrSi_2N_2O_2:Eu^{2+}$

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$SrSi_2N_2O_2:Eu^{2+}$ is known mainly as an efficient and stable phosphor used in phosphor-converted white LEDs. Since its potential applications in the lighting industry were first reported, significant efforts have been made to enhance its luminescence efficiency, improve its thermal stability, and reduce production costs. One proposed method involves co-doping with lanthanide or transition metal ions, and Mn doping was reported as the most effective. The increased luminescence intensity has been attributed to energy transfer between Mn^{2+} and Eu^{2+} ions [1-3].

We investigated a series of $SrSi_2N_2O_2:Eu$ samples synthesized with the addition of different Mn precursors using two fabrication methods: standard solid-phase synthesis and two-step high-pressure synthesis. Since even small contamination with other Sr-Si- N-O phases can affect the final material's spectroscopic qualities, it was essential to obtain samples with a pure triclinic $SrSi_2N_2O_2$ phase, free of contamination by other phases, to avoid interpretive confusion.

Our results for samples synthesized by the standard solid-state method confirmed that adding Mn-O-based compounds during the standard solid-state synthesis of $SrSi_2N_2O_2:Eu^{2+}$ significantly increases the quantum yield of this phosphor. But surprisingly, we also found that Mn ions are not incorporated into the crystal lattice. We discovered that Mn-O-based compounds used in the standard solid-state synthesis of $SrSi_2N_2O_2:Eu$ result in an increased number of defects, which enhance the energy storage capacity of this material. This leads to increased luminescence, thermoluminescence, and persistent luminescence. Moreover, we found that it improves the mechanoluminescence properties of this phosphor, extending the potential applications of $SrSi_2N_2O_2:Eu$ beyond white LEDs.

In contrast, the two-step high-pressure synthesis resulted in the samples of pure triclinic $SrSi_2N_2O_2$ doped with Eu, and Eu and Mn. However, the effective introduction of Mn into $SrSi_2N_2O_2:Eu$ caused the reduction of its luminescence quantum yield. Additionally, it changed the energy distribution of the trap states compared to samples doped solely with Eu.

Acknowledgments: Polish National Science Center project No: 2019/33/B/ST8/02142

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P-24

LUMINESCENT PROPERTIES OF ALKALI-GERMANATE GLASSES WITH CDS QUANTUM DOTS

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Semiconductor quantum dots (QDs) have attracted considerable attention due to the various unique and interesting optical and electronic properties compared to their bulk counterparts [1]. Semiconductor QDs with desired size in glass can be obtained by specifically selected annealing temperature and duration. The higher the temperature or the longer the duration, the larger the size of the QDs [2].

Alkali-germanate glass had the composition of xR_2O-$(80-x)GeO_2$, where R=Li or Na, x=10; 15; 20 mol.%. Glass-ceramics synthesis was carried out via homogeneous crystallization followed by interfacial-controlled growth at 560°C. The original glass showed the presence of two luminescence bands: one wide band with a maximum at 650 nm and one narrow band with a maximum at 851 nm. After heat treatment (HT), the intensity of the broad short-wave band decreased, and the long-wave band increased. At the same time, the short-wavelength shifted by 765 nm, and the long-wavelength by 858 nm.

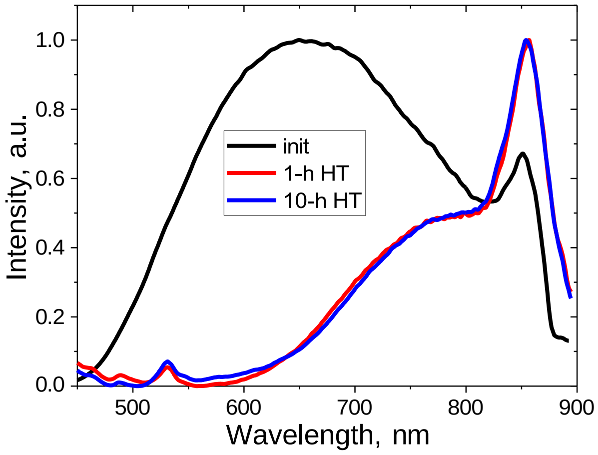

Fig.1. Luminescence spectra of alkali-germanate glasses with CdS quantum dots immediately after synthesis (black curve), after short (red curve) and long (blue curve) heat treatment at 560°C.

The work was supported by Russian Science Foundation (No. 24-43-20020).

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P-25

LUMINESCENT PROPERTIES OF SILVER ION EXCHANGE LAYERS OF SILICATE GLASSES

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Silver nanostructures in the form of ions, clusters and nanoparticles in a glass matrix are of scientific and practical interest. Silver nanostructures can be used as nonlinear optical devices, luminescent temperature sensors and selective UV radiation detectors, photocatalysts for producing hydrogen from water, as well as purifying water and air. The formation of silver nanostructures in glass can be realized either during high-temperature synthesis of glass from charge components (in this case, the silver concentration is a few percent) or in the low-temperature ion exchange process, for example, sodium ions in glass are replaced by silver ions from molten salt (in this case, the silver concentration can reach several tens of percent). In this work, silver nanostructures and, first of all, silver molecular clusters were created in silicate glass through ion exchange and their spectral and luminescent properties were studied.

Ion exchange took place in a 0.1% $AgNO_3$ / 99.9% $NaNO_3$ melt for 10 minutes at a temperature of 320 °C. The luminescent properties of molecular silver clusters were studied in the excitation wavelength range from 250 to 480 nm (Figure 1). It has been established that the silver clusters luminescence consists of two components with nanosecond and microsecond lifetimes. The technique of layer-by-layer chemical etching of surface layers in glass made it possible to establish that larger clusters are concentrated closer to the glass surface, and their concentration and size decrease as the penetration depth in the ion-exchange layer increases. By selecting the parameters of ion exchange in glass, it is possible to change the concentration and size of molecular silver clusters along the depth of the ion exchange layer, and thus control the luminescent characteristics of the clusters.

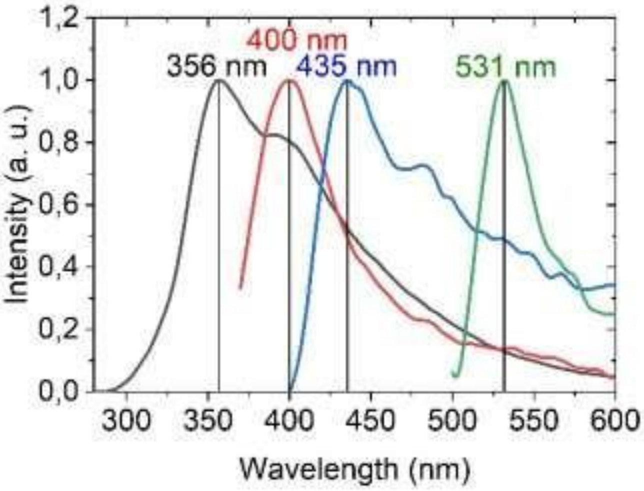

Figure 1 - Luminescence spectra upon excitation at excitation wavelengths of 250 nm (black line), 340 nm (red line), 370 nm (blue line) and 480 nm (green line). The wavelength of the luminescence maximum is indicated above the spectrum.

The work was carried out with financial support from the Russian Science Foundation (project № 20-19-00559).

P-26

PHOSPHORESCENT FIBRE OPTIC TIP TEMPERATURE SENSOR

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We report the construction and performance of an optical fiber tip temperature sensor based on phosphorescent strontium (Sr) aluminates' ON/OFF time responses. The sensor makes use of the fact that as temperature increases the phosphorescence intensity drops and the ON/OFF time responses become slower [1]. The 600 μm core quartz polymer lead-in fiber tip is polished through 45° and reflects the incoming UV excitation light from a 405 nm LED to the phosphorescent material placed at the tip of the receiving lead-out fiber as shown in Fig. 1a) below. The phosphorescence spectrum is measured approximately each 0.18 s at different temperatures using the Time Acquisition capability of the USB2000 Ocean Optics mini-spectrometer and the results for one of the Sr aluminate samples is shown in Fig.1b). The responses clearly show the decrease of the intensity with temperature T and the increase of the duration of both ON and OFF time responses $R(t)$ and $D(t)$. As a measure of these two types of changes we take the normalized ratio [2].

$$\mathrm{N} = 100\frac{R_i - D_i}{R_i + D_i}\ \% \qquad (1)$$

where R_i is the intensity at the i-th moment t_i during the *rise* phase while D_i is the is the intensity at the i-th moment t_i during the *decay* phase. As temperature increases R_i goes down while D_i goes up so the normalized ratio represents a more sensitive measure for temperature changes. Fig. 1c) displays the N(T) dependences for i = 1 (blue rhombs) and for i = 2 (red squares). As is clearly seen the N(T) dependence is monotonically decreasing with temperature in the 0-80C temperature range and can serve as a measure for temperature changes. The particular range of operation and sensitivity of the sensor depends on the appropriate choice of the phosphorescent material.

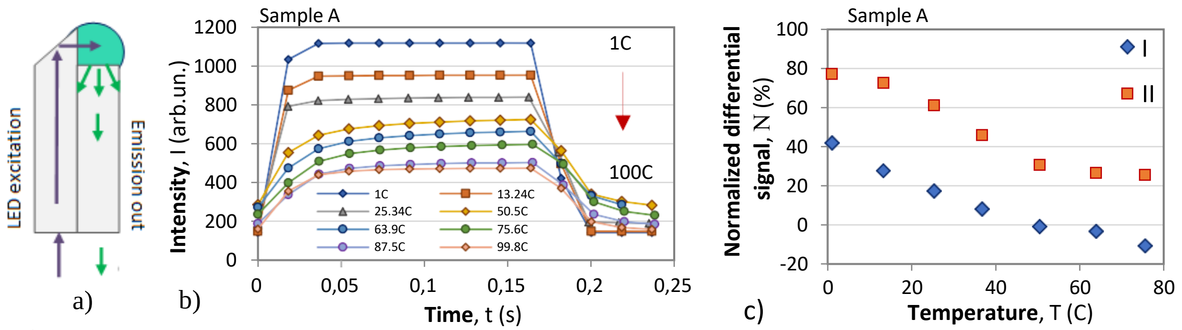

Figure 1.

a) construction of the tip sensor; b) ON/OFF time rise and decay time responses; c) temperature dependence of the normalized difference N(T)

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P-27

WAVELENGTH REFERENCED POLARIMETRIC FIBRE OPTIC CURRENT SENSOR WITH SMARTPHONE INTERROGATION

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We present the performance of a smartphone interrogated polarimetric fibre optic current sensor in which a wavelength referencing and calibration is used to avoid jitter and rescaling caused by autofocusing of the mobile phone. The sensor makes use of the broadband spectrum of the white LED and the additional fluorescence in the BSO crystal caused by the blue excitation line [1], low cost polarizers and a transmission diffraction grating (1000 lines/mm) placed in front of the smartphone's camera. A large core (1 mm) plastic lead-in and lead-out fibre was used in the tested construction. The shifts of the modulated spectral response detected by the smartphone are caused by the external magnetic field along the BSO crystal and by ambient temperature. However, it is sensitive to instabilities caused by smartphone autofocussing and needs wavelength referencing for calibration.

Two types of sources were used to reference and calibrate the spectra: LEDs emitting at the extremities of the smartphone spectral range (395 nm and 700 nm) and laser diodes (LD) at 405 nm, 658 nm as well as a 532 nm DPSS laser.

Three different optical schemes were used to launch the signals from the above reference sources: i) side tunnelling into the plastic fibre; ii) side injection into the plastic fibre and iii) parallel output reference fibres. Each of the schemes can be used with any of the sources – LEDs or LDs. We show that the latter scheme in combination with laser diodes offers the most accurate determination of the position of the reference wavelength and allows the best calibration. Fig.1a) below shows the spectral distribution along the pixels in the presence of jitter and rescaling observed as fluctuations of the position and the distance between the reference wavelengths 405 nm and 532 nm. Fig. 1b) to the right is the spectral distribution after individually realigning each of the spectra to the reference wavelengths which eliminates the induced noise.

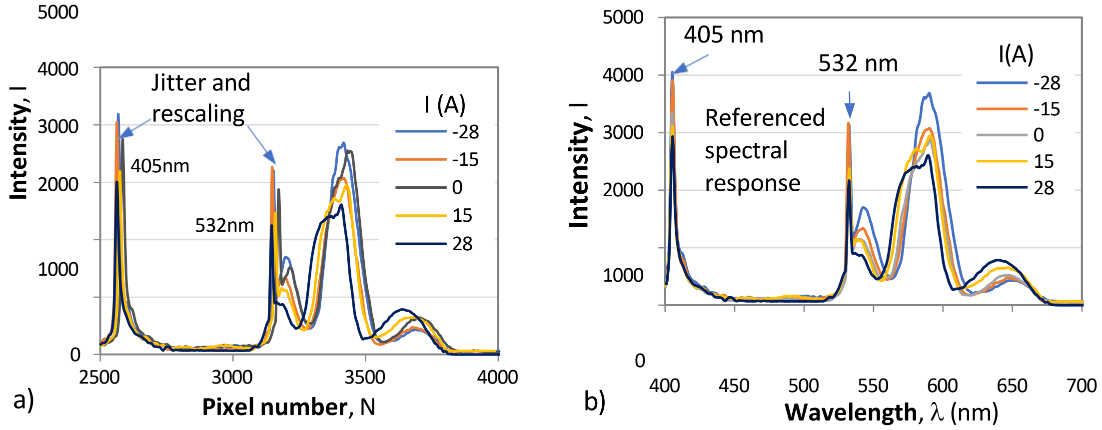

Figure 1. Sensor responses : a) as obtained from the mobile phone; b) after referencing with respect to 405 nm and 532 nm laser lines.

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P-28

Rare earth doped strontium aluminates for contactless smartphonereadable temperature sensors

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The present work studies the photoluminescent characteristics and temperature dependent time responses of rare earth (RE) doped strontium aluminates synthesized at different conditions. The synthesis was performed by solid-state high-temperature methodology in air and in a weak reduction atmosphere. We observe the influence of some factors such as boric acid presence, doping and co-doping agents, and synthesis duration on the photoluminescent spectra and time responses. We demonstrate the possibility to measure 3D excitation-emission spectra as well as their rise and decay time responses [1] using common smartphones equipped with adiffraction grating. We perform a detailed 3D excitation-emission matrix (EEM) analysis comparing measurements using a standard (Fig. 1a) and a mobile phone spectrometer (Fig. 1 b) outlining the basic differences and advantages of each method. While smartphones have a different and non-uniform spectral response compared to a standard spectrometer, it is shown that they offer several advantages such as efficient suppression of the UV excitation light anda possibility for contactless measurement of ambient temperature from the temperature dependent ON/OFF time responses under pulsed LED UV excitation as shown in Fig.1 c) below. In this work we continue the research on Sr aluminates for optical fiber temperature sensors and demonstrate the possibility for contactless smartphone based interrogation.

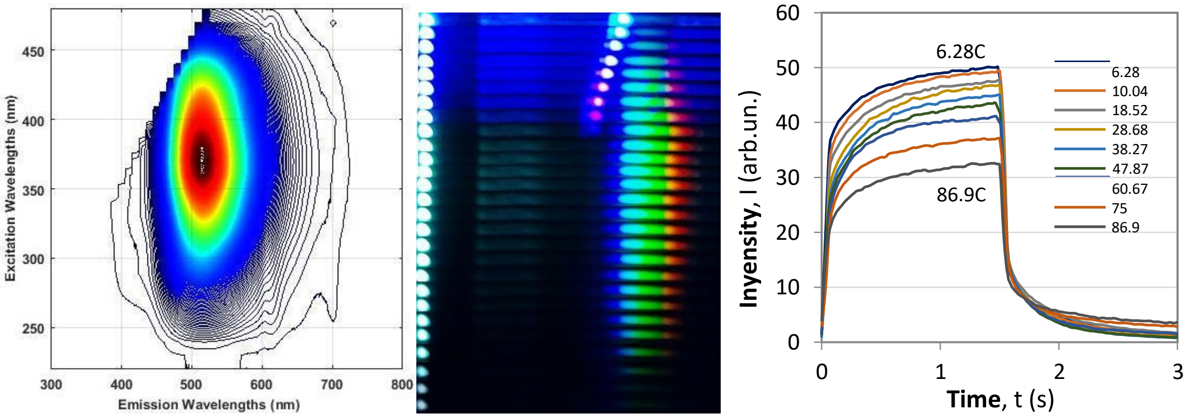

Figure 1. Spectral and time responses of a Sr aluminate sample: a) 3D excitation emission spectra as measured by a spectrometer; b) the spectra from a) as measured by a smartphone (Samsung A51) and c) the time responses of the sample at increasing temperatures.

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P-29

RED MUD AS COLOURING AGENT FOR STONEWARE PASTES

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Red mud (RM), a byproduct of alumina production by the Bayer process, is classified as hazardous waste and is, nowadays, one of the most abundant industrial waste worldwide. Currently, more than 4 billion tons of this material are stored in ponds or as dried mounds, underscoring the urgency of addressing this issue.

This work aims to recycle RM as colouring agent for stoneware products. To achieve this goal, several proportions of RM (0–10 wt%) were incorporated into ceramic pastes. The developed products with RM display an appealing reddish/brown hue while meeting the required technical specifications, including firing shrinkage, weight loss, density, water absorption and flexural strength, all falling within the established industrial limits. Furthermore, leaching tests, conducted in industrially prepared cups, revealed that all the values remained well below the permitted maximum thresholds. Therefore, this work provides a viable alternative for the management of considerable amounts of this waste as coloring agent for ceramic pastes, thereby contributing to a more sustainable production process.

P-30

OPTICAL AND STRUCTURAL PROPERTIES OF Eu^{3+} DOPED $La_3Al_5O_{12}$ GROWN BY MICROWAVE-DRIVEN HYDROTHERMAL TECHNIQUE

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Research into producing Eu^{3+} doped nanopowders has very high potential due to the materials' unique luminescent properties. Eu^{3+} ions can be used in modern light sources, displays, and bioimaging technology, making these materials crucial in the optical, electronics, and medical industries [1]. Optimization of synthesis methods reduces production costs and improves the purity and properties of the materials. In addition, this research contributes to the understanding of structural and physicochemical properties, paving the way for new technologies and innovative applications [2].

Given the growing use of nanomaterials, more research on quick, cheap and simple production methods is being conducted. At present, many methods of obtaining nanomaterials require high vacuum, very high temperature, and high purity of reagents to ensure crystals of sufficiently good quality. A very promising method for producing nanomaterials is the microwave-driven hydrothermal technique, which is superior to other methods for obtaining materials due to its high energy efficiency and shorter synthesis time. This technique minimizes energy and resource consumption making it environmentally friendly. In addition, it allows control over reaction conditions, allowing for better properties of the final product [3].

In this study optical and structural properties of $La_3Al_5O_{12}$ (LaAG) nanopowders doped with Eu^{3+} ions are investigated as a function of hydrothermal crystallization conditions. Parameters for the growth of structures, such as temperature, reaction time, and reactant concentration, have been studied to achieve the good reproducibility and reliability of hydrothermal technology. A detailed optical and structural analysis of the material was performed proving the potential of the doped nanopowder as an orange-red phosphor [4]. These studies provide a beter understanding of synthesis mechanisms, leading to process optimization and ensuring the required quality of the final product in each production run.

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TEMPERATURE AND PRESSURE DEPENDENT EMISSION OF MIXED Eu^{3+} AND Tb^{3+} COORDINATION COMPOUNDS WITH N-PHOSPHORYLATED CARBOXAMIDE

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One of the methods of sensitizing the Ln^{3+} emission is so-called antenna effect, achieved by synthesis of lanthanide coordination compounds with carefully designed organic ligands. These multifunctional structures possess interesting luminescent and magnetic properties, often dependent on external stimuli such as temperature or pressure.

The ligand used in this study - N-(diphenylphosphoryl)-quinoxaline-2-carboxamide – was designed in such a way as to obtain coordination compounds exhibiting temperature- dependent luminescence for some of the lanthanide ions due to back-energy transfer from Ln^{3+} to the ligand triplet state. In order to enable ratiometric temperature readout, mixed coordination compounds were synthetized ($[Na_2Tb_xEu_{1-x}L_4(DMF)_2][CF_3SO_3]$, where x=0.99, 0.995). These compounds showed strong temperature-dependance of terbium ion emission, however, their luminescent properties were also strongly influenced by pressure. In hopes of limiting this effect, PMMA thin layers containing 2% and 5% (w/w) of said coordination compounds were prepared and studied. Obtained PMMA thin layers exhibited interesting luminescent properties, with terbium emission strongly enhanced compared to monocrystalline samples and highly dependent on temperature. This work presents spectroscopic properties of before-mentioned coordination compounds in a form of single crystals and PMMA thin layers together with thermometric parameters. Luminescent measurements (emission and excitation spectra as well as emission lifetimes) were performed in the temperature range between 11 and 300 K.

P-32

PHOTON-INDUCED EFFECTS ON COLOR CENTERS OF DIAMONDS

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Diamond is a material with many unique properties suitable for the different applications from power electronics to quantum computing. It has an ultra-wide band gap (5.47 eV), high electron and hole mobility, high thermal conductivity, high reflectivity, transparency from RF to UV radiation, and has compelling potential advantages over the most known semiconductors, such as the narrow-bandgap silicon (Si), in radiation-resistant, high-power, and high-frequency electronics, as well as in deep-UV optoelectronics, synchrotron optics, quantum information, quantum sensing and extreme-environment applications [1].

It was previously shown that diamonds under the influence of optical radiation [2,3], X-ray radiation [4,5], radio frequency radiation [6,7] are capable of changing their properties. This fact can be used for various practical applications, such as the creation of optical and X-ray detectors, quantum sensors, optoelectronic devices, etc. In addition, in [8], an NV color center laser was demonstrated, and it was shown that the additional effect of optical radiation changes the lasing properties [9].

In this work, we studied the effect of optical and X-ray radiation on the concentrations of various conductive and color centers in diamonds (related with phosphorus, nitrogen, boron, germanium, silicon and others). It has been shown that optical radiation significantly affects the charge states of color centers, and these effects are observed not only when exposed to high-energy photons (deep UV, X-rays), but also when exposed to relatively low-energy ones (IR and visible light). Moreover, many effects demonstrate a significant memory effect, even at room temperature - up to weeks. To restore charge states, the crystal must be annealed. We envision this could be used in applications such as optical recording memory, optical and quantum sensors, Gamma, X-ray and deep-UV imagers.

The work was supported by the Ministry of Science and Higher Education of Russian Federation, Youth laboratory under the leadership of Boldyrev K.N. is acknowledged.

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P-33

HETEROMETALLIC LANTHANIDE-PENTACYANIDOCOBALTATE FRAMEWORKS AS NIR-EMISSIVE AND SHG-ACTIVE STIMULI-RESPONSIVE SOLIDS

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The combination of multiple optical properties in a single-phase material ought to benefit the development of new sensors and smart devices tailored to specific requirements, especially when the incorporated properties are sensitive to physical and chemical stimuli.[1] Among the broad spectrum of optical functionalities, the manipulation of near-infrared light, including its efficient generation as well as its application for inducing visible light, provides a platform for crucial applications such as bioimaging, security, and optical communication.[2]

In this context, a strong scientific need emerged to search for novel materials that can efficiently generate NIR light through photoluminescence as well as those that can transform NIR light into visible one through the second harmonic generation (SHG) effect or other non-linear optical (NLO) properties.[1,3] In the best-case scenario, both phenomena, i.e., NIR emission and SHG activity, can be combined to achieve multifunctional luminophores. We present the results of our work devoted to lanthanide(III) complexes, mainly employing Nd(3+) ions, which are coordinated to heteroligand pentacyanidocobaltate(III) ions, $[Co^{III}(CN)_5(X)]^{3-}$ (X = azido, nitrito, etc.). It results in a series of heterometallic cyanido-bridged coordination polymers that link tunable NIR photoluminescence originating from f-f electronic transitions employing also the sensitization pathway from Co(III) complexes with tunable SHG activity realized by breaking the crystal's symmetry by pentacyanidocobaltate(III) ions. The more extended multifunctionality of these materials, including magnetic and solvent vapor sorption properties, is also accessible for these systems which will be discussed in this contribution (Figure 1).

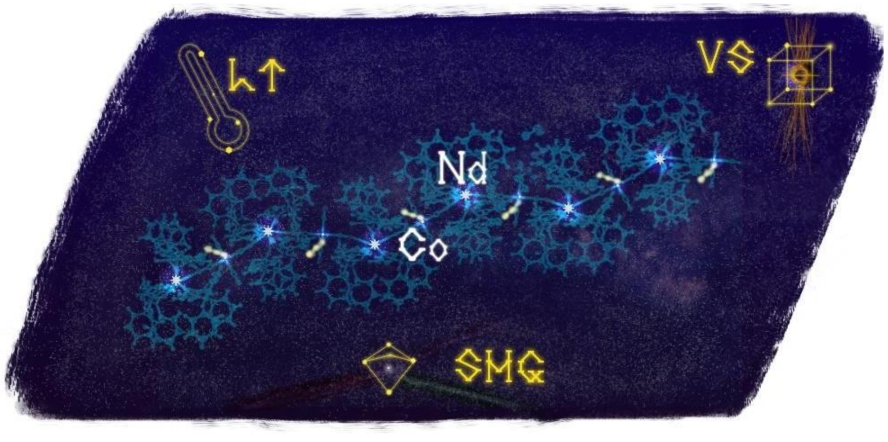

Figure 1. Graphical representation of functionalities combined within the reported systems: luminescent thermometry (LT), second harmonic generation (SHG), and vapour sorption (VS).

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P-34

PHOTOLUMINESCENT COORDINATION POLYMERS BASED ON BIPYRIDINE-CYANIDO RUTHENATES(II) AND F-BLOCK METAL COMPLEXES

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Photoluminescent coordination polymers containing emissive metal complexes in their structure, including d-block heavy metal ions and trivalent lanthanide cations, are of great research interest due to their potential in the construction of light-emitting diodes (LEDs), sensors, or optical communication devices, as well as advanced multifunctional materials [1]. Due to the above points, there is a keen interest in the synthesis of crystalline luminescent materials, whose emission can be easily adjusted by external stimuli. It was shown that a plethora of functionalities can be implemented in crystalline solids built of cyanido metal complexes of selected d-block metals, which can potentially act as sensitizing metalloligands for emissive lanthanide(III) (Ln) centers [2–4]. We decided to use the highly emissive ruthenium(II) complex, $[Ru(bpy)(CN)_4]^{2-}$ (bpy = 2,2'-bipyridine) to sensitize the Ln^{III}-centered photoluminescence. Moreover, the discussed Ru(II) complex exhibits optical properties sensitive to external factors (both physical and chemical), which makes it a useful molecular building block in the construction of Ru^{II}–Ln^{III} heterometallic materials with switchable luminescent properties [5]. We present new luminescent coordination polymers based on selected lanthanide(III) complexes, $[Ru(bpy)(CN)_4]^{2-}$ anions, and selected supporting organic O,O'-donor ligands (Figure 1). The potential lanthanide-emission-modulating nature of $[Ru(bpy)(CN)_4]^{2-}$ anions is discussed.

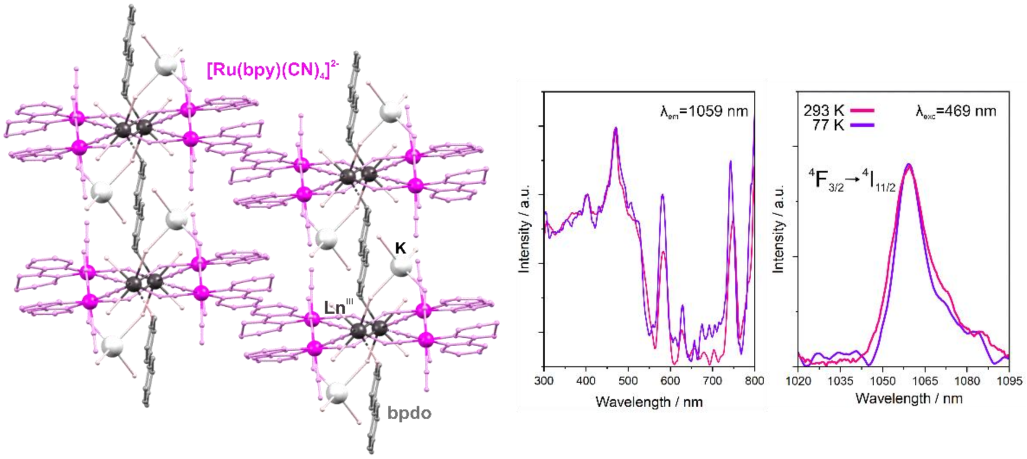

Figure 1. Crystal structure of one of the presented coordination systems, $\{[K(H_2O)_2][Nd^{III}(H_2O)_3(bpdo)_{0.5}][Ru^{II}(bpy)(CN)_4]_2\}$, depicted with its excitation and emission spectra, recorded at high (293 K) and low (77 K) temperatures (bpy = 2,2′-bipyridine; bpdo = 4,4′- bipyridine-N,N′-dioxide).

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P-35

HETEROMETALLIC DECANUCLEAR COPPER(I)-RHENIUM(V) CLUSTERS EXHIBITING EFFICIENT TUNABLE LUMINESCENCE

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Development of novel highly efficient photoluminescent materials has been a hot topic of scientific interest in the last decades[1], as their properties allow applications in, e.g., light-emitting diodes (LEDs, OLEDs), chemical sensors, and radiation detectors. Materials containing luminophores based on metal ions, especially those incorporating earth-abundant metals, have recently gained special attention[2], due to the need to replace commonly used expensive materials utilizing such elements as Pt, Ir, or Ru. Such metal-complex-based luminophores are also attractive as a source of multifunctional luminescent solids combining light emission with magnetic or electrical functionalities.[3,4] The materials based on Cu(I) complexes are especially attractive in this context, as they combine high quantum yields and structural diversity, being also rather effortless to prepare. We decided to combine such highly emissive copper(I) complexes $[Cu^{I}_{2}(dppy)_{3}(MeCN)]^{2+}$ (dppy = diphenylphosphinopyridine) with anionic metalloligands $[Re^{V}(CN)_{4}(N)(L)]^{2-}$ (L = organic ligand, N^{3-} = nitrido ligand), which are also strongly emissive and their emission can be tuned by temperature or the embedded ligand L, as well as other external stimuli.[5] As a result, we obtained four decanuclear coordination clusters of the general formula $\{[Cu^{I}(dppy)]_{2}[Cu^{I}(dppy)_{2}]_{4}[Re^{V}(CN)_{3}(dppy)(N)]_{2}[Re^{V}(CN)_{4}(L)(N)]_{2}\}\cdot n$MeOH (abbreviated as **$\{Cu^{I}_{6}Re^{V}_{4}\}$**; L = methanol or pyridine-based ligand), which exhibit efficient orange, green-yellow or almost white photoluminescence, tunable by temperature, excitation wavelength. and the presence of an additional organic ligand L.

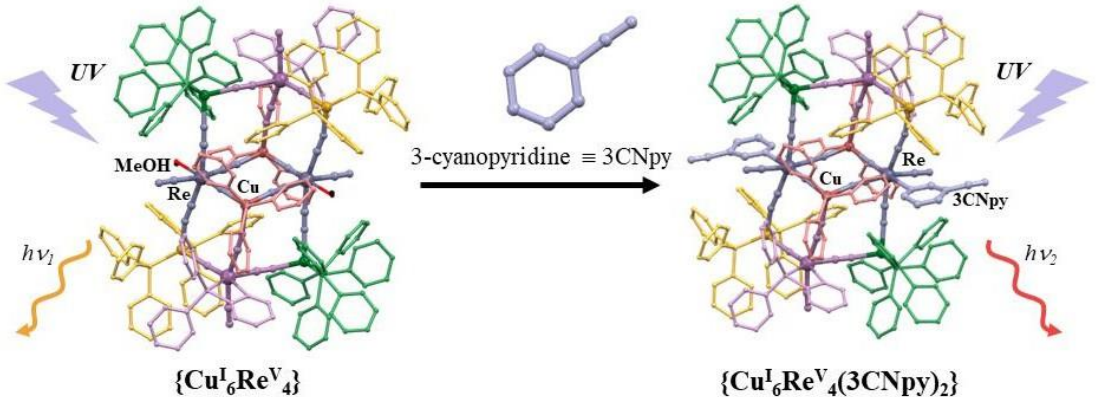

Figure 1. Visualization of the crystal structure of **$\{Cu^{I}_{6}Re^{V}_{4}\}$** clusters which optical properties can be modified by introducing a pyridine-based ligand, such as indicated 3CNpy.

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P-36

AB INITIO EVALUATION OF OPTICAL PROPERTIES IN LANTHANIDE(III)-BASED LUMINESCENT MATERIALS: MULTICONFIGURATIONAL AND TDDFT APPROACHES

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Theoretical studies play an increasingly important role in molecular material sciences as they are crucial for understanding and elucidating complex phenomena that decide the desired optical properties of designed materials. Robust and relatively simple approaches are of great interest since they allow for a highly efficient search for novel materials with particular optical properties beforehand, conducting tedious, manual experimental work. In this regard, we present the evaluation of relativistic multiconfigurational (CASSCF type) and TDDFT-based *ab initio* methodologies within a straightforward electric dipole kind approach and including excited-state geometry optimization for predicting spectral properties such as UV-vis absorption and photoluminescence of lanthanide(III) complexes.[1–4] We exploit minimal vibrational effects on well-screened 4f-electrons to simulate temperature effects by adopting a model that completely disregards electron-phonon interactions and assumes a purely statistical Boltzmann population of excited states within a given manifold. We assess the accuracy and utility of our selected approaches for predicting spectral characteristics for future optical devices, such as emitting diodes and luminescence thermometers, correlating the results of theoretical investigations and experimental data for various lanthanide-based molecular materials. Our approaches are tested using the example of luminescent solids based on lanthanide(III) complexes, including the heterometallic Eu(III)-Ag(I) systems (Figure 1).

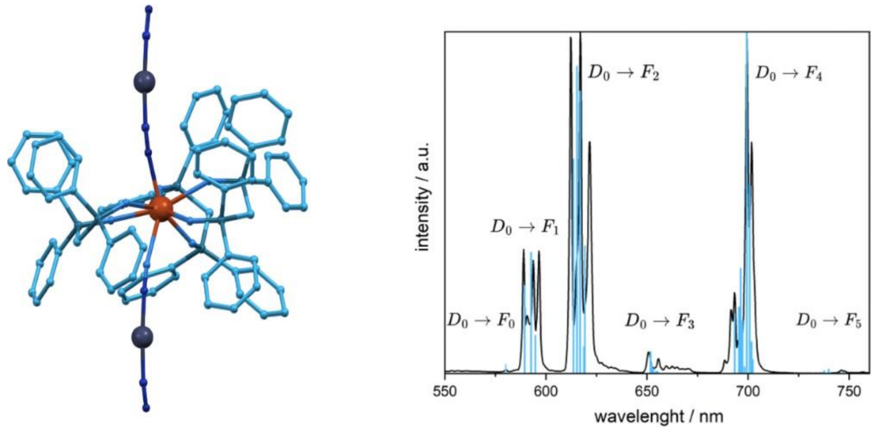

Figure 1. The visualization of the crystal structure investigated Eu(III)-Ag(I) coordination polymer represented by the $[Eu^{III}(dppmO_2)_3Ag^{I}(CN)_2]^{2+}$ fragment (left, $dppmO_2$ = bis(diphenylphosphino) methane dioxide) and its experimental photoluminescence spectra with calculated intensities (right).

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P-37

CHROMIUM(III)-CENTERED SPIN-FLIP LUMINESCENCE IN HETEROMETALLIC HYBRID MATERIALS FOR THE CONSTRUCTION OF OPTICAL SENSORS

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Photoluminescent materials exhibiting emission characteristics sensitive to temperature, relative humidity, or chemical stimuli have gained broad scientific interest in the last few years due to their possible sensor applications.[1,2] While constructing optical sensors, a popular strategy involves incorporating more than one luminescent building block, which results in more precise sensing parameters.[3,4] The promising strategy in this context could be the incorporation of compounds exhibiting spin-flip luminescence, where the metal-centered emission originates from intra-configurational excited states characterized by a single spin flip. The prime examples of chromophores exhibiting this phenomenon are those based on octahedral Cr^{III} complexes. Their strong metal-centered emission can be achieved, e.g., by incorporating a strong ligand field or adequate tailoring of the crystal field symmetry.[5]

In these regards, we present a series of heterometallic coordination frameworks, based on the hexacyanidochromate(III) anion, an organic emissive linker ligand 4,4'-bpdo (4,4'-bipyridine N,N'-dioxide) and $M^{II}(NO)_3$ salts (M^{II} = Ca, Sr, Ba for **1**, **2** and **3** respectively, Figure 1). **1** and **2** form a framework based on the *s*-metal ions bridged with 4,4'-bpdo ligands, with $[Cr(CN)_6]^{3-}$ anions and solvent molecules located in the pores. The presence of larger Ba^{2+} ions in **3** results in the formation of a different framework, where the $[Cr(CN)_6]^{3-}$ anion is coordinated. Distinct spin-flip luminescence emission has been observed for **1** and **2**, whereas for **3**, while still present, the signal is notably worse. Further investigation shows that the lifetime of the Cr^{III}-centered spin-flip emission in **2** changes from 1 to 19 ms upon decreasing relative humidity from 90 to 0%. Moreover, a strong temperature dependence has been observed, mainly relying on the enhancement of the 4,4'-bpdo centered emission upon decreasing the temperature down to 10 K. Both these features make **2** a promising candidate for a multifunctional optical sensor.

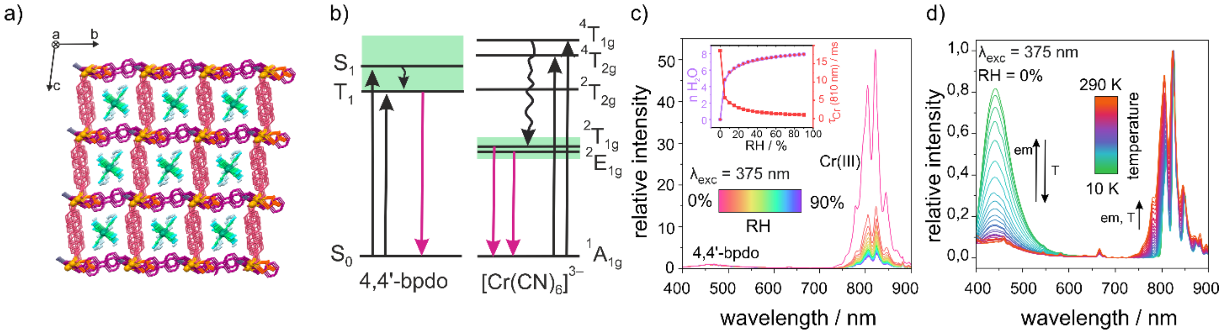

Figure 1. a) Fragment of the framework of **1** and **2**; b) scheme of energy transitions of presented series; c) the RH-dependent luminescence of **2** (outer, RH = relative humidity)); the RH-dependent lifetime of Cr^{III} centered emission alongside the sorption-desorption curve (inner); d) the temperature-dependent luminescence of **2.**

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P-38

Nd^{3+},Yb^{3+},Tm^{3+} triply-doped LiLuF$_4$ nanothermometers fully operating in the near-infrared range

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The field of luminescence thermometry has progressed substantially in the last 10 years. Remote temperature sensing, coupled with micro- or nanometric spatial resolution, is responsible for many potential applications, such as the characterization of microelectronics, plasmonics, and catalysis. Furthermore, nanocrystals designed for low cytotoxicity may be incorporated into biohybrid materials and used as *in vitro* or *in vivo* thermometers [1]. In this last case, it is important that the thermometers operate in the near-infrared (NIR) range, as visible light is strongly absorbed/scattered by biological tissues [2]. Therefore, nanosized thermometers operating fully in the NIR range need to be further investigated.

In this context, LiLuF$_4$ nanocrystals were synthesized by a decomposition method [3]. These materials were doped with three NIR optically active lanthanide ions: Nd^{3+}, Yb^{3+}, and Tm^{3+}, to achieve both excitation (808 and 980 nm) and emission (1320, 1450, and 1800 nm) in the NIR range. In general, the synthesized LiLuF$_4$ bipyramidal nanocrystals are monodisperse, showing some degree of aggregation due to the removal of oleate ligands (Figure 1a). These nanocrystals were synthesized with different Nd^{3+}, Yb^{3+}, and Tm^{3+} dopant contents, and they all exhibited NIR emission after 808 nm laser excitation (Figure 1b). Tm^{3+} $^3H_4 \rightarrow {}^3F_4$ emission (1452 nm) was observed for the material single-doped with Tm^{3+}, whereas both Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (900– 1100 nm) and Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1320 nm) emissions were triggered after exciting at the Nd^{3+} $^4F_{5/2} \rightarrow {}^2H_{9/2}$ (808 nm) absorption transition. Different Nd/Yb/Tm ratios are being current explored to yield highest NIR emission intensities and optimal thermometer performance in the NIR region.

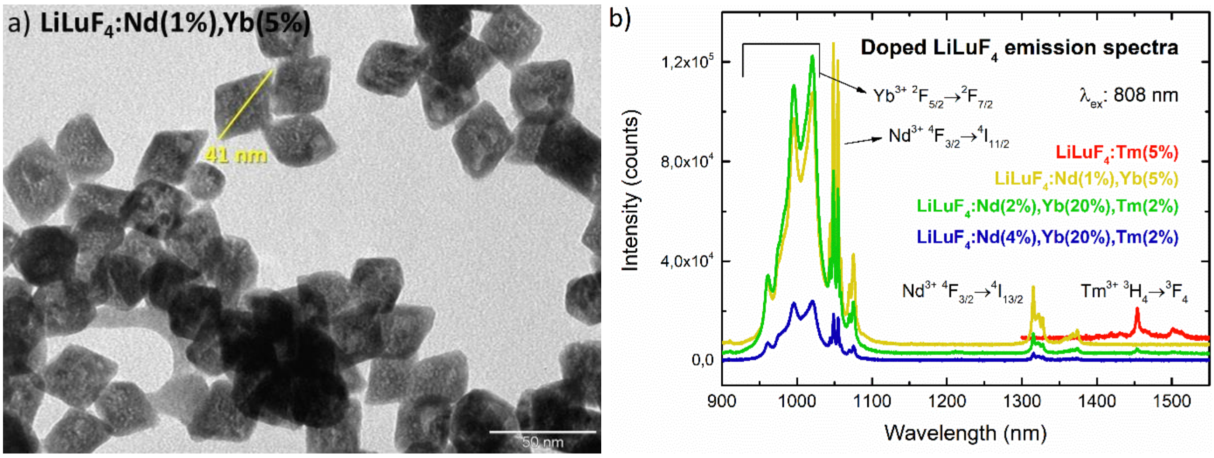

Figure 1. a) TEM of the LiLuF$_4$:Nd^{3+}(1%),Yb^{3+}(5%) nanocrystals. **b)** Emission spectra (λ_{ex}: 808 nm) of LiLuF$_4$ nanocrystals with different Nd^{3+}, Yb^{3+}, and Tm^{3+} dopant concentrations.

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P-39

APPLICATION OF AMPHIPHILIC ACETYLACETONE-BASED CARBON DOTS IN LIGHT EMISSION DIODES

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The ongoing development of carbon dots (CDs) for different applications calls for researching novel methods for their synthesis and surface functionalization. For the fabrication of photonic devices, apart from the obvious requirement of bright luminescence, CDs also should be soluble in the non-polar solvents used for the ink-printing of their functional layers. Herein, we introduce amphiphilic CDs synthesized from a mixture of benzoic acid and ethylenediamine in acetylacetone[1], which satisfy both of the abovementioned requirements. These CDs are quasi-spherical nanoparticles that are 20–50 nm in size, with aliphatic, carbonyl, amide, imine, and carbamate groups at the surface. This wide spectrum of surface groups renders them amphiphilic and soluble in a variety of substances, such as toluene, chloroform, alcohol, and water, with relative polarity ranging from 0.002 to 1. By variation of the molar ratio of benzoic acid and ethylenediamine, the highest quantum yield reported so far of 36% in isopropanol is achieved for the amphiphilic CDs. As a demonstration of the use of developed amphiphilic CDs in LEDs, green-emitting charge-injection devices were fabricated with a broad emission band centered at 515 nm, maximal luminance of 1716 cd m^{-2}, and CCT of 5627 K. These LEDs are the first ones based on amphiphilic CDs. Furthermore, these CDs can be used as luminescent inks and as an active material for solar concentrators.

Acknowledgement
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P-40

BIOACTIVE COMPONENTS IN THE LEAVES OF MORINGA OLEIFERA AND THEIR EXCITATION EMISSION MATRICES

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Moringa oleifera is known as the “miracle tree” or the” tree of life” due to its rich phytochemical composition. Extracts from the plant have anti-inflammatory, hepatoprotective, cardioprotective, and wound-healing effects.

The present study aims to quantitatively evaluate the polar and non-polar metabolites in the *Moringa oleifera* leaves from India and get their three-dimensional excitation-emission matrices. Gas chromatography and fiber optic spectroscopy were used to achieve the goals.

The selective fluorescence excitation in leaves was investigated using over 50 excitation wavelengths. Two areas are distinguished in the obtained excitation-emission matrices:

- The first in the 400 - 500 nm interval, associated with carotenoids and flavins:
- The presence of chlorophyll is recorded in the second region 650 - 733 nm.

The content of sucrose - 28.95 mg/g dw and fructose - 20 mg/g dw predominates among the sugars studied in the dried leaves. Of the phytosterols, sitosterol 7.10 mg/g dw predominates, of the fatty acids bechanic acid 6.17 mg/g dw and pentadecenoic acid 6.87 mg/g dw.

The results of the emission excitation matrices can be used in future studies to obtain fingerprints of plant leaves obtained in different regions of the world by excitation in the blue part of the visible spectrum. Furthermore, it can be used to estimate the time of harvesting the leaves when they have the highest content of biologically active substances.

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P-41

FLUORESCENCE FROM ORGANIC DYES INDUCED BY A LIGHT-EMITTING-DIODE FOR APPLICATION IN EXCITATION-EMISSION FLUORESCENCE SPECTROSCOPY

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Abstract: Our experimental study aims to investigate if the fluorescence characteristics of an organic dye with high quantum yield can serve as a light source for application in excitation-emission matrix (EEM) fluorescence spectroscopy. We used a high-power light-emitting diode (LED) to excite the Coumarin 1 dye dissolved in ethanol. The LED emits an output wavelength at 365 nm which is close to the absorption maximum of Coumarin 1 dye. For the spectral tuning of the fluorescence, a Czerny–Turner monochromator with a diffraction grating was used. We investigated two excitation configurations to check the effectiveness of LED-induced fluorescence: excitation through an optical-fiber-coupled LED and direct excitation from the LED. A diffuse reflector composed of barium sulfate ($BaSO_4$) and polyvinyl alcohol (PVA) was used to demonstrate the possibility of both increasing the excitation efficiency as well as the fluorescence signal collection. Fluorescence spectra of the test objects Coumarin 6 dye, extra-virgin olive oil (EVOO), and the polycyclic aromatic hydrocarbon (PAH) Perylene, were acquired. The results showed that the direct excitation from the LED is very effective and results in much stronger fluorescence compared to excitation through an optical-fiber-coupled LED. The use of a diffuse reflector leads to an increase in the efficiency of the LED-induced fluorescence, which is expressed in an increase in the output light intensity. The obtained results reveal the practical possibility of applying the LED-induced fluorescence from organic dyes as a broadband light source for sample analysis by EEM fluorescence spectroscopy.

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P-42

APPLICATION OF FLUORESCENCE SPECTROSCOPY AND CHEMICAL ANALYSES FOR THE CHARACTERIZATION OF FRUITS FROM EUROPEAN PLUM (*Prunus domestica* L.) VARIETIES

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The comparison of conventional methods with non-invasive methods (including spectral methods) is an up-to-date interdisciplinary topic. Knowledge from agricultural, chemical, and physical sciences is combined in this study.

This study aims to investigate the possibility of using fluorescence spectroscopy for evaluation of the fruit quality. Plum (*Prunus domestica* L.) is a traditional fruit species grown in Bulgaria and Romania. Thus, plum genetic recourses with different ripening time and fruit characteristics, originating from both countries, are used. The standard variety Stanley, which is grown worldwide, is also included.

The emission spectra of the different genotypes were generated using the experimental setups developed based on fluorescent signals. The spectral installation for the generation of emission fluorescence spectra is mobile and has applicability in local product quality assessments. In its optical adjustment, a system engineering approach based on the classical principles of modern optoelectronics was applied. The experimental studies were carried out on eighty samples (10 fruits of each variety) of plum. The plum varieties' fluorescence emission spectra were connected with chemical analyses of sugars, acidity, and pH.

The proposed study includes an analysis related to the optimization of plum quality time with the application of mobile fluorescence spectroscopy. The method is fast, not requiring special preparation of the sample with chemical reagents. The results of this study can be implemented in the breeding process in its initial stages when it is necessary to qualify and select a large set of hybrids in a short time.

SENSING OF PHYSIOLOGICAL REACTIONS OF FERRITIN WITH DIELECTRIC METASURFACES

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Abstract

Ferritin is an iron-storing protein that plays an essential role in biochemical reactions and underlies the existence of all living organisms. It can act as a `buffer' that can alter and restore the iron concentrations to maintain a regular iron metabolism essential to life. By exploiting this mechanism, ferritin can play a crucial role in monitoring and diagnosing neurodegenerative diseases by detecting the threshold concentration of iron. Here, we use the low-loss resonances of nanostructured dielectric metasurfaces to build a label-free, cost-efficient, and non-toxic biosensor for sensing low ferritin concentrations. The optimised SiO_2 metasurfaces underwent a maximum redshift of the far-field resonance as high as 13 nm after the deposition of ferritin. Upon irradiation of UV light on the realisation of Fe (II) from ferritin, our analysis confirmed the ability of the dielectric metasurfaces to detect changes to the ferritin morphology. Exposing the metasurfaces to different UV radiation duration can be utilised as an accurate sensor for physiological changes in proteins. These results guide the future of portable biosensors for real-time and non-invasive monitoring of metabolic activity.

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P-44

Optical properties of lanthanide-doped zirconia core/shell nanoparticles

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Europium and terbium-doped nanoparticles are being studied widely due to their strong emission intensity, sharp emission lines, and long lifetimes [1]. These properties makes europium a good candidate for time-gated imaging, which increases the signal-to-noise ratio by avoiding peptide auto-fluorescence [2]. Lanthanide-doped zirconia nanoparticles have already been proven to lower the detection limit of avidin down to 3.0 nM by using FRET quenching techniques [3].

We recently prepared core/shell structures of sub 5 nm ZrO_2/ZrO_2 and ZrO_2/HfO_2 nanoparticles. If lanthanide-doped nanoparticles are shelled, the emission spectra of europium change: the splitting of the $^5D_0 \rightarrow {}^7F_2$ transition is suppressed (Figure 1A). Also, the biexponential lifetime decay of 1.2 ms and 2.7 ms (at 606 nm) becomes a slower monoexponential decay of 5.3 ms (Figure 1B). These changes in optical properties prove that all the europium ions are in the same chemical environment after shelling. [4]

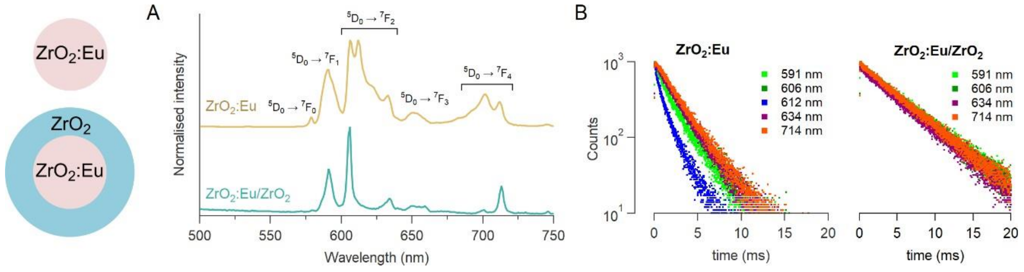

Figure 1: (A) Photoluminescence emission spectra of ZrO_2:Eu cores and ZrO_2:Eu/ZrO_2 core/shells, measured under direct excitation at 394 nm. (B) Lifetime decay at various emission wavelengths for both type of particles. Excitation at 238 nm (maximum of charge transfer bands).

Time-resolved emission spectra and co-doping with lanthanum and niobium give insights into what parameters the optical properties are influenced by: at first glance, oxygen vacancies themselves do seem to have less impact on the emission spectra, and the vicinity to the surface plays a bigger role on color purity.

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P-45

A DFT STUDY OF INTERFACIAL CHARGE TRANSFER COMPLEXESBETWEEN TiO_2 AND A SERIES OF FLAVONOID COMPOUNDS

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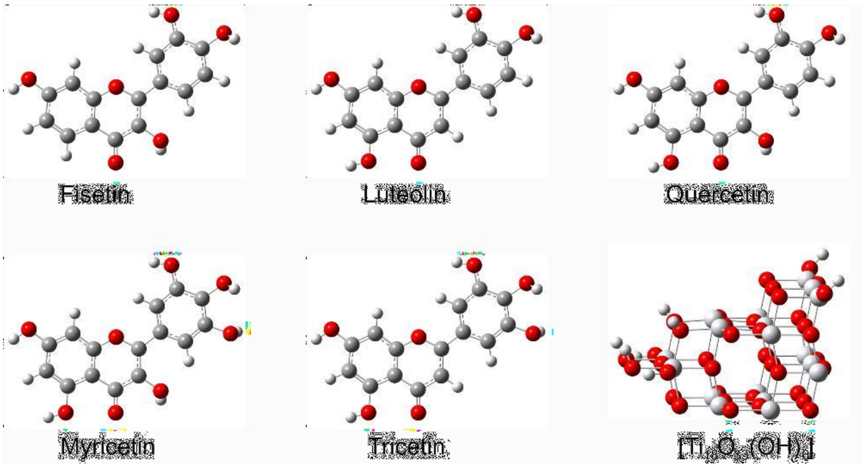
To improve the optical absorption of wide bandgap oxide materials in the visible spectrum range and increase their application in photo-driven processes, the interfacial charge transfer (ICT) complex formation is a straightforward approach [1,2]. Compared to pristine TiO_2 (anatase), the optical absorbance of the synthesized ICT complexes between TiO_2 and five different flavonoids is red-shifted. We used DFT modeling to validate experimental findings and examine the effects of surface modification of TiO_2 nanoparticles by flavonoid compounds. To this end, the $[Ti_{18}O_{33}(OH)_6]$ cluster was employed, whose structure was designed based on the anatase TiO_2 (101) crystal plane. The ground-state geometries of the five $[Ti_{18}O_{31}(OH)_8]$/flavonoid clusters were optimized using the CAM-B3LYP (Coulomb-attenuating method) functional, in combination with valence double-ζ polarized 6-31G(d,p) basis set. Excellent agreement is found between the DFT-calculated bandgap values and the empirically estimated bandgaps of the TiO_2/flavonoid hybrids. In this work, the antioxidant properties of TiO_2/flavonoid ICT complexes are also investigated by using spectroscopic methods and different computational approaches. The bond critical points (BCP) and delocalization indexes (DI) and the thermochemistry of the O-H bonds cleavage indicate enhanced radical scavenging activity of TiO_2/flavonoid hybrids compared to the free flavonoids.



The structures of five flavonoids and TiO_2-cluster used for calculations

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P-46

Luminescence of Eu doped material incorporated into PMMA fiber

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Keywords: Europium, PMMA, luminescence, films, fiber, niobates

This study is focused on uncovering and characterizing the variables influencing the luminescence of PMMA fiber containing Eu(III) dopants. For the purpose of this work $YNbO_4$:Eu is produced through a solid-state synthesis and effectively integrated into a PMMA solution. This solution is then converted into fibers of 1µm diameter using an electrospinning apparatus. Over time, the collected fibers develop into a film, as depicted in Figure 1a. The emission spectra of the samples exhibit a significant intensity, prominently featuring a characteristic red emission attributed to the Eu^{3+} ions (Figure 1b).

Hybrid materials possessing optical attributes are increasingly garnering attention, particularly in sensing, imaging, and energy applications. The potential to manipulate the organic-inorganic structure presents promising opportunities for advancing efficient luminescent devices within these hybrid materials.

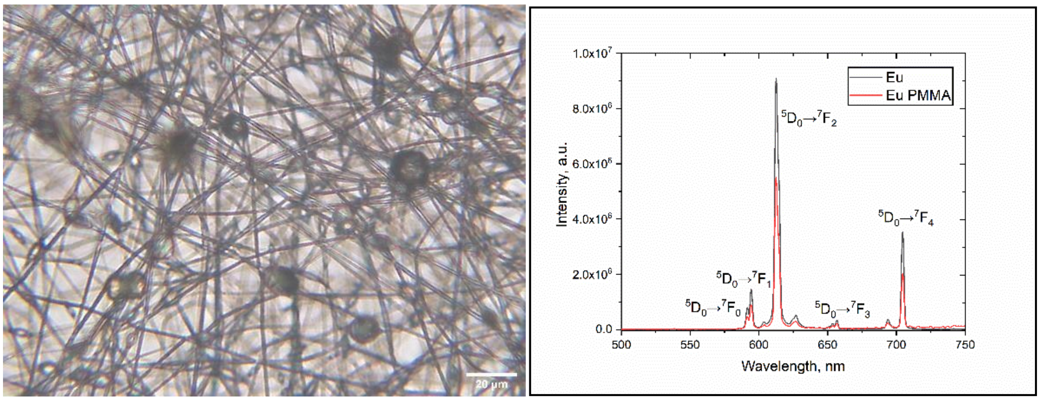

Figure 1. a) A microscopic image of the sample captured at 40x magnification b) Emission spectra of $YNbO_4$:Eu with and without PMMA under 394nm excitation

P-47

IMPROVING SENSITIVITY OF LUMINESCENCE THERMOMETRY WITH $YNbO_4:Sm^{3+}$ BY EXPLOITING EMISSION FROM HIGH ENERGY $^4G_{7/2}$ EXCITED LEVEL

Ljubica Đačanin Far, Aleksandar Ćirić, Katarina Milenković, Mina Medić, Jovana Periša,
Tatjana Dramićanin, Miroslav Dramićanin
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The luminescence intensity ratio (*LIR*) is the most widely used method of luminescence-based thermometry. It usually involves the ratio of two closely positioned emissions of a lanthanide ion originating from the two thermalized excited levels, and its value is defined by the Boltzmann-type equation [1]. In this approach, the relative sensitivity of a temperature reading depends directly on the energy difference between adjacent excited levels. One way of increasing the relative temperature sensitivity is by using the higher excited energy levels with a larger energy gap. However, drawbacks may arise, as these levels tend to have very low intensities, especially at lower temperatures, shortening the usable temperature range and reducing the overall temperature resolution [2].

We obtained a good temperature sensitivity around 500 K using the traditional energy levels of Sm^{3+} in our previous research on samarium-doped yttrium niobate, prepared by a simple solid-state reaction [3]. Hereby, we prepared powders of $YNbO_4:Sm^{3+}$ (6 mol%) using a vibrational ball mill for homogenization and thermal treatment for solid-state reaction between the precursors. For the first time, we used the higher excited energy level of Sm^{3+} — the $^4G_{7/2}$ level — for the *LIR* analysis. The results proved that relative sensitivity within the 500–650 K temperature range doubled, compared to the one obtained using the $^4F_{3/2}$ excited level.

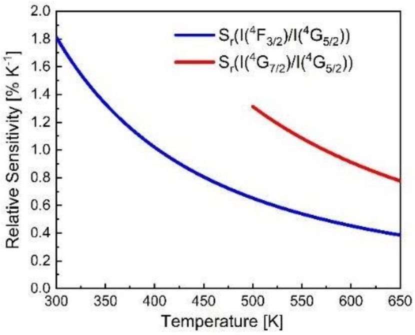

Figure 1. Relative temperature sensitivities obtained by *LIR* analysis using excited levels: $^4F_{3/2}$ (blue curve) and $^4G_{7/2}$ (red curve)

References:
[1] S.A. Wade, S.F. Collins, J. Appl. Phys. 94 (2003) 4743–4756.
[2] A. Ćirić, J. Aleksić, T. Barudžija, Ž. Antić, V. Đorđević. M. Medić, J. Periša, I. Zeković, M. Mitrić, M.D. Dramićanin, Nanomat. 10 (2020) 627(10pp).
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Acknowledgment

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P-48

Exploring Luminescence Thermometry Using Principal Component Analysis: Insights from Pr^{3+}-Doped YF_3

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Luminescence thermometry has gathered significant attention for its non-invasive and highly sensitive temperature sensing capabilities, crucial in diverse fields such as biomedical sciences and materials engineering. This study focuses on the luminescence properties of Pr^{3+}-doped YF_3 material as a promising candidate for advanced temperature sensing applications, employing principal component analysis (PCA) to enhance spectral analysis.

Pr^{3+}-doped YF_3 powders were produced by fluorinating oxides with NH_4HF_2 under mild sintering conditions in an Ar-10%H_2 reducing environment. The material has an orthorhombic crystal structure, as evidenced by X-ray diffraction. The morphology exhibits micron-sized agglomerates of quasi-spherical nanoparticles with a wide range of particle sizes, average around 120 nm.

Pr^{3+} demonstrates versatile luminescence across the ultraviolet, visible, and deep-red spectra, attributed to its inter-configurational ($4f5d \rightarrow 4f^2$) and intra-configurational ($4f^2 \rightarrow 4f^2$) emission transitions, which are markedly influenced by host materials. The luminescence spectra of these nanoparticles were studied over a temperature range of 93–473 K, identifying distinct emission bands attributed to Pr^{3+} ions. Principal Component Analysis (PCA) was employed to analyze the luminescence data, revealing temperature-dependent spectral changes and extracting significant features that reflect thermal sensitivity.

Furthermore, the temperature sensitivity and stability of Pr^{3+}-doped YF_3 nanoparticles were evaluated comprehensively, affirming their potential for accurate temperature sensing within the temperature range of 200-400 K. The findings underscore the robustness and applicability of PCA-assisted luminescence thermometry using Pr^{3+}-doped YF_3 nanoparticles, highlighting their utility in advancing temperature sensing technologies across various scientific and technological domains.

In conclusion, this study not only contributes to the fundamental understanding of luminescence thermometry mechanisms but also positions Pr^{3+}-doped YF_3 nanoparticles as promising candidates for next-generation temperature sensing devices, offering insights into their practical implementation and future research directions.

Acknowledgment
This research was supported by the Science Fund of the Republic of Serbia, #GRANT No 7017, TECHNOLOGY FOR REMOTE TEMPERATURE MEASUREMENTS IN MICROFLUIDIC DEVICES – REMTES. Authors acknowledge funding of the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia under contract 451-03-66/2024-03/ 200017.

P-49

Effect of Eu^{3+} doping on structure transitions in $Y_2Mo_3O_{12}:Eu^{3+}$ and its application as temperature sensing probe

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A set of Eu^{3+} -doped molybdates, $Y_{2-x}Mo_3O_{12}:xEu^{3+}$ (x = 0.04; 0.16; 0.2; 0.4; 0.8; 1; 1.6; 2) were synthesized by an optimized solid-state method. Their structural, diffuse reflectance, luminescent emission, and lifetime characteristics were analyzed as a function of Eu^{3+} ions concentration. Temperature-dependent luminescence properties of the sample with the highest red Eu^{3+} emission, $Y_2Mo_3O_{12}$: 80 mol% Eu^{3+} were investigated as well. XRD results showed a single orthogonal phase obtained by doping with 2 and 8 mol% of Eu^{3+} ions. Single tetragonal structures were identified by doping with 50 and 80 mol% of Eu^{3+} ions. After doping with 100 mol% Eu^{3+} we collected a single, α-$Eu_2Mo_3O_{12}$. Luminescence thermometry showed good value of relative sensitivity, Sr = 2.8 % K^{-1} at 300 K (see Figure 1.). So, for the first time, here we talk about the appearance of the structural orthorhombic-tetragonal transition in $Y_{2-x}Mo_3O_{12}:xEu^{3+}$ caused by distinct concentration of Eu^{3+} ions and single tetragonal phase of doped $Y_2Mo_3O_{12}$: 80 mol% Eu^{3+} that has good sensing properties and can be very convenient for future application in temperature sensing technology. Due to the high energy gap this Eu^{3+} doped sensor probe is best employed for higher temperatures, $S_r = 0.99$ % K^{-1} at 500 K.

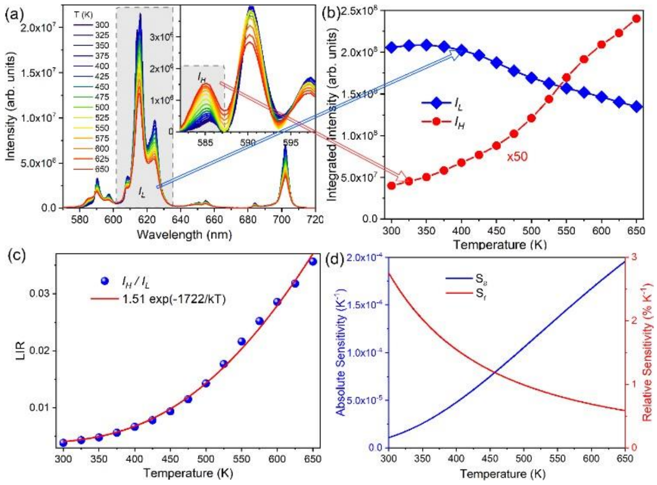

Figure 1. (a) Temperature-dependent $Y_2Mo_3O_{12}$:80mol%Eu^{3+} emission spectra. (Inset) separation of $^5D_1 \rightarrow {}^7F_3$ transition by peak sharpening method. (b) Integrated intensities of $^5D_0 \rightarrow {}^7F_2$ and $^5D_1 \rightarrow {}^7F_3$ emissions, (c) their LIR and fit to the Boltzmann relation, and (d) corresponding absolute and relative sensitivities. The fits are performed by LumThools. [1]

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P-50

MICROWAVE-ASSISTED SOLVOTHERMAL METHOD FORRbY_3F_{10} DOPED WITH Eu^{3+}

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Lanthanide-doped nanoparticles are increasingly utilized in various industries, including bioimaging, thermometry, sensors, and lighting. Photosynthetically active radiation (PAR) refers to the portion of the light spectrum that plants use for photosynthesis, encompassing wavelengths from 400 to 700 nm. The development of LEDs that convert electrical energy into PAR has gained popularity, highlighting the importance of advanced nanoparticle synthesis in optimizing lighting solutions.

The selection of host material is crucial for achieving intense and efficient luminescence in nanoparticles. Fluoride hosts are often preferred due to their relatively low phonon energies, which minimize non-radiative energy losses and enhance luminescence efficiency. Ternary fluoride systems allow for a variety of compositions, which can be tuned to optimize luminescent properties.

Using the microwave-assisted solvothermal method, we synthesized the fluoride host material RbY_3F_{10} doped with Eu^{3+}. This approach offers several advantages over previously reported methods: the use of soluble salts as precursors instead of highly corrosive HF. Additionally, the combination of microwaves with the classic solvothermal technique allows for synthesis on an hour timescale, in contrast to the days typically required by traditional solvothermal methods.

The use of a water/ethylene glycol mixture as a solvent can significantly influence the solubility and reactivity of the precursors. By varying the chelating agents like EDTA, Na_2EDTA, and citric acid we can control the coordination environment around the metal ions. Also, different pH levels can lead to variations in the ionic species present, which can influence the nucleation and growth of the crystals.

It was discovered that the combination of EDTA and citric acid at particular pH levels provided the optimal conditions for pure phase RbY_3F_{10} doped with Eu^{3+}. According to X-ray diffraction measurements, the phosphor crystallizes in a cubic form with a Fm-3m (225) space group. Powder morphology was revealed by scanning electron microscopy to be spherical particles in the nanodomain. Under 405 nm excitation wavelengths, the emission spectra show dominant Eu^{3+} emission peaks in the orange, red, and deep-red spectral regions. Up to 50 mol% of the concentration of Eu^{3+} is reached before the intensity of the emission of Eu^{3+} increases but extra crystal phase becomes apparent. The results of our study indicate that RbY_3F_{10}:Eu phosphors show potential for use in PAR lighting technology because of their strong emissions in the red and deep-red spectral regions.

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P-51

SYNTHESIS AND PHOTOLUMINESCENT PROPERTIES OF Bi^{3+}-CODOPED $SrF_2:Eu^{3+}$ PHOSPHOR NANOPARTICLES

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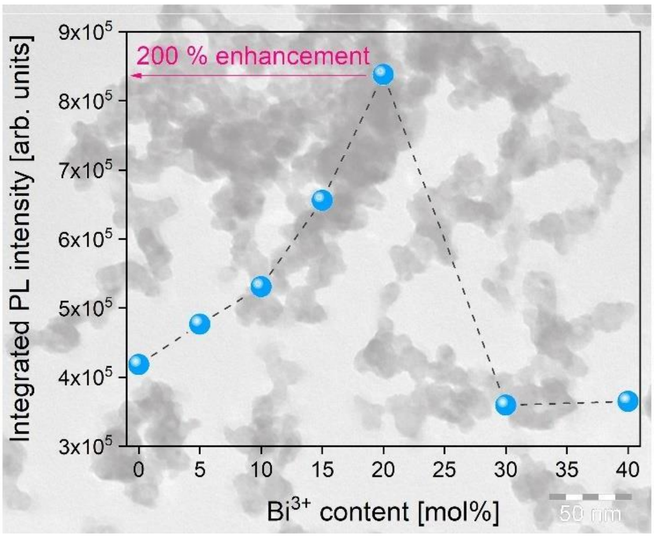
The trivalent europium ion (Eu^{3+}) is a well-known luminescence center with narrow peaks in the red emission range originating from the 4*f*–4*f* transitions, making it an appropriate phosphor for horticultural LEDs. Co-doping with Bi^{3+}, which acts as a sensitizer, enhances Eu^{3+} emission under UV and blue irradiation. Herein, we report the improved photoluminescence properties of Eu^{3+}-doped, Bi^{3+}-sensitized SrF_2 phosphors. Samples with optimized 10 mol% Eu^{3+} and various Bi^{3+} concentrations (5, 10, 15, 20, 30, and 40 mol%) were prepared using the solvothermal microwave-assisted method. X-ray diffraction analysis showed that all phosphors crystallize in a cubic structure with an Fm-3m (225) space group. Transmission electron microscopy shows that samples comprise well-defined nano-sized sphere-like particles with an average size of around 20 nm. Upon 265 nm excitation photoluminescence spectra show characteristic Eu^{3+} emission, with the most intense $^5D_0 \rightarrow {}^7F_1$ orange followed by $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$ red and $^5D_0 \rightarrow {}^7F_4$ deep- red emissions. The emission intensity increases with the increase of Bi^{3+} concentration up to 20 mol%, after which emission decreases. The integrated intensity of Eu^{3+} emission in the 20%Bi^{3+} co-doped SrF_2 is more than two times larger compared to the Bi^{3+}-free sample. Our findings demonstrated that Eu^{3+}-doped, Bi^{3+}-sensitized SrF_2 phosphors have considerable potential for application in plant lighting technology.



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P-52

Advancing luminescence thermometry: Employing multiple fluorescence intensity ratios of $Y_3Al_5O_{12}$:Er^{3+}/Mn^{4+} nanocrystals for supersensitive temperature sensing

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The potential of Er^{3+} and Mn^{4+} co-doped $Y_3Al_5O_{12}$ for luminescence intensity ratio (LIR) thermometry is investigated. The sample was prepared by the modified Pechini method, and the cubic structure was confirmed by X-ray diffraction with an average crystallite size of ~ 23 nm. Temperature-dependent photoluminescent emission spectra (λ_{exc} = 380 nm, 200-450 K temperature range) of the co-doped sample consist of emission bands in the green spectral region originating from Er^{3+} transition, and red spectral region from Mn^{4+} transitions. Results show a rise in the emission intensity of the Er^{3+} $^2H_{11/2}\rightarrow{}^4I_{15/2}$ transition, while the intensity of the Er^{3+} $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition slowly decreases with temperature increase. At the same time, the emission intensity of the Mn^{4+} $^2E\rightarrow{}^4A_2$ transition shows a sharp decrease. The luminescence intensity ratio, the most frequently exploited luminescent thermometry readout method, was tested using: i) emissions from thermalized $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^2H_{11/2}\rightarrow{}^4I_{15/2}$ Er^{3+} ions transitions (LIR1) ii) emissions from Er^{3+} $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition and the Mn^{4+} $^2E\rightarrow{}^4A_2$ manyfold (LIR2), and iii) emissions from Er^{3+} $^2H_{11/2}\rightarrow{}^4I_{15/2}$ transition and the Mn^{4+} $^2E\rightarrow{}^4A_2$ manyfold (LIR3), with relative sensitivities of 1.13 $\%K^{-1}$ at 300 K, 6.45 $\%K^{-1}$ at 300 K, and 8.01 $\%K^{-1}$ at 300 K, respectively. LIR2 and LIR3 have about 5- and 6-times greater sensitivity than LIR1 in the whole range, respectively.

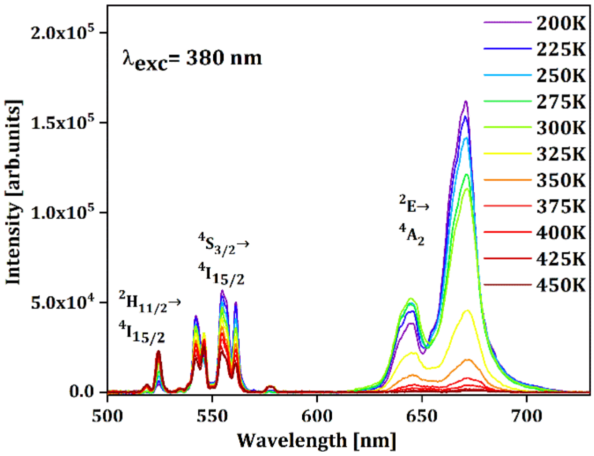

Figure 1. Temperature-dependent emission spectra of $Y_3Al_5O_{12}$: Er^{3+}, Mn^{4+} sample recorded under 380 nm excitation.

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SYNTHESIS, LUMINESCENT PROPERTIES, AND THERMAL STABILITY OF Eu^{3+}-DOPED Sr_2GdF_7 RED-EMITTING NANOPHOSPHOR FOR HORTICULTURE LEDs

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Eu^{3+}-activated inorganic phosphors are traditionally used for general lighting and displays because they usually emit intense orange ($^5D_0 \rightarrow {}^7F_1$) or red ($^5D_0 \rightarrow {}^7F_2$) light with a wavelength shorter than 630 nm. However, Eu^{3+}-activated phosphors with a dominant deep-red emission due to $^5D_0 \rightarrow {}^7F_4$ transition are relatively rare and such special features of Eu^{3+} luminescence mainly meet the need of phytochrome photoreceptors in plants. Herein, the hydrothermal synthesis method is used to prepare Eu^{3+}-activated Sr_2GdF_7 nanophosphors. Transmission electron microscopy shows quasi-spherical nanoparticles with the average particle size estimated to be ~24 nm. Unlike other Eu^{3+}-activated phosphors, photoluminescent measurements show strong red emission with intensity continually increasing with the Eu^{3+} content from 5 mol% to 80 mol%, without concentration quenching. The most noticeable emission peaks are around 600 nm (red) and 700 nm (deep red), with the latter being more pronounced. The temperature-dependent photoluminescent measurements in steady-state and time-domain demonstrate excellent stability of nanophosphors. The $Sr_2Gd_{0.95}Eu_{0.05}F_7$ sample exhibits a lifetime and emission intensity almost completely temperature-independent up to 200 °C, while the decrease in both values is noticed for higher doping concentration in the $Sr_2Gd_{0.2}Eu_{0.8}F_7$ sample. However, the temperature stability of all samples is high up to around 100°C, which is the manufacturer's maximum operating temperature for LEDs, or up to 150°C, as commonly reported in the literature. For the most intense $Sr_2Gd_{0.2}Eu_{0.8}F_7$ sample the lifetime and emission intensity at 100°C remain at 95% and 83% of its initial value at room temperature, respectively, showing a slow reduction trend. This rare combination of temperature stability, high efficiency, and the rare case of dominant deep-red emission label these nanoparticles as potential phosphors for a variety of applications. To show the application potential of this system in LEDs, the powder sample with the highest emission intensity, $Sr_2Gd_{0.2}Eu_{0.8}F_7$, was mixed with a ceramic binder and placed on top of a 365 nm near- UV chip.

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Temperature stability of luminescent Eu^{3+}-activated Sr_2GdF_7 colloid incorporated in PVA fiber

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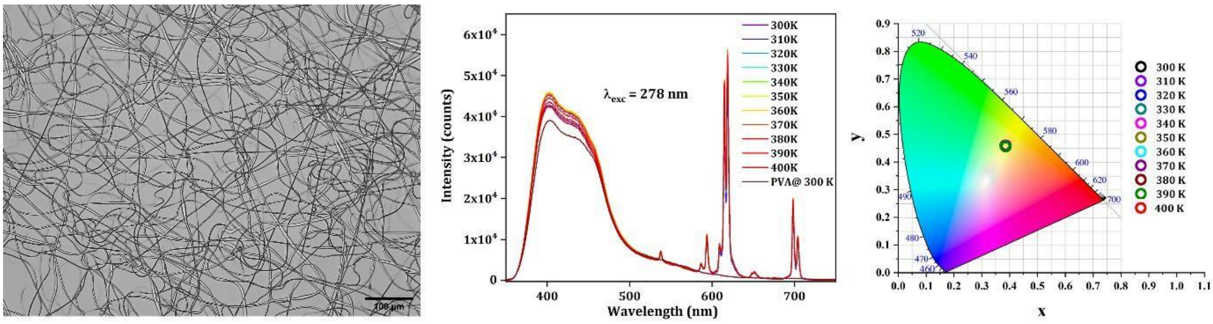
In this work, the hydrothermal synthesis was used to prepare Eu^{3+}- activated Sr_2GdF_7 colloid (SGF:Eu). XRD analysis performed on the powder obtained from colloid confirmed that SGF: Eu crystallizes in the cubic crystal structure. The colloid was mixed with PVA solution and converted into 1μm diameter fibers by electrospinning method (SGF:Eu@PVA). The collected SGF:Eu@PVA fibers in a thin film form were further characterized by photoluminescent spectroscopy. Temperature-dependent photoluminescent emission spectra (λ_{exc} = 278 nm, 300-400 K temperature range) showed strong emission characteristics for Eu^{3+} ions in the red spectral region, as well as wide PVA emission in the blue spectral region. It can be concluded from the obtained spectra that there is no significant change in the emission intensity with the temperature alteration, indicating that the fiber is temperature stable in the measured range. CIE chromaticity coordinates were derived from the photoluminescent spectra and for all the temperatures, CIE coordinates are almost identical ($x = 0.38$, $y = 0.46$) and placed in the yellow-greenish portion of the diagram. These results indicate that there is a potential usage ofthis phosphor for applications requiring stable luminescent properties under varying conditions.



(a) (b) (c)

Figure 1. (a) SGF:Eu@PVA fibers, (b) Temperature-dependent photoluminescent emission spectra (λ_{exc} = 278 nm, 300-400 K temperature range), (c) CIE diagram with calculated coordinates.

Acknowledgment:

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P-55

SYNTHESIS AND LUMINESCENT PROPERTIES OF Pr^{3+}-DOPED Sr_2LaF_7 PHOSPHOR NANOPARTICLES

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Herein, the hydrothermal synthesis is used to prepare Pr^{3+}-activated Sr_2LaF_7 phosphor nanoparticles with the following composition $Sr_2La_{1-x}Pr_xF_7$ (x = 0.002, 0.01, 0.02, 0.03, 0.05. 0.10, and 0.25). X-ray diffraction confirmed a cubic structure with the Fm-3m space group. Transmission electron microscopy shows quasi-spherical nanoparticles with the average particle size estimated to be ~32 nm. The room temperature diffuse reflectance of the samples recorded in the 350–800 nm range shows typical optical features of Pr^{3+} which correspond to the $^3H_4 \rightarrow {}^3P_{0,1,2}$ (broadband from 425 to 500 nm) and $^3H_4 \rightarrow {}^1D_2$ (band positioned around 590 nm) electronic transitions. Visible emissions from Pr^{3+} electronic transitions were detected under 450 nm excitation. Pr^{3+}-doped Sr_2LaF_7 shows a strong blue emission (from the $^3P_0$ to $^3H_4$ state) accompanied by weaker green ($^3P_{0,1}$ to $^3H_5$), red (from the $^3P_{0,1,2}$ to $^3H_6$ + $^1D_2$ to $^3H_4$ and $^3P_1$ to $^3F_3$ + $^3P_0$ to $^3F_2$ states), and deep-red (from the $^3P_{0,1}$ to $^3F_4$ state) emissions. The relative intensities of blue and red emission can be modified by Pr^{3+} concentrations, which give rise to overall emission colors. The sample Sr_2LaF_7: 2 mol% Pr^{3+} exhibits the most intense emission; however, the emission quenches as the Pr^{3+} concentration increases. In addition, the warm white emission was obtained for heavily doped Sr_2LaF_7: 25 mol% Pr^{3+} sample with CIE chromaticity coordinates of (0.357, 0.364) and a correlated color temperature of 4634 K. These findings indicate that $Sr_2LaF_7:Pr^{3+}$, as a single-phase phosphor, has promising application potential for white light-emitting diodes. Our future work will focus on mechanisms interpretation responsible for Pr^{3+} *f*-*f* emissions in Sr_2LaF_7 and similar rare earth fluoride hosts.

Figure 1

Acknowledgment

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P-56

Synthesis, structure, and luminescent properties of Eu^{3+} doped $BaIn_2O_4$ powders

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$BaIn_2O_4$ was synthesized by a solid-state process at high temperatures and doped with different concentrations of Eu^{3+} ion (x=1, 3, 5, 7, 10). The pure structure of this material was identified using the method of X-ray diffraction. The $BaIn_2O_4$ sample was found to have a monoclinic structure with space group P21/a determined by XRD measurement. SEM analysis was also done. ***Figure 1*** shows the photoluminescence (PL) of the $BaIn_2O_4$ sample at various Eu concentrations, suggesting that the emission intensity increases with increasing Eu concentration. The emission at 614 nm indicates that the highest intensity occurs at a doping concentration of 10% in Eu^{3+}. $BaIn_2O_4$ doped Eu^{3+} phosphors are considered to be promising luminescent material for WLEDs.

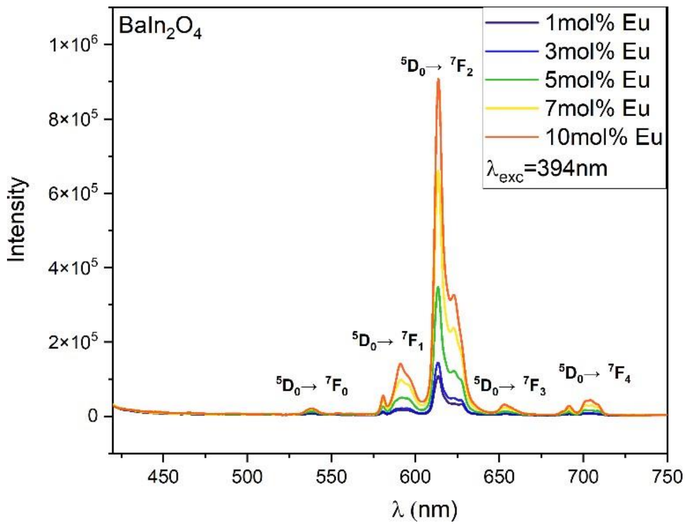

Figure 1. Effect of dopant concentration on photoluminescence emission $BaIn_2O_4$: Eu^{3+}

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P-57

Highly water-soluble and biocompatible hyaluronic acid functionalized upconversion nanoparticles as ratiometric nanoprobes for label-free detection of nitrofuran and doxorubicin

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Antibiotic detection is crucial and challenging because the widespread consumption of antibiotics has shown extensive harmful effects on food, environment and human health. Here, we propose highly water-soluble and biocompatible hyaluronic acid (HYA) functionalized upconversion nanoparticles (UCNPs) for ratiometric detection of multiple antibiotics. The ultraviolet upconversion luminescence (UCL) from UCNPs was significantly quenched by nitrofurazone (NFZ)/nitrofurantoin (NFT), and blue UCL was quenched by doxorubicin (DOX), while red UCL remained unchanged for internal reference. The UCNPs-HYA nanoprobes exhibit excellently sensitive and selective NFZ, NFT and DOX detection in linear range of 2.5–100 μM, 2.5–80 μM, and 2.5–200 μM with the LOD at 0.28 μM (55 μg/kg), 0.20 μM (48 μg/kg) and 0.17 μM (97 μg/kg), respectively. The nanoprobes achieved detecting real samples of NFZ in lake water, liquid milk and chicken meat with satisfactory results, and UCL bioimaging of DOX in HeLa cells. The UCNPs-HYA ratiometric nanoprobes are promising for food samples detection and potential biosensing in the cellular environment.

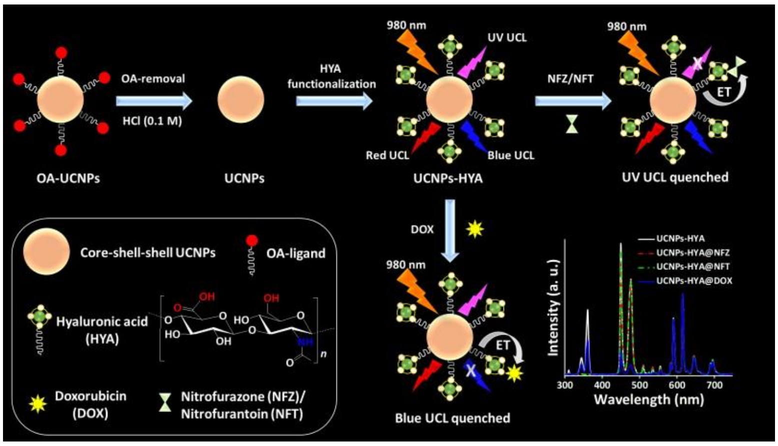

Fig. 1. Schematic representation of the UCNPs-HYA ratiometric UCL nanoprobe for highly selective and sensitive multi-antibiotics sensing of NFZ, NFZ and DOX.

Acknowledgement

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P-58

ULTRA-BROADBAND NEAR-INFRARED EMISSION IN PEROVSKITE-LIKE $Mg_4Sb_2O_9:Cr^{3+}$ PHOSPHORS

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Near-infrared (NIR) spectroscopy based on phosphor-converted NIR light-emitting-diode (LED) has extensive applications in modern life, stimulating the exploration of ultra-broadband NIR phosphors with high efficiency. Herein, Cr^{3+}-doped perovskite-like $Mg_4Sb_2O_9$ phosphor was synthesized, which exhibits a NIR emission with peak wavelength of 855 nm, and a full width at half maximum of about 207 nm. Upon 442 nm excitation, the quantum efficiency and absorption efficiency were determined to be 59.1% and 48.3%, respectively; while the luminescence intensity remained 61.5% of room temperature at 373 K, indicating an excellent efficient and a moderate thermal stability of this material. The fabricated NIR pc-LED through combining the optimized phosphor with a 455 nm LED chip presents an output power of 20.1 mW and a photoelectronic conversion efficiency of 3.6% under a driving current of 175 mA. These results suggest that $Mg_4Sb_2O_9:Cr^{3+}$ phosphor with excellent luminescent performance may have good potential for applications in NIR pc-LEDs.

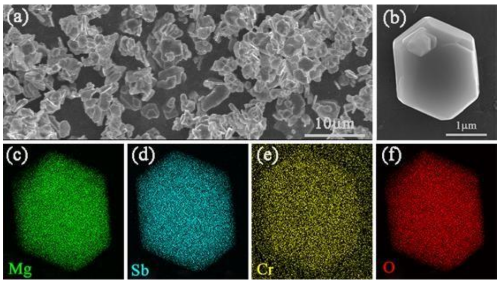

Fig. 1 SEM image and EDS mapping images of $Mg_{3.92}Cr_{0.08}Sb_2O_9$.

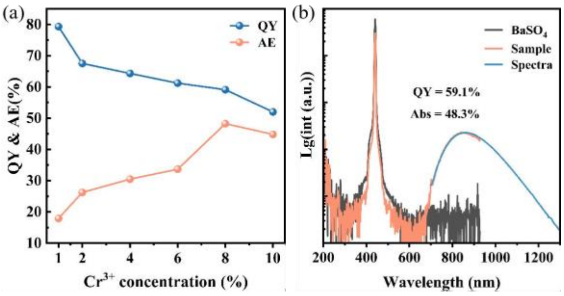

Fig.3. (a) Cr^{3+} concentration dependence of the photoluminescence QY and absorption efficiency of $Mg_{4-x}Sb_2O_9:xCr^{3+}$ phosphors. (b) The photoluminescence quantum yield spectrum of $Mg_{3.92}Sb_2O_9:0.08Cr^{3+}$ phosphor.

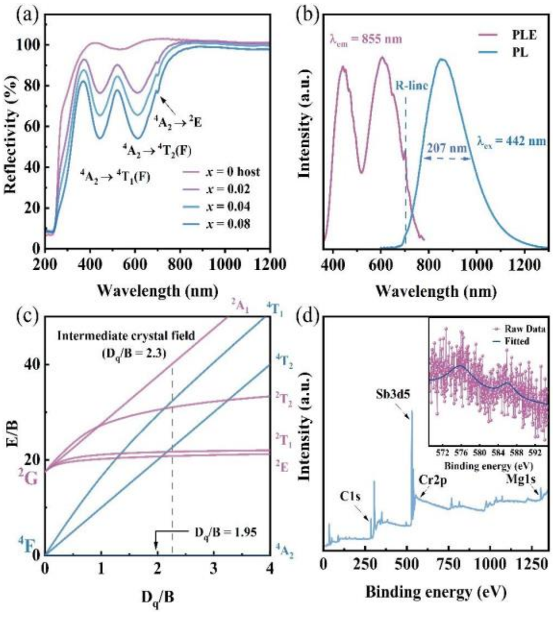

Fig.2. (a) Diffuse reflection spectrum of $Mg_{4-x}Sb_2O_9:xCr^{3+}$. (b) PLE spectrum, and PL spectrum of $Mg_{3.92}Sb_2O_9:0.08Cr^{3+}$. (c) Tanabe–Sugano diagram for the Cr^{3+} in $Mg_4Sb_2O_9$. (d) XPS survey spectrum and high-resolution XPS spectra of $Mg_{3.92}Sb_2O_9:0.08Cr^3$

LUMINESCENCE MANOMETRY BASED ON Ni^{2+} IONS EMISSION

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Automated pressure measurements, allowing for remote, non-contact, real-time readouts, are increasingly in demand, and techniques to achieve this are being actively explored. Optical pressure sensing, which relies on utilizing pressure-dependent spectroscopic properties of phosphors, is a promising approach to meet these requirements while ensuring high precision and accuracy in the pressure measurements. The potential of luminescence manometry has been demonstrated with sensors based on luminescence of lanthanide and transition metal ions. [1,2] Among transition metal ions, Ni^{2+} ions seems to be ideal candidates for use as luminescent manometers due to the strong dependence of the energy of $^3T_{2g}$ excited state of the Ni^{2+} on the strength of the crystal field, which correlates with metal-oxygen distances that are influenced by applied pressure. [3] Given the lack of literature on the use of Ni^{2+} ions in pressure sensing, our studies aim to fill this gap. We carried out research on the pressure-dependent properties of spinel $ZnGa_2O_4$ doped with Ni^{2+} ions. The emission band associated with the $^3T_{2g}\rightarrow{}^3A_{2g}$ electronic transition of Ni^{2+} ions was utilized for pressure sensing. Due to the large spectral shift of the emission band, an innovative for luminescence manometry ratiometric approach based on the luminescence intensity ratio of a broad emission band integrated into two spectral ranges was utilized. The results obtained demonstrated the high potential of Ni^{2+} ions in pressure sensing, thus establishing a new class of highly sensitive luminescent manometers.

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P-60

STRUCTURAL, SPECTROSCOPIC AND MAGNETIC PROPERTIES OF TRINUCLEAR *Ln*$^{3+}$ COORDINATION COMPOUNDS WITH A CARBOXAMIDE DERIVATIVE

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The development of modern technologies is impossible without an extensive search for novel multifunctional materials, refinement of the existing ones, as well as the expansion of theoretical knowledge. Lanthanide (*Ln*$^{3+}$) chelates are an example of multifunctional compounds enabled to combine luminescent properties with the single-ion magnets (SIM) behavior. This is due to the 4f electron configuration, which results in a large unquenched orbital moment and a weak interaction of the crystal field on *Ln*$^{3+}$ ions. For the advance of *Ln*-based bifunctional SIMs, it is essential to use the tools of theoretical chemistry that will allow rationalization of experimental outcomes and generalization of mutual magnetic- luminescence correlations.

The work concerns the effect of an alkali metal cation on the structural, spectroscopic and magnetic properties (SIM – single ion magnet) of *Ln*$^{3+}$ compounds with carboxamide derivative. The influence of the cation was determined for two series of $[M_2Ln(L)_4(CF_3SO_3)(DMF)]$ ($M^+ = Na^+, Cs^+$; $Ln^{3+} = Dy^{3+}, Eu^{3+}, Gd^{3+}, Sm^{3+}, Tb^{3+}$; $L = [C_4H_3N_2\text{-}C(O)\text{-}N\text{-}P(O)(C_6H_5)_2]^-$; DMF = N,N-dimethylformamide) compounds. Crystal structure, photophysical data (emission lifetimes (τ), radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates, experimental intensity parameters (Ω_λ), energy transfer rates, emission quantum yields (theoretical and experimental), emission sensitization efficiencies (η)) as well as magnetic parameters (the dynamic and static susceptibilities and magnetizations) have been determined for $[Cs_2Ln(L)_4(CF_3SO_3)(DMF)]$. They have been discussed in detail and compared with the structural-luminescence-magnetic properties of $[Na_2Ln(L)_4(CF_3SO_3)(DMF)]$ [1].
In-depth analysis of experimental and theoretical results provided insight into the magneto-optical and structural correlation, facilitating the bifunctional compounds design.

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P-61

PHONON PROPERTIES OF NANODIMENSIONAL Cr_2O_3 THIN FILMS

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Cr_2O_3 thin films on glass substrate were prepared by reactive sputtering technique. Here we investigate the influence of deposition parameters on both thickness and optical features on the films.

Structural and optical properties were investigated applying atomic force microscopy (AFM), UV-Vis, Raman and far–infrared spectroscopy. In the analysis of the far – infrared reflection spectra, numerical model for calculating the reflectivity coefficient for system which includes films and substrate has been applied. Density functional theory (DFT) is used in phonon assignment. We reveal the existence of surface optical phonon (SOP) mode, too.

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PLASMON-PHONON INTERACTION AND SURFACE OPTICAL MODE IN $Cd_{1-x}Fe_xTe_{1-y}Se_y$ SINGLE CRYSTALS

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The interaction between electrons and phonons represents a notable phenomenon in the realm of condensed matter physics, exerting a substantial influence on diverse electronic and optical characteristics of materials [1]. Within this context, an exhaustive investigation of the Raman and Far – Infrared reflectivity spectra of $Cd_{1-x}Fe_xTe_{1-y}Se_y$ single crystals can yield valuable insights into the various impacts of Plasmon – phonon interactions on the fundamental physics of II – IV semiconductors.

Spectral analysis was executed employing a suitable fitting procedure. In the analysis of Far – infrared spectra, a dielectric function incorporating the presence of Plasmon – LO phonon interaction was employed [2]. Three principal lines in the spectra, contingent upon the composition, were discerned at approximately 140 cm^{-1}, 170 cm^{-1} and 200 cm^{-1}. 140 cm^{-1} feature corresponds to the longitudinal – transverse (LO – TO) splitting of the CdTe – like mode. The 170 cm^{-1} feature is associated with CdSe, while the 200 cm^{-1} feature is linked to the local Fe mode. These features were elucidated within the framework of the modified random – element – isodisplacement (MREI) mode [3 – 4]. The calculated phonon frequencies demonstrated a high level of agreement with experimentally determined values.

Additionally, in all samples, a surface layer characterized by a low concentration of free carriers (depleted region) was formed [5]. Consequently, a surface optical mode (SOP) was registered at approximately 150 cm^{-1} in samples with a predominant CdTe component (y less that 15%) and at around 190 cm^{-1} in samples with a majority CdSe content (y greater that 95%).

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Addressing trap depth and distribution in novel $Li_2ZnSn_3O_8$:Dy^{3+} stannatematerials for improvement application of their persistent luminescence

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The development of new inorganic persistent luminescent materials containing rare earth ions as activators has been drawing significant attention for innovative solid-state lasers, biological and forensic markers, thermal sensors, security devices, and other several products in the photonic technology area. In this context, even though the most studied persistent phosphors are rare-earth (RE) doped aluminates, silicates, and sulfides matrices, the study and development of RE^{3+}-doped stannates are equally fundamental since they are inexpensive, thermally stable, and have a favorable band gap to allow the phenomenon of persistent luminescence[1]. Moreover, there is a growing interest in the pursuit of the adjusted synergy between the deployment of energy and time-saving synthesis methods and the enhancement of the optical characteristics of these phosphors, such as a more intense and longer persistent emission, that is required for those photonic applications. In this sense, the Microwave-Assisted Solid-state Synthesis (MASS) method has been highlighted by its efficient punctual heating process, generating high-purity materials, besides being able to be performed using cheap and off-the-shelf equipment[2]. It is also important to notice that, as much as known mechanisms can explain qualitatively the persistent luminescence in inorganic materials, this phenomenon still needs to be studied for the luminescent stannate systems from the perspective of specific material trapping defects depth distribution to be fully understood and exploited[3]. Therefore, in this work, material samples of the novel stannate $Li_2ZnSn_3O_8$:x%Dy^{3+} (x = 0.5, 1.0, 2.5, 5.0, 7.5, 10.0, 12.5, and 15) were prepared by the MASS methodology, employing a domestic equipment, after gridding Li_2CO_3, ZnO, SnO_2, Dy_2O_3 precursor oxides. The materials were characterized by thermal analysis, powder X-ray diffraction, and Raman spectroscopy. The PXRD patterns indicate the formation of the desired $Li_2ZnSn_3O_8$ matrices phases, showing high crystallinity. The persistent luminescence properties of the materials were determined based on cathode-, photo-, and thermoluminescence spectroscopic techniques focusing on the determination of trap density, depth, and nature, which assists in establishing connections between the persistent luminescent behavior and defects in these stannates, facilitating the fine-tuning of materials to suit distinct applications with particular requirements (such as luminescent coating, and anti-counterfeiting tags).

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The more the better: Multiparametric data analysis enhances the performance of Eu^{III}- based thermometers

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Being the foremost thermodynamic state variable, measuring temperature demands meticulous monitoring across a myriad of fields[1]. Its precise measurement holds increasing significance in cutting-edge technologies, such as the processing capability of networked devices. In this context, remote temperature sensing via luminescence thermometry is currently in the spotlight among the available procedures[1]. This method relies on temperature-induced changes in the spectroscopic attributes of an ensemble of probes[2]. Such dependence may lead to variations in the thermal response based on the chosen spectroscopic properties. Mindful of this interplay, the present study endeavors to enhance thermal sensitivities by unifying the traditional ratiometric approach with temperature-independent emission lifetimes through multiparametric data analysis, specifically employing multiple linear and logistic regression. Accordingly, these methods are often used in machine learning to incorporate explanatory variables to forecast the outcome of a response variable. As a proof-of-concept, the phosphor SrY_2O_4:Tb$^{IV/III}$(2at.%),Eu^{III}(9at.%) was selected, with the synthesis method based on a modified Pechini route at 1100 °C/5 h under a partial CO atmosphere. Notably, Tb$^{IV/III}$ was used as a co-dopant to distort the host lattice and amplify the intensity of Eu^{III} emission bands given its spectroscopic inertness in the visible region for the fourthly oxidized state. XRD analysis confirmed the absence of spurious phases, with all peaks assigned to SrY_2O_4. Chemical mapping of the dopants was envisioned through EDS analysis performed on SEM images, which revealed a high dopant homogeneity. However, XPS analysis unveiled a 25/75% Tb^{III}/Tb^{IV} ratio, being this small amount of Tb^{III} undetectable in the emission spectrum. To further mitigate any Tb^{III} emission, the sample emission spectrum was recorded under excitation at the $^5D_2 \leftarrow {}^7F_0$ Eu^{III} 4*f* transition. Examining the phosphor' emission spectrum reveals the characteristic set of $^5D_0 \rightarrow {}^7F_{0-4}$ emission bands, where a thorough inspection enables observing the $^5D_1 \rightarrow {}^7F_2$ Eu^{III} band (541 nm). The thermally coupled nature of $^5D_0/^5D_1$ pair allowed the development of a ratiometric temperature probe with a maximum relative sensitivity (S_r) of 1.2% K^{-1} in the 390 – 500 K range. Simultaneously, using the $^5D_0$ emission lifetime, monitored by the $^5D_0 \rightarrow {}^7F_2$ (612 nm) emission, and $^5D_2 \leftarrow {}^7F_0$ (464 nm) excitation, maximum values of 0.55% K^{-1} were obtained across the same interval. While this result aligns with the existing literature, one may inquire about the sensitivity achievable through integrating both metrics. In this sense, a 2-fold gain (2.4% K^{-1}) was acquired by multiple linear regression of their respective thermometric parameters within the 390 – 460 K interval. Switching to logistic regression, a 2.2-fold enhancement (2.6% K^{-1}) was harnessed across the same temperature range. These outcomes underscore the significance of this approach in advancing luminescence thermometry by improving the thermal sensing capabilities of simple thermometric systems.

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P-65

Light-element based materials for persistent luminescence and photochromic applications

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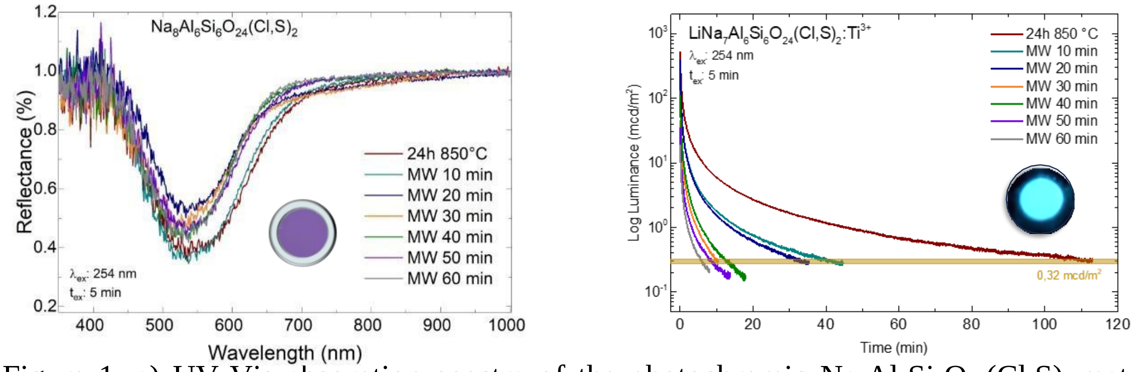
Advanced photonic and luminescent materials have a wide range of applications in modern society, including solid-state lighting and high-energy radiation detectors. However, the majority of commercially available materials for these purposes contain heavy metals, which have a negative impact on the environment. On the other hand, naturally occurring optical minerals, such as hackmanites, have inspired the development of new environmentally friendly alternatives. Natural or synthetic hackmanites with the composition $M_8Al_6Si_6O_{24}(X,S)_2$ (M: Li^+, Na^+; X: Cl^-, Br^-), which contain only light elements, can exhibit photochromism or persistent luminescence (PersL) phenomena, expanding their application potential.[1–3]

In this work, we have demonstrated the versatility of Hackmanite-based compounds prepared by conventional Solid-state and the rapid and energy-saving Microwave-Assisted Solid-State (MASS) methods. The materials were prepared by varying the composition in order to obtain Photochromic or Persistent Luminescent properties. The using of Li^+ and doping with a small amount of Ti^{3+} favors the PersL phenomenon. On the other hand, the no-doped materials presented photochromic properties. Overall, the MASS method allowed the obtention of the material in less than 60 min of synthesis. This is a great advantage when compared with the 24 h of conventional solid-state synthesis.



a) Photochromic

b) Persistent Luminescent

Figure 1. a) UV-Vis absorption spectra of the photochromic $Na_8Al_6Si_6O_{24}(Cl,S)_2$ materials, and b) absolute luminance decay of PersL $LiNa_7Al_6Si_6O_{24}(Cl,S)_2:Ti^{3+}$ materials.

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P-66

EFFECT OF Ca DOPANT CONCENTRATION ON THE VARIATION OF OPTICAL PROPERTIES OF ZrO_2 CERAMICS WITH GREAT PROSPECTS IN THE FIELD OF SOLID OXIDE FUEL CELLS

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The interest to ceramic materials based on zirconium dioxide when used as solid oxide fuel cells is primarily due to their high resistance to thermal expansions characteristic for high-temperature operation modes, as well as a mixed type of conductivity, which determines good indicators of capacitance, and as a consequence, operability. However, despite the great prospects of this class of materials as solid oxide fuel cells, the problem of deformation-induced polymorphic transformations such as m–ZrO_2→t–ZrO_2, t–ZrO_2→c–ZrO_2, can have a double effect on the change of thermophysical and capacitive characteristics of this type of ceramics. To restrain the processes of polymorphic transformations, as a rule, various additives in the form of magnesium, yttrium or calcium oxide dopants are used, the use of which allows to stabilize the crystal structure of zirconium dioxide due to partial substitution of zirconium by dopant, which in turn leads to the formation of stable phases in the composition of ceramics, not subject to polymorphism, the main reason for the occurrence of which, in addition to deformation effects, is the presence of a large number of oxygen vacancies in the composition. This paper presents the results of investigation of the influence of variation of $CaCO_3$ dopant concentration on the processes of polymorphic transformations in ZrO_2 ceramics under variation of synthesis conditions (annealing temperature). To determine the concentration of oxygen vacancies, the method of estimation of changes in the optical density and absorption spectra was applied, on the basis of which the concentration dependences of oxygen vacancies in the composition of ceramics on the concentration of dopant were obtained. It was determined that the increase in dopant concentration leads to more pronounced processes of polymorphic transformations associated with changes in the concentration of oxygen vacancies in the composition, and as a consequence, changes in optical properties.

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VARIABILITY OF THE PHASE COMPOSITION OF OXY-NITRIDE CERAMICS AND ITS INFLUENCE ON OPTICAL AND THERMOPHYSICAL PROPERTIES

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Interest in oxy-nitride ceramics, which have sufficiently high porosity, providing high specific surface area, low density and low coefficient of thermal expansion during prolonged heating allows the active use of such ceramics as high-temperature filters for liquids and gas, heat insulators, catalysts, as well as various optical absorbers and light filters. In this case, the presence of silicon nitride in the composition, as a rule, provides higher thermal conductivity values, in contrast to single- or multi-component oxide ceramics, which have rather low thermal conductivity values.

This paper presents the results of determining the influence of the variation of the phase composition of $(1-x)Si_3N_4 - xAl_2O_3$ ceramics when changing the ratio of nitride and oxide components in a wide range of values, on the determination of optical (width of the forbidden zone, refractive index, metallization criterion, optical density) and thermal conductive (thermal conductivity coefficient, the value of heat losses) properties of ceramics.

According to the assessment of phase transformations in $(1-x)Si_3N_4 - xAl_2O_3$ ceramics at variation of component ratio, it was found that thermal annealing in oxygen-containing medium at Al_2O_3 concentration equal to the order of 0.3 - 0.5 M results in the formation of orthorhombic $Al_2(SiO_4)O$ phase, the increase of contribution at concentrations higher than 0.5 M of which causes the increase of thermal conductivity associated with the concentration dependences of defect inclusions and vacancies. In the course of the conducted studies it was determined that the change in phase composition associated with the formation of $Al_2(SiO_4)O$ phase leads to an increase in the thermal conductivity coefficient from 1.8 to 2.8 W/(m×K), while the displacement of Si_3N_4 phase from the ceramics composition associated with the processes of thermal decomposition of $Si_3N_4 \rightarrow SiO_2$ leads to a decrease in the thermal conductivity coefficient associated with the dominance of Al_2O_3 phase.

At assessment of change of optical density of investigated $(1-x)Si_3N_4 - xAl_2O_3$ ceramics it has been established that dominance in composition of $Al_2(SiO_4)O$ phase at equal molar ratio of ceramics components, leads to increase of optical density up to 0.16, also dominance of Al_2O_3 phase in composition of $(1-x)Si_3N_4 - xAl_2O_3$ ceramics forms additional absorption bands, connected with presence of oxygen vacancies in composition of ceramics.

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Molten Salt Assisted Synthesis of Double Tungstates TowardsOptimized Optical and Morphological Properties

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The density of defects is one of the most important material parameters governing the efficiency of photocatalytic and luminescent materials [1,2]. On the one hand, in these types of materials defects often function as recombination centers for photogenerated charge carriers subsequently reducing the respective quantum efficiency. On the other hand, defects can prove indispensable in some application fields, i.e. they might serve in the surface activation of photocatalysts, and form necessary energetic states in storage phosphors. Therefore, the effective control over defect formation, by means of new and optimized synthetic procedures, has gained renewed interest. Double tungstates and molybdates form a group of luminescent materials well known for some interesting optical properties such as low concentration quenching and high thermal quenching temperatures [3]. In this study several double tungstates were synthesized using a molten salt assisted solid state synthesis resulting in powders of facetted microcrystals. This type of synthesis resulted in products with high optical quality. Furthermore, some double tungstates featuring selected lanthanides were studied in detail regarding their temperature dependent luminescent behavior and their feasibility in the field of lanthanide based luminescence thermometry.

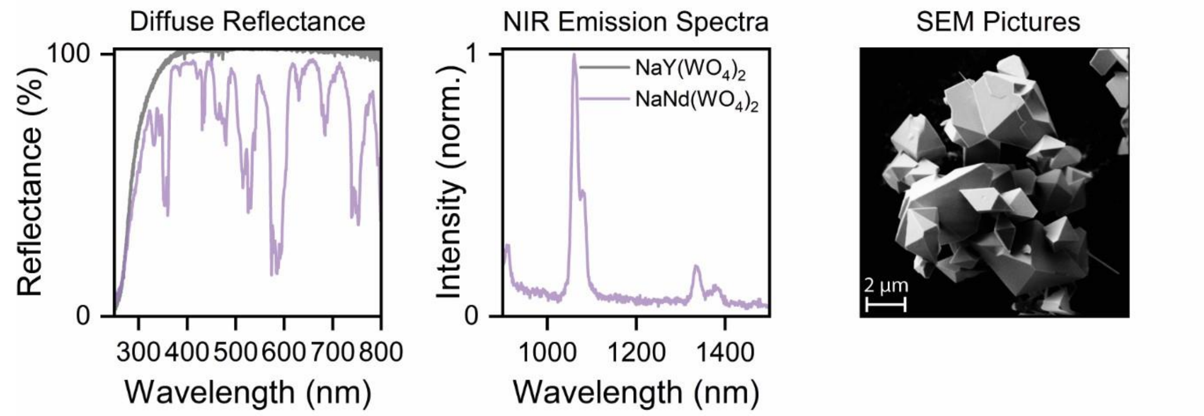

Figure 1: Optical and morphological properties of two exemplary double tungstates synthesized by using a molten salt. Diffuse reflectance spectra of $NaY(WO_4)_2$ and $NaNd(WO_4)_2$ (left). NIR emission spectrum of $NaNd(WO_4)_2$ (middle). Scanning electron microscope image of facetted $NaY(WO_4)_2$ microcrystals (right).

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MACHINE LEARNING USED IN PREDICTION OF UV 5d-LEVELS ABSORPTION OF LUMINESCENT MATERIALS DOPED WITH Pr^{3+} OR Ce^{3+} IONS.

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Artificial intelligence (AI) and Machine learning (ML) become versatile and powerful instruments in complex predictions and smart searches for new materials. Their application in different areas including Material sciences and Materials informatics stimulates the efficient development of various materials, e.g. A Lab - an autonomous laboratory for the solid-state synthesis of inorganic powders [1]. Also, recent research demonstrates a structure-based ML model for emission wavelength prediction in Mn^{4+}-activated fluorides [2]. Other work demonstrates the ML model for describing crystal structures based on interatomic distances - Grouped Representation of Interatomic Distances (GRID) [3].

Considering the mentioned evolution of ML and the potential of ultraviolet (UV) 4f-5d upconversion emission of Pr^{3+} ions for antimicrobial disinfection [4], we developed here several ML instruments that analyze a set of structural data of host materials and predict the 5d-levels absorption of Pr^{3+} and Ce^{3+} dopants. The obtained data are correlated with experimental data of 5d-levels absorption of Pr^{3+} and Ce^{3+} ions in AF_3, A_2O_3 hosts, published earlier by P. Dorenbos [5]. These results will serve in future work for a better understanding of the UV upconversion emission from 4f-5d of Pr^{3+} and Ce^{3+} dopants in various hosts.

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Identification of oxidation states of Ce and Mn in luminescent borosilicate glasses using a combination of EPR and XPS technique

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For fabrication of the luminescent crystalline and glass materials, one of the sensitizer- activator pairs, which is frequently studied is a combination of Ce^{3+} and Mn^{2+} ions. The Mn^{2+} ion has a sensitizing effect. In various glass matrices the intensive luminescence of Ce^{3+} around 350 nm and broad luminescence of Mn^{2+} around 580 nm [1], [2], [3], [4], energy transfer between ions and also the influence of the crystal field on luminescence were studied. The balance between Mn^{2+} and Mn^{3+} is mostly established in the glass, but oxidation states Mn^{4+} and Mn^{5+} have also been detected. Similarly, cerium occurs in Ce^{3+} and Ce^{4+} oxidation states, but only the first of these ions exhibits the indicated luminescence [5]. Since it is clear that both ions can occur in various oxidation states, it is generally necessary to know and be able to influence the oxidation states of the ions in the glass matrix. Absorption and luminescence spectra are often used to determine these states.

In this contribution, we focused on the use of the EPR (electron paramagnetic resonance), XPS (X-ray photoelectron spectroscopy) method in combination with absorption and luminescence spectrometry for the determination of the oxidation states of manganese and cerium in glass matrix. The oxidation states of manganese were monitored by EPR, because Mn^{2+} has a characteristic signal with hyperfine structure. It is also possible to detect Mn^{4+} and Mn^{5+} ions and distinguish them from the Mn^{2+} ion using this method. Mn^{3+} ion generally cannot be detected by this technique. On the other hand, the XPS method is suitable for the detection of oxidation states of cerium and their quantification. For the study, the four sets of glass matrices were prepared. The general composition of the glass was SiO_2–B_2O_3–Al_2O_3– Na_2O–MeO (Me = (Mg, Ca, Ba)). The Ce content was kept constant (1 mol. % CeO_2) and Mn content was changed. Three sets of glasses with 0.2, 1 and 2 mol. % of MnO were prepared. In these individual sets, the variable content of elements affecting the glass basicity was present. In addition, the glasses with 1 mol. % of MnO were also prepared with addition of 1 mol. % of SnO, a reducing agent. Analysis of the glasses using a combination of the above- mentioned methods led to the following conclusions: i) it is possible to determine the oxidation state of cerium ions, b) it is possible to prove the presence of manganese ions $Mn^{2+,}$ $Mn^{3+,}$ $Mn^{4+,}$ in glass c) it is possible to prove the influence of tin on red-ox. balance of both ions.

Acknowledgement: This work was supported by the Czech Science Foundation, grant No. GA23-05507S.

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LUMINESCENT NANOMATERIALS FROM SPRUCE BIOMASS

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Traditional luminescent materials require raw materials derived from fossil resources and complex processing, which has a direct impact on the environment. One of the most important tasks of modern society is to find more renewable and sustainable sources of energy to produce materials. One ideal alternative precursor is lignocellulosic biomass, consisting of cellulose, hemicellulose and lignin. The use of cellulose and hemicellulose has been widely explored and used, while the potential of lignin has not yet been fully explored. Lignin is a natural polymer with a complex aromatic structure such as p-hydroxyphenyl, guaiacyl, and syringyl. It could be a promising source of carbon precursors and its aromatic structure could be a good basis for the synthesis of luminescent materials. However, lignin is not sufficiently used as a precursor for the synthesis of luminescent materials due to its complex and multilayered structure. In our study, we used spruce biomass and isolated lignin, and performed a detailed analysis of the lignin structure. The isolated lignin was then converted into lignin carbon quantum dots, which showed luminescent properties. Luminescent materials produced from spruce biomass are inexpensive and environmentally friendly materials with great potential for further functionalization and application.

Fig. 1. Luminescent nanomaterials prepared from the biomass of spruce.

Acknowledgment: This work was done in the frame of the project “Novel materials based on lignin from biomass with enhanced luminescent activity” (J2-50061), funded by the Slovenian Research Agency (ARIS) and Polish National Science Centre (NCN) under Weave call.

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THEORETICAL MODELING OF ABSORPTION AND EMISSION SPECTRA OF CORE/SHELL QUANTUM DOT

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Investigation of optical properties of core/shell quantum dots (QDs) has been an important topic for decades due to their potential application in quantum computing, quantum information [1] and for designing new generations of solar cells [2]. Optical properties of the spherical CdSe/ZnS core/shell QD [3] are the subject of the present work.

The energy level structure of QD were obtained by solving the radial Schrödinger equation in effective mass approximation with corresponding boundary conditions. The interaction of QD with laser light was modeled in the scheme of four-level system under dipole and rotating wave approximation. The optical Bloch equations for density matrix elements were derived and solved. Absorption spectrum is obtained by calculating optical susceptibility while the emission spectrum is studied through changes in the population of the excited levels.

It is found that changing some model parameters can strongly affect the calculated quantities. We focused here on observing the effect of core and shell thickens on the positions of absorption picks and excited level populations and found that changes in the core/shell radii can significantly change the population of the excited sided level.

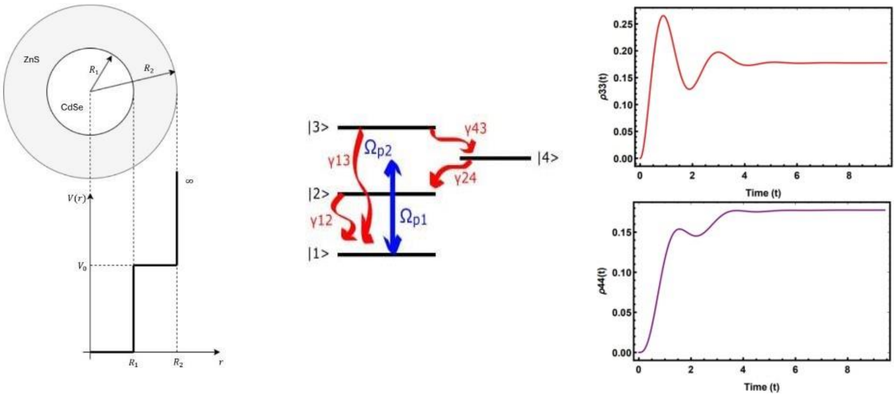

Figure: Details of the CdSe/ZnS core/shell QD (left), model based on four-level system (middle) and dynamics of the excited level populations (right).

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ENERGY DISTRIBUTION OF TRAP LEVELS IN FELDSPARS

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Feldspars are common minerals in the earth's crust. Radioluminescent properties of these minerals were intensively studied due to potential application in dating various geological processes up to a million of years. Typical measurements are based on thermoluminescence (TL) or optically stimulated luminescence (OSL) methods. There are various types of these natural minerals, however all of them have very complex structure containing a variety of defects. Consequently, the TL and OSL characteristics are represented by multi-component curves that are difficult to deconvolute and interpret in terms of elemental processes of trapping and recombination related to particular defect levels.

In general, TL provides an information relating population and energy distribution of trap levels in dielectric solids. Typical measurements are performed using a photomultiplier as a light detector. Therefore, information regarding the spectral properties of the emitted light is unknown. Advanced measurement technique, known as the spectrally resolved thermoluminescence (SR-TL) allows to record spectral distribution of luminescence during heating. There spectral characteristics reveal important properties of the recombination mechanism and the energy distribution of recombination centers.

The SR-TL data were analyzed numerically to obtain energy distribution of traps and recombination centers. For this purpose a novel algorithm was developed. The results are somewhat surprising and reveal a quasi-continuous distribution of activation energies of trap levels. A similar result was found with regard to recombination centers.

The OSL decay curves were measured using green light as well as infra-red (IR) light for stimulation of irradiated samples. Obtained curves, for both types of optical stimulation, cannot be interpreted in terms of first, second or even general order of kinetics. The spectrum of relaxation times is very broad. A novel analysis allows to determine the distribution of the relaxation times under optical stimulation. This also seems to be a quasi-continuous, confirming the previous SR-TL findings.

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TIME-RESOLVED LUMINESCENCE PROPERTIES OF SWIFT HEAVY ION IRRADIATED CERIUM-DOPED $Gd_3Ga_2Al_3O_{12}$ SINGLE CRYSTALS

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Scintillators are utilized in high-energy physics and fusion applications as ionizing radiation detectors. Cerium-doped $Gd_3Ga_2Al_3O_{12}$ (GGAG:Ce) is a promising scintillator material standing out due to its high light yield and high density. Its relatively long afterglow of Ce^{3+} emission is countered by co-doping GGAG:Ce with divalent ions, such as Mg^{2+}, which accelerates the Ce^{3+} luminescence emission.

As scintillators are naturally subjected to radiation damage, their influence on the material properties and their stability under radiation should be thoroughly studied and the properties must be optimized. Radiation damage strongly influences the stability of scintillator parameters under ionizing radiation thus deteriorating their performance. The goal of this work was to evaluate the influence of swift heavy ions on GGAG:Ce,Mg single crystals, which were irradiated with several different fluences in the range $6.6 \cdot 10^{10} – 1 \cdot 10^{14}$ cm^{-2}. The irradiation of the crystals has been carried out using the DC-60 heavy ion accelerator (Astana, Kazakhstan). Optical and luminescence spectroscopy including time-resolved luminescence spectroscopy was utilized to study the induced radiation defects in GAGG. Special attention was paid to the study of the luminescence properties of irradiated crystals under vacuum ultraviolet (VUV) excitations of synchrotron radiation. Synchrotron-based experiments were conducted on the P66 beamline at DESY (Hamburg, Germany) and the FinEstBeAMS beamline at MAV IV Laboratory (Lund Sweden).

All irradiated crystals studied contain induced optical absorption bands. Detailed analysis of the induced absorption bands and their thermal stability allows us to attribute them to F-type centers. Time-resolved luminescence properties of the virgin and irradiated single crystals were studied. Non-radiative losses caused by the induced radiation defects lead to a strong degradation of the excitation spectra in the VUV range. Energy absorption and electron-hole pair generation mechanisms will be proposed along with the energy transfer processes. The degradation of the Ce^{4+} centers as witnessed in the XANES spectra and its influence on the luminescence properties will be discussed.

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Vladimir Pankratov and Zhakyp T. Karipbaev were supported by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP19680626)

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FROM Ce^{3+} to Ce^{4+}AND BACK: HARNESSING DEFECT ENGINEERING FOR ENHANCED CATHODOLUMINESCENCEIN GARNET SCINTILLATORS

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“Defect engineering” method was used for cerium-activated lutetium aluminum garnets co-doped with various Ca^{2+} concentration (LuAG:Ce,Ca) and co-doped with various Si^{4+} concentration (LuAG:Ce,Ca,Si). The first aim of this work was to enhance cathodoluminescence (CL) performance by stabilizing $Ce^{3+} \rightarrow Ce^{4+}$ through Ca^{2+} co-doping, particularly accelerating CL decay, as previously demonstrated in garnets [1, 2]. The second aim is to demonstrate that the stabilization of Ce centers can be reversed through Si^{4+} co-doping, thereby reversing the trend of CL characteristics.

Samples were prepared by liquid phase epitaxy using a lead-free $BaO\text{-}B_2O_3\text{-}BaF_2$ flux [3]. CL analysis was conducted using a specialized CL apparatus [4]. CL decays (Figure 1) and other CL and optical characteristics were examined.

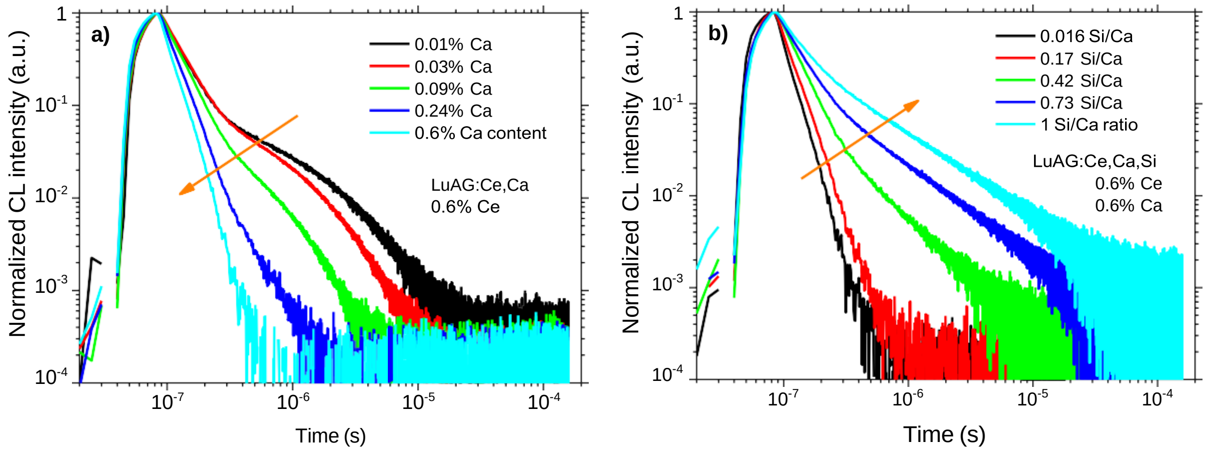

Figure 1: Cathodoluminescence (CL) decays of single-crystalline films after a 50 ns excitation time. a) LuAG:Ce,Ca films with various Ca co-doping. b) LuAG:Ce,Ca,Si films with various Si co-doping.

Ca^{2+} co-doping resulted in a significant acceleration of CL decay (Figure 1a), while Si^{4+} co-doping led to the opposite trend (Figure 1b). However, the CL decay shape of Si^{4+} co-doped samples differed. Additionally, co-doping caused a decrease in CL intensity (see at the conference). The influence of Si^{4+} co-doping and the effect of Ce^{3+}/Ce^{4+} ratio on the CL of the LuAG:Ce,Ca epitaxial films will be discussed.

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