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The 6th International Conference on
RARE EARTH MATERIALS

20th – 23rd October, 2024

ABSTRACT BOOK

6th International Conference
Rare Earth Materials
Advances in Synthesis, Studies and Applications

Vilnius, Lithuania
October 20th – 23rd 2024

BOOK OF ABSTRACTS

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Lithuanian Academy of Sciences
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PREFACE

Dear Colleagues,

October 20–23, 2024, we are organizing the **INTERNATIONAL SCIENTIFIC CONFERENCE "RARE EARTH MATERIALS: ADVANCES IN SYNTHESIS, STUDIES, AND APPLICATIONS"**. This marks the 6th International Conference focused on the synthesis, research, and application of rare earth materials across various industries. The conference continues under the acronym "REMAT" (previously REMAT 2008, 2011, 2013, 2015, and 2018), and this year it will be known as **REMAT 2024**.

We are excited to share that this year's conference will be held in Lithuania for the first time, in collaboration with colleagues from the Institute of Low Temperature and Structure Research (PAS), Wrocław, Poland, the Center for Physical Sciences and Technology and Vilnius University. The conference aims to showcase the latest scientific advancements in the synthesis, properties (including optical, electrical, catalytic, magnetic, adsorptive, and more), and applications of rare earth metal materials.

This conference is vital for the scientific community, particularly for young researchers and doctoral students from the Vilnius University Faculty of Chemistry and Geosciences, as well as for the wider Lithuanian society. The international scientific committee comprises esteemed scientists from various countries, including Brazil, Denmark, Spain, Italy, Israel, Japan, China, Poland, Lithuania, the Netherlands, France, Finland, Germany, the USA, and others.

The conference will take place at the Center for Physical Sciences and Technology (Sauletekio av. 3), with an anticipated attendance of approximately 100 scientists and researchers. We extend our heartfelt gratitude to the sponsors recognized on the conference website, without whom this event would not be possible.

We would like to give a special thanks to our co-organizers, Prof. Wieslaw Strek and Prof. Dariusz Hreniak from the Institute of Low Temperature and Structure Research (PAS), Wrocław, Poland, for their invaluable support in making **REMAT 2024** a reality in Lithuania.

We hope that **REMAT 2024** will foster fruitful discussions, the establishment of new friendships, and fruitful collaborations.

Chair

Professor Aivaras Kareiva

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Conference programme

Sunday October 20th, 2024

Arrival	
17:00 – 20:00	Badge pickup and registration, Restaurant “Valdovu sodas”, Katedros a. 4, Vilnius, Lithuania (entrance from the side of Grand Duke Palace)
18:00 – 20:00	Meet together with a glass of beverage, Restaurant “Valdovu sodas”, Katedros a. 4, Vilnius, Lithuania (entrance from the side of Grand Duke Palace)

Monday October 21st, 2024, Center for Physical Sciences and Technology, Sauletekio av. 3, Vilnius

8:00 – 9:00	**Registration at the lobby**	
	Room A101, Name of Topic: Rare-earth metal driven optical phenomenon **Chair: Prof. Aivaras Kareiva, Vilnius University, Lithuania**	
9:00 – 9:20	**Opening ceremony:** • Prof. Aivaras Kareiva, Vilnius University, Lithuania • Prof. Wieslaw Strek, Institute of Low Temperature and Structure Research (PAS), Poland • Prof. Dariusz Hreniak, Institute of Low Temperature and Structure Research (PAS), Poland • Prof. Ramunas Skaudzius, Center for Physical Sciences and technology, Lithuania	
9:20 – 10:00	**Keynote speaker Prof. Artur Bednarkiewicz** (Institute of Low Temperature and Structure Research (PAS), Poland) “*Photon Avalanching – mechanism, applications and future challenges*”	
10:00 – 10:30	**Invited speaker Prof. Michele Back** (Ca' Foscari University of Venice, Italy) **“Detecting Phase Transitions Through Luminescence”**	
10:30 – 11:00	**Coffee break at the lobby**	
	Room A101, Name of Topic: Rare-earth metal driven optical phenomenon **Chair: Prof. Ramunas Skaudzius,** Center for Physical Sciences and technology, Lithuania	**Room D401, Name of Topic: Magnetism and novel applications and uses of rare-earth materials** **Chair: Prof. Rimantas Ramanauskas,** Center for Physical Sciences and technology, Lithuania
11:00 – 11:30	**Invited speaker Prof. Stefan Lis** (Adam Mickiewicz University in Poznan, Poland) *“Chosen inorganic nanoluminophores containing Ln ions focused on sensor and analytical applications”*	**Invited speaker Dr. Dovydas Karoblis** (Vilnius University, Lithuania) *“Molten salt synthesis of various perovskite, pyrochlore and Ruddlesden-Popper systems”*
11:30 – 11:50	**Oral presentation Prof. Jerzy Sokolnicki** (University of Wroclaw, Poland) *“Oxonitridosilicate phosphors for LEDs”*	**Oral presentation Prof. Philippe Smet** (Ghent University, Belgium) *“Study and quantification of divalent lanthanides in persistent phosphors”*

11:50 – 12:10	Oral presentation **Prof. Dagmara Stefanska** (Institute of Low Temperature and Structure Research (PAS), Poland) *"Potential of Aluminosilicate in White WLED Light Production"*	Oral presentation **Dr. Mykhailo Chaika** (Institute of Low Temperature and Structure Research (PAS), Poland) *"Advancements and challenges in sintering of Cr^{4+}:YAG transparent ceramics"*
12:10 – 12:30	Oral presentation **Dr. Guna Doķe** (University of Latvia, Latvia) *"Persistent luminescence and trap properties of UV emitting materials based on RE-doped silicates"*	Oral presentation **Mr. Manuel Hofinger** (Johannes Kepler University, Austria) *"Influence of Ytterbium and potentiostatic anodization on the corrosion of co-eavporated Magnesium Thin-Film"*
12:30 – 14:00	**Joint Conference Photo** **Lunch at the lobby**	
	Room A101, Name of Topic: Rare-earth metal driven optical phenomenon **Chair: Prof. Dariusz Hreniak,** Institute of Low Temperature and Structure Research (PAS), Poland	**Room D401, Name of Topic: Magnetism and novel applications and uses of rare-earth materials** **Chair: Prof. Maria Luisa Saladino,** University of Palermo, Italy
14:00 – 14:30	Invited speaker **Dr. Rocio Rojas Hernandez** (Tallinn University of Technology, Estonia) *"Zinc Aluminate Nd, Ce based material in form of core shell particles and sub-micrometer films for NIR Emitting applications"*	Invited speaker **Dr. Andrius Pakalniškis** (Vilnius University, Lithuania) *"The Formation and Magnetic Properties of Metastable Hexagonal Phase in Doped $LuFeO_3$"*
14:30 – 14:50	Oral presentation **Prof. Marcin Nyk** (Wroclaw University of Science and Technology, Poland) *"Lanthanide-doped nanomaterials with nonlinear optical and multimodal functionalities"*	Oral presentation **Dr. Martin Straka** (UJV Rez, a.s., Czech Republic) *"Separation of Dy from acidic solutions using ionic liquids"*
14:50 – 15:10	Oral presentation **Dr. Dagmara Kulesza** (University of Wroclaw, Poland) *"High-Precision Luminescence Thermometry Beyond 1000 °C with $Ca_3Sc_2Si_3O_{12}$:Pr Garnet"*	Oral presentation **Mr. Jallouli Necib** (Tallinn University of Technology, Estonia) *"Synthesis and Luminescence of Rare-Earth-Free Zn_2SiO_4 via Solid-State and Molten Salt Methods"*
15:10 – 15:30	Oral presentation **Dr. Mateusz Oleszko** (Institute of Low Temperature and Structure Research, Poland) *"Luminescent properties of Laser Induced White Light source based on $Yb_3Al_5O_{12}$ nanocrystal"*	Oral presentation **Prof. Kei Kamada** (Tohoku University, Japan) *"2 inch diameter growth of Eu doped $BaCl_2$ /KCl/NaCl eutectic scintillator for X-ray imaging applications"*
15:30	**Excursion**	

Tuesday October 22nd, 2024, Center for Physical Sciences and Technology, Sauletekio av. 3, Vilnius

8:00 – 9:00	**Registration**	
	Room A101, Name of Topic: Rare-earth metal driven optical phenomenon **Chair: Prof. Artur Bednarkiewicz, Institute of Low Temperature and Structure Research (PAS), Poland**	
9:00 – 9:40	**Keynote speaker Prof. Thomas Justel** (Munster University of Applied Sciences, Germany) *"A Century of Luminescent Materials - From Down to up-Conversion"* (On-line presentation)	
9:40 – 10:10	**Invited speaker Prof. Markus Suta** (Heinrich Heine University Dusseldorf, Germany) *"Designing luminescent thermometers with lanthanoid ions - An approach to gain a better understanding of non-radiative transitions"*	
10:10 – 10:30	**Oral presentation Dr. Justyna Zeler** (University of Wroclaw, Poland) *"Towards Designing of Primary Optical Thermometers"*	
10:30 – 11:00	**Coffee break at the lobby**	
	Room A101, Name of Topic: Rare-earth metal driven optical phenomenon **Chair: Prof. Michele Back,** Ca' Foscari University of Venice, Italy	**Room D401, Name of Topic: and Magnetism and novel applications and uses of rare-earth materials** **Chair: Prof. Narcis Avarvari,** CNRS-University of Angers, France
11:00 – 11:30	**Invited speaker Prof. Chong-Geng Ma** (Chongqing University of Posts and Telecommunications, China) *"Engineering defect spectroscopy in metal halide perovskites via first-principles electronic structure calculations"*	**Invited speaker Prof. Joan Josep Carvajal Marti** (University Rovira i Virgili, Spain) *"Preparation and characterization of $GdVO_4$:Tb,Eu/carbon dot composites through hydrothermal deposition synthesis"*
11:30 – 11:50	**Oral presentation Mr. Leonardo Saraiva** (São Paulo State University, Brasil) *"Excited-state absorption meets multiparametric thermometry: Merging strategies for enhanced thermal sensing"*	**Oral presentation Dr. Silvia Ruggieri** (University of Verona, Italy) *"NIR-CPL/CD active Yb(III) complexes bearing both central and axial chirality"*
11:50 – 12:10	**Oral presentation Mr. Artur Harnik** (Laser research center, Lithuania) *"Luminescent microstructures: laser 3D printing and luminescence study"*	**Oral presentation Prof. Henning Höppe** (Universität Augsburg, Germany) *"Weak Coordination in Silicate-Analogous Host Structures"*
12:10 – 12:30	**Oral presentation Ms. Egle Ezerskyte** (Vilnius University, Lithuania) *"Bimodal, Shape-Tunable, Eu^{3+}-Doped $GdPO_4$ Nanoparticles and Their Impact on Zooplankton Daphnia Magna"*	**Oral presentation Mr. Davide Lascari** (Università degli Studi di Palermo, Italy) *"Thermodynamic and kinetic studies on REE ions recovery onto biochar of dead Posidonia oceanica leaves"*

12:30 – 14:00	**Lunch at the lobby**	
	Room A101, Name of Topic: Rare-earth metal driven optical phenomenon **Chair: Prof. Zivile Stankeviciute,** Vilnius University, Lithuania	**Room D401, Name of Topic: Magnetism and novel applications and uses of rare-earth materials** **Chair: Prof. Sarah Stoll**, Georgetown University, USA
14:00 – 14:30	Invited speaker **Prof. Eugeniusz Zych** (University of Wroclaw, Poland) *“The Presence and the Future of Luminescence Thermometry”*	Invited speaker **Prof. Paula Gawryszewska** (University of Wroclaw, Poland) *“PMMA thin layers based on lanthanide chelates with N-phosphorylated carboxamides: multicolor emission, temperature and pressure sensing properties”*
14:30 – 14:50	Oral presentation **Dr. Joanna Trojan-Piegza** (University of Wroclaw, Poland) *“On the nature of the Lu-based garnets highly sensitive luminescence thermometer”*	Oral presentation **Dr. Guna Krieke** (Vilnius University, Lithuania) *“Photochromic and radiochromic effect in $M_3MgSi_2O_8:Eu^{2+}$ (M = Ca-Ba)”*
14:50 – 15:10	Oral presentation **Dr. Nadiia Rebrova** (Institute of Low Temperature and Structure Research (PAS), Poland) *“Visible-to-UVC upconversion of new phosphates activated by praseodymium ions”*	Oral presentation **Mr. Andreas Greul** (Johannes Kepler University, Austria) *“Structural and Electrochemical Investigation of Al-Eu Compositional Thin Film Libraries”*
15:10 – 15:30	Oral presentation **Mr. Justinas Januskevicius** (Vilnius University, Lithuania) *“Synthesis and investigation of $LaScO_3$:Yb, Er – a new versatile ratiometric optical temperature sensor”*	Oral presentation **Ms. Natalia Charczuk** (Institute of Low Temperature and Structure Research (PAS), Poland) *“Nanosized silicate-phosphate hydroxyapatite co-doped with Gd^{3+} and Eu^{3+} ions as a drug carrier”*
15:30 – 17:00	**Coffee break and Poster session at the lobby**	
18:00 – 22:00	**Conference dinner, Park Town (Lvivo st. 101, Vilnius)**	

Wednesday October 23rd, 2024, Center for Physical Sciences and Technology, Sauletekio av. 3, Vilnius

8:00 – 9:00	**Registration**	
	Room A101, Name of Topic: Rare-earth metal driven optical phenomenon and Magnetism and novel applications and uses of rare-earth materials **Chair: Prof. Joan Josep Carvajal Marti, University Rovira i Virgili, Spain**	
9:00 – 9:40	**Keynote speaker Prof. Narcis Avarvari** (CNRS-University of Angers, France) *“Lanthanide complexes and coordination polymers with emissive, conducting and magnetic properties”*	
9:40 – 10:10	**Invited speaker Prof. Maria Luisa Saladino** (University of Palermo, Italy) *“Novel luminescent multi-component composites for anti-counterfeiting systems”*	
10:10 – 10:30	**Oral presentation Prof. Sarah Stoll** (Georgetown University, USA) *“Nanosheets of rare-earth chalcogenides”*	
10:30 – 11:00	**Coffee break at the lobby**	
	Room A101, Name of Topic: Rare-earth metal driven optical phenomenon **Chair: Prof. Markus Suta,** Heinrich Heine University Dusseldorf, Germany	**Room D401, Name of Topic: Magnetism and novel applications and uses of rare-earth materials** **Chair: Prof. Jerzy Sokolnicki,** University of Wroclaw, Poland
11:00 – 11:30	**Invited speaker Prof. Fabio Piccinelli** (University of Verona) *“Inorganic and hybrid organic-inorganic materials exhibiting chiroptical activity”*	**Invited speaker Prof. Jorma P.K. HÖLSÄ** (University of the Free State) *“Doping, Defects and Persistent Luminescence of Rare Earth Doped Materials”*
11:30 – 11:50	**Oral presentation Mr. Mikolaj Kaminski** (University of Gdansk, Poland) *“Energy transfer pathway between Cr^{3+} and Er^{3+} in $MgGa_2O_4$”*	**Oral presentation Mr. Leonhard Yuuta Dorsch** (Leipzig University, Germany) *“The hydrogenation behaviour of the Zintl phases EuTt (Tt = Si, Ge ,Sn)”*
11:50 – 12:10	**Oral presentation Dr. Marta Kuwik** (University of Silesia in Katowice, Poland) *“Compositional dependence of the spectroscopic properties of multicomponent phosphate glasses doped with rare earth ions”*	**Oral presentation Prof. Leonid Vasylechko** (Lviv Polytechnic National University, Ukraine) *“Crystal Structure Design of High-Entropy Rare-Earth Aluminate Perovskites”*

12:10 – 12:30	Oral presentation **Mr. Ryosuke Kawabata** (Tohoku University, Japan) *“Growth, scintillation properties, and pulse shape discrimination capability of Na-substituted CaI$_2$:Eu scintillator”*	Oral presentation **Mr. Adrian Kowalinski** (Wrocław University of Science and Technology, Poland) *“Electronic waste recycling using a coordination chemistry approach”*
12:30 – 12:50	Oral presentation **Dr. Natalia Pawlik** (University of Silesia, Poland) *“The studies of rare-earths luminescence in sol-gel glass-ceramics containing fluoride crystals”*	Oral presentation **Dr. Agnieszka Gładysz-Płaska** (Maria Curie-Skłodowska University in Lublin, Poland) *“Study of the tetrad effect in adsorption systems”*
12:50 – 13:10	Oral presentation **Dr. Nataliia Kariaka**, (Taras Shevchenko National University of Kyiv, Ukraine) *“Cation dependent Eu^{III} luminescence in carbacylamidophosphate based tetrakis-complexes”*	
13:10 – 13:20	**Conference closing, Snacks, Farewell, Room A101**	

Poster Session ReMat 2024, October 22nd, 2024

01	**Ruhany Azeez** Dissolution Kinetics of Rare Earth Elements from Estonian Phosphate Rock during Processing with Hydrochloric Acid
02	**Elžbieta Bajorinaitė** Could Phosphogypsum Waste Be a Source of Rare-Earth Elements?
03	**Vitalii Boiko** Synthesis parameter effect on the optical properties and structure of Eu doped ZnGa$_2$O$_4$ persistent phosphors
04	**Alėja Marija Daugėlaitė** Upconverting Nanocomplexes Loaded Mesenchymal Stem Cells for Two-Step Photodynamic Therapy
05	**Igor Djerdj** High-Entropy Oxides: Game-Changers in CO$_2$ Hydrogenation Photocatalysis
06	**Justina Gaidukevič** Europium Oxide-Modified Reduced Graphene Oxide Composite for Serotonin Detection
07	**Yuriy Gerasymchuk** Zirconium phthalocyanine and reduced graphite oxide composite materials for photocatalytic purification of waste water
08	**Mariusz Hasiak** Lanthanide-Doped Gd-Ge-Si Alloys: Microstructure, Magnetic Properties, and Magnetocaloric Performance
09	**J. Hölsä** Charge Compensation and Persistent Luminescence: CaWO$_4$:Eu^{3+}

10	**J. Hölsä** Defects and Persistent Luminescence of Tb^{3+} Doped $Ca_2Ga_2GeO_{7+\delta}$
11	**Greta Inkrataitė** Praseodymium doped garnets as new generation scintillators
12	**Ewa Kasprzycka** Quinolones as sensitizers of visible emitting lanthanide(III) ions
13	**Artūras Katelnikovas** Synthesis and Optical Properties of Eu^{3+}, Sm^{3+}, and Ce^{3+}-Doped $Na_7Mg_{13}La(PO_4)$12 Phosphors
14	**Vaidas Klimkevičius** Surface Functionalization of UCNPs for Excellent Colloidal Stability and Cellular Uptake
15	**Gabrielė Klydžiūtė** Synthesis and Characterization of Layered Double Hydroxides (LDH) Replacing the M^{2+}/M^{3+} Ions with Zinc, Copper and Lanthanum
16	**Amadeusz Łaszcz** Impact of High-Temperature Heat Treatment on the Functional Properties of Gd-Doped Ni-Mn-Ga Magnetic Shape Memory Alloy
17	**Janina Legendziewicz** Thermoluminescence application in architecture studies of the Gothic cathedral in Opole
18	**Greta Linkaitė** Synthesis of Biphasic Calcium Phosphate Granules from Gypsum Under Static and Rotating Conditions
19	**Agnieszka Lipke** The influence of phosphates on the tetrad effect in the adsorption systems with red clay or zeolites
20	**Anna Lukowiak** Photoluminescence of RE-doped bioactive glass
21	**Marvin Michak** In situ investigations on H/O exchange reactions in yttrium hydride oxide YHO
22	**Christoph Middelhoff** Novel Gain Media for a Potential UV-B Up-Conversion Laser
23	**Agata Musiałek** Laser induced white emission and photocurrent of GaN nanoceramics
24	**Turlybek Nurakhmetov** Luminescence and electron-hole trapping centers of phosphates and sulfates activated by transition and rare-earth ions
25	**Kazuya Omuro** Next-Generation X-Ray Imaging Scintillators: Challenges and Opportunities in Ce^{3+}-Doped $(Lu_{1-x}Tb_x)$3$Al_2Ga_3O_{12}$ Garnet Crystals
26	**Tim Pier** On the Photoluminescence of Pr(III) Substituted Pyrophosphate Polymorphs
27	**Rosina Celeste Ponterio** Microorganisms as Promising Biotechnological Candidates for Rare Earth Elements Recovery
28	**Maciej Ptak** Structural, phonon, and optical properties of inorganic perovskites tuned by aliovalent doping
29	**Olzhas Shalkhar** New insight in the sol-gel synthesis of lanthanide-substituted garnets

30	**Dmytro Shyshkin** Synthesis of Nickel-Rhenium-Phosphorous Catalysts and their Application for Oxygen Evolution Reaction
31	**Jonas Stadulis** Luminescent Properties of Eu^{2+}-doped $Sr_5(PO_4)_3Cl$ Synthesized in Air Atmosphere
32	**Mariusz Stefanski** Broad Luminescence Generated by IR Laser Excitation from $CsPbBr_3$:Yb^{3+} Perovskite Ceramics
33	**Simona Streckaite** The limiting factors of quantum-cutting efficiency of ytterbium-doped lead halide perovskites: dimeric and monomeric ytterbium species
34	**Robert Tomala** Laser induced white emission as a tool for pressure sensing
35	**Marlies Van Bael** Controlling oxygen vacancies in CeO_{2-x} for CO_2 reduction
36	**Diana Vištorskaja** The Sol-Gel Synthesis and Characterization of Novel Garnet-Type Luminescent Materials
37	**Patrycja Zdeb** Visible-to-UVC Upconversion in Pr^{3+}-Doped Phosphors: A Step Towards Innovative UVC Light Sources

Keynote lecture abstracts

Lanthanide complexes and coordination polymers with emissive, conducting and magnetic properties

N. Avarvari[1,*]
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Tetrathiafulvalenes (TTF) and anilates (An) are outstanding redox-active units which, upon suitable functionalization, can provide electroactive coordination polymers (CP) or metal-organic frameworks (MOF). Their association with lanthanide ions may provide luminescent, conducting and magnetic materials. Accordingly, we have used TTF based ligands, such as TTF-tetracarboxylates to prepare Dy(III) based electroactive MOFs with single molecule magnet (SMM) properties [1], and anilate ligands for dinuclear Dy(III) complexes (Fig. 1) [2] and for NIR emissive coordination polymers [3]. On the other hand, the use of chiral ligands allowed us the preparation of Eu(III) complexes showing circularly polarized luminescence (CPL) [4].

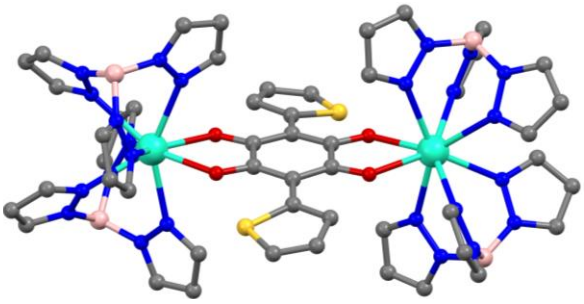

Fig. 1. Anilate-based Dy(III) dinuclear complex.

References

1. F. Manna, M. Oggianu, P. Auban-Senzier, G. Novitchi, E. Canadell, M. L. Mercuri, N. Avarvari, *submitted*.
2. F. Manna, M. Oggianu, J. R. Galán-Mascarós, F. Pop, B. Le Guennic, M. L. Mercuri, N. Avarvari, Dalton Trans., **53** (2024) 8369-8381.
3. S. A. Sahadevan, N. Monni, A. Abhervé, D. Marongiu, V. Sarritzu, N. Sestu, M. Saba, A. Mura, G. Bongiovanni, F. Quochi, N. Avarvari, M. L. Mercuri, Chem. Mater., **30** (2018) 6575-6586.
4. A. Abhervé, M. Mastropasqua Talamo, N. Vanthuyne, F. Zinna, L. Di Bari, M. Grasser, B. Le Guennic, N. Avarvari, Eur. J. Inorg. Chem., (2022) e202200010.

Photon Avalanching – mechanism, applications and future challenges

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Lanthanide ions doped inorganic nanoparticles (LnNP) are potential candidates and alternative labels to fluorescent molecules and quantum dots. Among the other, they display narrowband absorption and emission lines, multicolour emission, long luminescence lifetimes and are perfectly photostable. In sensitized configuration, they are also capable to efficiently convert NIR excitation to visible range (so called upconversion UC), thus avoiding background fluorescence and enhance signal to background ratio towards super-sensitive biosensing & imaging. They also display non-linearity of luminescence intensity versus pump intensity, which enables imaging beyond diffraction limit with simple, customized confocal setups.

Among upconversion processes leading to the anti-Stokes emission, the photon avalanche (PA) became an interesting research topic since 1979, when it was first observed in Pr^{3+} doped $LaCl_3$ [1]. There are several essential requirements necessary to enable observation of PA in a given system – these include (i) the presence of efficient ESA transition and negligible GSA at the pumping wavelength and (ii) the presence of efficient the cross-relaxation (CR) processes required to populate intermediate excited level. As a consequence, the luminescence intensity of PA increases by several, typically 2-3 orders of magnitude when exciting with power density slightly (e.g. twice) above the PA threshold. Only recently its PA emission was also demonstrated for $NaYF_4$ nanoparticles doped with Tm^{3+} at the room temperature under 1064 and 1450 nm photoexcitation and 800 nm emission [3].

In this lecture, current state-of-the-art on PA emission and the PA emission in nano, micro and bulk $LiYF_4$ crystals will be summarized. Moreover, peculiarities of photon avalanche emission in wider context as the paradigm shift in luminescent nano-bio-labels will be discussed. The wide application potential of PA (e.g. super-resolution imaging [3], biosensing [4], nano-thermometry [5] etc.) makes it extremely interesting to further studies of the PA in various lanthanides and various matrices of various sizes – these applications will be evaluated and future directions will be emphasized for material scientists.

References

1. J. S. Chivian, W. E. Case, and D. D. Eden, Appl. Phys. Lett. (1979) 35, 124–125.
2. M. F. Joubert, Opt. Mater. (Amst). (1999) 11, 181–203.
3. Ch. Lee et al., Nature (2021), 589, 230-235; A.Bednarkiewicz et al. (2019) Nanoscale Horizons, 4(3), 706-719.
4. A. Bednarkiewicz, E. Chan, K. Prorok, Nanoscale Adv., 2020,2, 4863-4872.
5. M. Szalkowski et al., Optical Materials: X (2021)12, 100102; L. Marciniak et al. J. Mater. Chem. C, 2018, 6, 7568

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A Century of Luminescent Materials - From Down to up-Conversion

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Systematic R&D projects concerning luminescent materials (also called phosphors or luminophors) started in the early 20th century [1]. During the last century, main activities concentrated on the search for luminescent materials for low- and high-pressure discharge lamps, cathode-ray tubes, plasma displays, and x-ray detectors. Suitable down-conversion materials and scintillators were rapidly found and in the meantime those materials applied have been developed to an impressive maturity level [2]. Therefore, the search for novel materials for established application areas has almost come to an end and remaining R&D activities concentrate on tailoring the particle morphology and surface chemistry to optimize device performance.

The advent of several lighting and display technologies since the 1990ties, i.e. large and flat display screens based on liquid crystals, OLEDs, or µ-LEDs, excimer discharge lamps, and solid state light sources, i.e. (In,Ga)N and (Al,Ga)N LEDs, has revitalized research on luminescent materials, both in industry and university laboratories worldwide. These new technologies require materials with a high stability, suitable PL spectra, and energy efficiency under harsh excitation conditions, i.e. under high power density, strong electric fields, and at elevated temperature. Such demand for stable and efficient luminescent materials drove the research on transition metal or rare-earth activated fluorides, oxides and nitrides as well as on quantum dots for more than 30 years now.

Moreover, the growing request for air, surface, and water disinfection devices, optical imaging or marking, and novel medical therapy approaches initiated the research on VUV phosphors [3], x-ray phosphors, nanoscale particles, and up-converters. After the discovery of NIR to visible up-converters in the 1960ties [4], the search for up-conversion schemes of blue light into UV radiation was promoted by the advances in efficiency and power density of blue LEDs and laser diodes. The recent improvements of respective blue-to-UV up-converters [5,6] resulted in the claim to use them for low dose UV disinfection of surfaces. In general, the development of novel UV phosphors either excited by blue light, x-rays, or low-voltage electrons resulted in several new studies and even launched products comprising such materials. These novel achievements as well as many breakthroughs during a century of R&D on luminescent materials will be highlighted by this contribution.

References

1. C. Feldmann, T. Jüstel, C.R. Ronda, P.J. Schmidt, Inorganic Luminescent Materials: 100 Years of Research and Application, Adv. Funct. Mater. 13 (2003) 511
2. T. Jüstel, H. Nikol, Optimization of Luminescent Materials for Plasma Display Panels, Adv. Materials 12 (2000) 527
3. T. Jüstel, D.U. Wiechert, J.-C. Krupa, VUV Spectroscopy of Luminescent Materials for Plasma Display Panels and Xe Discharge Lamps, J. Luminescence 93 (2001)
4. F. Auzel, Upconversion and Anti-Stokes Processes with f and d Ions in Solids, 104 (2004) 139
5. E.L. Cates, M. Cho, J.-H. Kim, Converting Visible Light into UVC: Microbial Inactivation by Pr3+-Activated Upconversion Materials, Envir. Sci. Techn. 45 (2011) 3680
6. F. Schröder, S. Fischer, T. Jüstel, On the concentration dependency of Pr doped Li2CaSiO4, Austr. J. Chem. 75 (2022) 760

Invited speaker lecture abstracts

Detecting phase transitions through luminescence

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Phase transitions (PTs) play a critical role in driving critical properties of materials. The ability to detect them is becoming increasingly important for a wide variety of applications, making contactless detection highly desirable. In this framework, the possibility of probing solid-solid PTs through luminescence has been utilized for semiconductors in chalcogenide quantum dots [1] and more recently for metal halide perovskites [2]. On the other hand, due to the direct link between the electronic and crystalline structures, the luminescence of suitable doping ions such as lanthanides incorporated in insulators of interest is attracting increasing attention. This is due to the sensitivity of luminescence centers to their environments [3] and the possibility of an *in-situ* view that can be exploited during material applications [4]. The use of site sensitive luminescent ions such as Eu^{3+} has been demonstrated to be a promising strategy for PT probing due to the effect of the predictable local crystal symmetry on the spectroscopic features [5]. Additionally, also the use of the lifetime of lanthanide ions has also been proposed [6]. However, complex data analysis or unreliable parameters have been limiting their use, making the search for a reliable technique a challenge.

In this presentation, using $LaGaO_3$ perovskite as prototype, the orthorhombic ↔ rhombohedral PT is investigated through the use of lanthanide doping. Different luminescent strategies are compared in order to discuss the most reliable one. In addition, the PT temperature and the hysteresis are probed and discussed with respect to conventional temperature dependence X-ray diffraction (XRD) and differential scanning calorimetry (DSC) techniques. The control of the PT temperature by cooping with suitable ions and the potential and limits of the technique are discussed.

References

1. S.H. Tolbert, A.P. Alivisatos, Science, **265** (1994) 373-376.
2. M.I. Dar, et al., Sci. Adv., **2** (2016) e1601156.
3. P.A. Tanner, Chem. Soc. Rev., **42** (2013) 5090-5101.
4. M. Back, J. Ueda, J. Xu, D. Murata, M.G. Brik, S. Tanabe, ACS Appl. Mater. Interfaces, **11** (2019) 38937-38945.
5. G. Canu et al., Sci. Rep, **9** (2019) 6441.
6. A. Stanulis, et al., Inorg. Chem., **58** (2019) 11410-11419.

Preparation and characterization of $GdVO_4$:Tb,Eu/carbon dot composites through hydrothermal deposition synthesis

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Carbon dots (CDs) are interesting because of their luminescent properties to replace other luminescent sources. CDs exhibit interesting features of easy preparation, high photostability, adjustable optical and surface properties, low toxicity, environmental friendliness, and superior biocompatibility [1]. CDs have been used as luminescent sensors, bioimaging, photodynamic therapy, optoelectronic devices, etc. [2].

The combination of CDs with lanthanide-doped nanoparticles allow developing new applications for the resulting composites, and improve the performance of these materials when considered separately. By using these composites in luminescent sensing applications, an internal reference is incorporated, allowing the application of self-referencing approaches based on ratiometric methods. Luminescent technology is one of the most effective technical methods for high-tech anticounterfeiting. In advanced anti-counterfeiting measures these composite materials can play an important role.

Here we show the results obtained when preparing $GdVO_4$:Tb,Eu/CDs composites using a hydrothermal deposition method of CDs on previously prepared $GdVO_4$:Tb,Eu nanoparticles. The resulting composites have been characterized in terms of morphology, X-ray diffraction and luminescence spectra. Some potential applications for these $GdVO_4$:Tb,Eu/CDs composites will also be examined.

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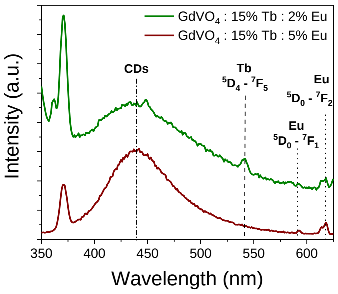

Fig. 1. Photoluminescence of GdVO4:Tb,Eu/CDs composites

References

1. Z, Shu, M. Du, M. Li, Y. Liu, L. Gan, X. Zhang, W. Gui, Luminescencece, **38** (2023) 1521-1528.
2. N. Navya, B.R. Radha Krushna, S.C. Sharma, A.R. Srinivasan, A. George, S.S. Mohapatra, C. Krithika, A. Bhanu, K. Manjunatha, S.Y. Wu, H. Nagabhushana, Mater. Today Sustain, **27** (2024) 100840.

PMMA thin layers based on lanthanide chelates with N-phosphorylated carboxamides: multicolor emission, temperature and pressure sensing properties

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Lanthanides are elements without which the development of modern technologies cannot be imagined. Their compounds are used in broadly understood materials engineering and serve in such fields as lighting, displays, sensors and luminescent markers, anti-counterfeiting agents, luminescent bar-codes [1]. Many of the applications mentioned require materials with tunable multiemission, which can be achieved using different lanthanide ions (Ln^{3+}). An excellent platform for Ln^{3+} compounds, due to its optical and mechanical properties, is PMMA (poly(methylmethacrylate) polymer), which has excellent transparency, UV and chemical resistance. Finding a ligand that sensitizes different Ln^{3+} ions is challenging, but it offers the advantage of using a single excitation source for multicolor emission materials, reducing costs and enabling practical application.

The work is devoted to PMMA thin layers with excellent luminescent properties containing single and multiple lanthanide chelates. This research presents series of PMMA thin layers (labeled **1Ln_PMMA**, where Ln = Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+} and **2Ln_PMMA**, where Ln = Eu^{3+}, Tb^{3+}) with high overall emission quantum yields of Q_{Eu}^{L} = 85%, Q_{Tb}^{L} = 66%, Q_{Sm}^{L} = 3 %, Q_{Dy}^{L} = 6% with introduced lanthanide (Ln^{3+}) coordination compounds of the type $[Na_2Ln(\mathbf{L^1})_4(OTf)(DMF)]$ and $[Na_2Ln(\mathbf{L^2})_4(DMF)_2][CF_3SO_3]$ (where **L¹** - N-(diphenylphosphoryl)-pyrazine-2-carboxamide, **L²** - N-(diphenylphosphoryl)-quinoxaline-2-carboxamide, OTf = $[CF_3SO_3]^-$, DMF = N,N-dimethylformamide). This is the first analysis comparing the photophysical properties of coordination compounds encapsulated in PMMA with single crystals, which includes the influence of such factors as the inhomogeneity of the Ln^{3+} coordination polyhedra and the refractive index. A model is proposed to estimate the change in Q_{Ln}^{L} when the Ln^{3+} chelat is incorporated into a PMMA medium, and it satisfactorily reproduces the experimental data with a maximum absolute error of 3% for the case of Eu^{3+} sample. At the same time, our work shows the influence of the PMMA matrix on the photophysical properties of Ln^{3+} with large (Eu, Tb) and small energy gap (Sm, Dy) between the emitting levels and adjacent levels with lower energy. **1Ln_PMMA** thin films containing multiple lanthanide chelates (Eu^{3+}, Tb^{3+}, Sm^{3+} and Dy^{3+}) exhibit multicolor tunable emission, and **2Ln_PMMA** thin films containing a mixture of Eu^{3+}, Tb^{3+} compounds show the properties of temperature and pressure sensors.

References

1. G. Tessitore, G.A. Mandl, S.L. Maurizio, M. Kaur, J.A. Capobianco, RSC Adv. **13** (2023) 17787–17811.

Doping, Defects and Persistent Luminescence of Rare Earth Doped Materials

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Up to date, here are only a few milestones in the development of persistent luminescence (*PersLum*) materials: the 1st one in the early 17th century when the famous *Bologna stone* (in 2013 shown to be barium sulfide BaS though actually barium sulfate $BaSO_4$ reduced by wood coal). As to the emitting specie(s), no certainty has been yet agreed upon though the copper ions (Cu^{2+} and Cu^+) have the upper hand. After a long silence, early in the 20th century, materials with inexpensive host materials and with even cheaper dopants dominated the PersLum markets. Then these materials were called as *afterglow materials* (which refers to very short lived emission (maybe only *a few seconds long* - just to give an estimate).

Later they were called *erroneously* as *phosphorescence materials* since all the luminescence is - at least partially - allowed since transitions occur between states with mixed wavefunctions, foremost those involving the rare earths (Ce^{3+}, Eu^{2+}, Eu^{3+}, Tb^{3+} etc). Some with a lot of (twisted) sense of humour have invented terms such as “Long persistent phosphorescence” or even longer - whatever that means…

In mid 1990s, rare earth dopants and even their hosts were introduced the most notable ones being the alkaline earth aluminates *MAl_2O_4 doped with Eu^{2+}*. It is still a conundrum why some of the *co-doping* R^{3+} ions (usually Dy^{3+}) seem to improve the (time, intensity of) PersLum time/intensity. Similar *oxidic materials* dominate both commercial and scientific interests. The first theoretical explanations provided achieved the *lowest ever quality with the Eu^+ species* introduced into the mechanisms. It remains to be seen if somebody can do worse than Eu^+. Hopefully not.

Soon it was observed that - even when recycled - the *rare earth hosts and dopants are* too expensive as persistent phosphors. Thus a return to non-rare earth materials seemed certain due to the fluctuating price and restricted availability of some rare earths.

At present, nanocrystalline/upconverting materials as well as theoretical methods occupy most people in *PersLum* field. As to the DFT calculations, it is though claimed that with a proper choice of software/algorithms, one can prove whatever one wants. Despite this, the calculated band gaps differ from the measured ones by 50 % or more. Such results are still published, which is an enigma. Also the *vacancy* based models (*simple but energy-wise impossible*) are still considered at the expense of more refined models favouring the opposite *charge compensation* with *oxide ions*. After all, the *materials are oxidic*, *manufacture involves heating in air* and structures have *space for small O^{2-} ions*. But ever more sophisticated and expensive apparatuses are required – the synchrotron radiation and neutron facilities worth milliards of euros. In addition to these, *human resources* are needed together with *out of the box ideas* (**Fig**). Last but not the least, in *PersLum* research, much closer co-operation should be expanded between the chemists, physicists, spectroscopists and structural experts. As it is impossible to only a few people to master all, interdisciplinary programs are needed. In brief, one needs to educate the material scientists!

Molten salt synthesis of Ruddlesden-Popper calcium manganites

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Many inorganic materials are prepared by simply heating a mixture of starting precursors at elevated temperatures, so-called solid state method. While the preparation simplicity is the biggest advantage, this technique suffers from several disadvantages, like formation of impurity phases, which cannot be separated from the final product, multiple heating and grinding stages, mass transport limitation, long reaction times and achievement of particles with specific morphology. In order to diminish these drawbacks, solid state reaction can be carried out in inorganic salts or mixture of the salts just above their melting point, better known as molten salt synthesis. By utilizing this method, the reaction time and the heating temperature are significantly decreased, particles with specific morphology can be obtained as well as no expensive reaction equipment is required.

In this work molten salt synthesis was used to prepare several calcium manganites with Ruddlesden-Popper structure. Few different parameters, like reaction temperature, heating time and precursors-to-chlorides ratio was investigated. It was determined that this technique allows to prepare Ca_2MnO_4 and $CaMnO_3$, which have distinctive shape (Figure 1), at temperature as low as 700 °C. Furthermore, the phase purity, sample morphology and magnetic properties were explored.

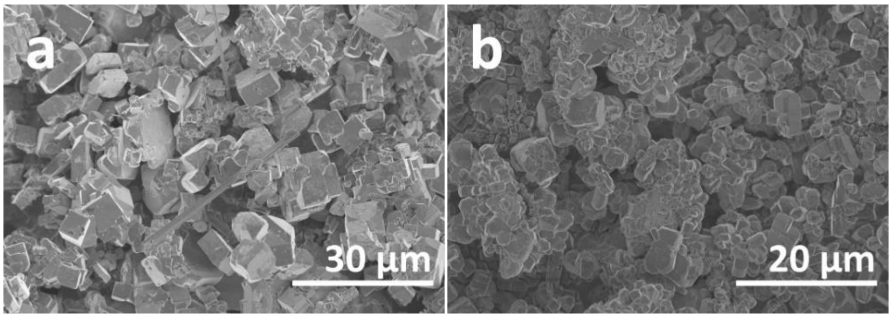

Fig. 1. SEM images of $CaMnO_3$ (a) and Ca_2MnO_4 (b) phases.

Chosen inorganic nanoluminophores containing Ln ions focused on sensor and analytical applications

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In this lecture, selected nanomaterials based on inorganic matrices (e.g.: fluorides, vanadates, borates, phosphates, silicates, etc.) doped with luminescent lanthanide (Ln) ions, characterized by efficient emission properties, are presented. As application materials, they should show: phase purity, high crystallinity and homogeneity, small particle size and narrow particle size distribution, and should not be agglomerated. Examples of effective nanoluminophores (NL) and up-converting (UCNL) doped with Ln ions and their surface functionalized, by coting with organic compounds, hybrid systems for sensor and analytical applications are discussed in detail. We have shown that the luminescence of selected Ln^{3+} or $Ln/^{2+}$-doped NLs can be successfully used in (nano)-manometry as optical pressure sensors [1], capable of measuring pressure and multifunctional optical sensors for (nano)-manometry and (nano)-thermometry [2], and bifunctional upconverting luminescent-magnetic (e.g. $FeS_2@NaYF_4:Yb^{3+}$, Er^{3+} core@shell nanocomposites) with tunable luminescence for temperature sensing [3]. We have fabricated luminescent-magnetic cellulose fibers modified with core/shell type NPs, based on the Ln^{3+} doped NLs. Such multifunctional NLs are excellent materials for textile and documents protection against counterfeiting [4] and temperature measurement [5].

NPs functionalized with organic compounds have also proved to be very useful for analytical purposes. We have developed novel, highly sensitive and selective fluorescence methods based on energy transfer from the analyte ion to the Eu^{3+} ion (in DPA capped-$LaF_3:Eu^{3+}$ NPs) [6], or Tb^{3+} ion (based on furoic acid capped $LaF_3:Tb^{3+}$ nanocrystals) [7] for the determination of metal species, i.e. Cu^{2+} or Al^{3+} in real water samples.

References

1. M. Runowski, A. Shyichuk, A. Tyminski, T. Grzyb, V. Lavín, S. Lis, ACS Appl. Mater. Interfaces 10 (2018) 17269-17279.
2. M. Runowski, N. Stopikowska, D. Szeremeta, S. Goderski, M. Skwierczyńska, S. Lis ACS Appl. Mater. Interfaces, 11 (2019) 13389–13396.
3. P. Woźny, K. S. Cerracedo, M. Perzanowski, J. Moszczyński, S. Lis, M. Runowski, J. Mater. Chem. C, in press
4. M. Skwierczyńska, P. Woźny, M. Runowski, M. Perzanowski, P. Kulpiński, S. Lis, J. Alloys Compd. 829 (2020) 154456
5. M. Skwierczyńska, N. Stopikowska, P. Kulpiński, M. Kłonowska, S, Lis, M. Runowski, Nanomaterials 12 (2022) 1926
6. V. N. K. B. Adusumalli, S Lis, YI Park, J Mater. Chem. C 10 (2022) 17494-17501
7. V. N. K. B. Adusumalli, S Lis, P Woźny, Y. I. Park, ACS Appl. Nano Mater. manuscript in the review

Engineering defect spectroscopy in metal halide perovskites via first-principles electronic structure calculations

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Since the 1960s, theoretical spectroscopy of defects, including doped transition-metal, rare-earth, and ns^2-type ions in solids, has played a crucial role in the discovery of novel luminescent materials [1]. However, applying these theories to metal halide perovskites (MHP) modified by those luminescent ions, which are currently a trending topic and widely used for various light-emitting applications, remains relatively limited.

In this presentation, we will showcase recent advancements in theoretical spectroscopy of defects, employing first-principles electronic structure calculations with selected MHP examples. Firstly, we will examine the calculated electronic structures of rare-earth-doped $CsPbX_3$ (X=F, Cl, Br). These structures provide valuable insights into the photon-electric upconversion mechanisms observed in $CsPbF_3$ doped with Yb^{3+}/Er^{3+} (or Tm^{3+}), as well as the enhanced absorption strength in the deep-ultraviolet range of Ce^{3+}-doped $CsPbCl_3$ compared to its pristine counterpart [2, 3]. Secondly, we will delve into modeling self-trapped exciton (STE) luminescence in $Cs_5Cu_3Cl_6I_2$ within a first-principles framework. This luminescence can be further enhanced by considering the passivation of anion vacancies, as suggested by chemical potential phase diagram calculations. Lastly, we propose band alignment engineering in MHPs doped with ns^2-type ions as a strategic approach to advance the development of next-generation MHP scintillators, as illustrated in Figure 1 [4].

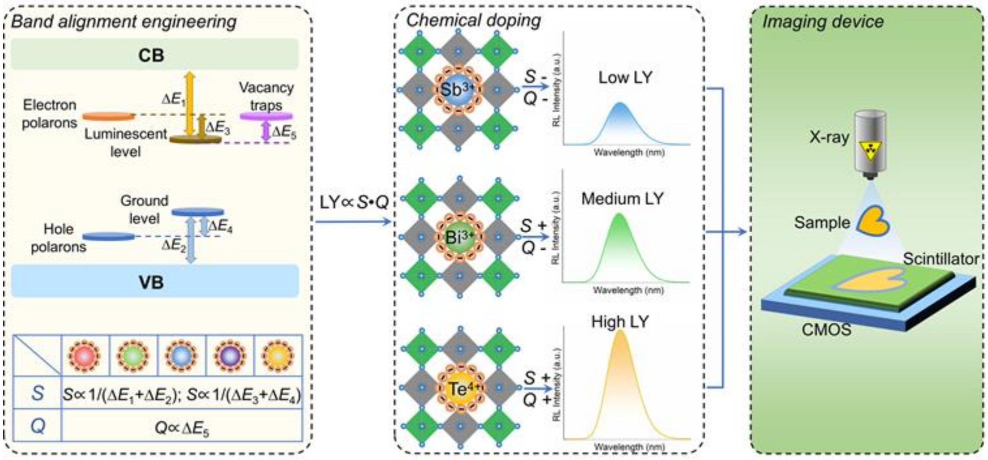

Fig. 1. Schematic diagram for novel design strategy including band alignment engineering, chemical doping and X-ray imaging device, where ΔE_1 and ΔE_2 are differences between valence/conduction bands and luminescent centers, ΔE_3 and ΔE_4 are differences between STE states and luminescent centers, ΔE_5 is difference between vacancy traps and luminescent centers.

References

1. M.G. Brik, C.-G. Ma, Theoretical spectroscopy of transition meatal and rare earth ions: From free state to crystal field. Jenny Stanford Publishing, Singapore, 2020.
2. N. Ding, W. Xu, D. Zhou, G. Pan, D. Li, Y. Ji, X. Chen, D. Yang, X. Bai, C.-G. Ma, H. Song, Nano Energy, 76 (2020) 105103.
3. D. Li, W. Xu, D. Zhou, Y. Ji, N. Ding, X. Chen, J. Zhu, R. Sun, S. Lu, C.-G. Ma, Z. Jia, G. Qin, X. Bai, H. Song, Adv. Opt. Mater., 9 (2021) 2100423.
4. K. Han, J.W. Qiao, S. Zhang, B.B. Su, B.B. Lou, C.-G. Ma, Z.G. Xia, Laser Photonics Rev., 17 (2023) 2200458.

The Formation and Magnetic Properties of Metastable Hexagonal Phase in Doped $LuFeO_3$

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Complex oxides are a group of materials that based on their crystal structure, elemental composition, and preparation method can obtain a wide variety of different properties. However, nowadays the requirements for practical applications of such compounds are more demanding than ever before. To fir these demands, many new areas of development are undertaken. One such area of development involves combining several different properties in one material. The most famous class of such materials is referred to as multiferroic. The combination of ferroelectricity and ferro/antiferromagnetism is of particular technological importance. However, the number of materials that exhibit such a combination of properties at or above room temperature is extremely scarce. This is mainly because ferromagnetism and ferroelectricity arise from opposite electronic configurations of the atoms [1]. Furthermore, quite often the coupling between electrical and magnetic orderings is also rather weak. As such a lot of research is still being done into looking for new and strongly coupled room temperature multiferroic materials.

One potential room temperature multiferroic compound is hexagonal $LuFeO_3$. Hexagonal $LuFeO_3$ is a polar compound where ferroelectricity is caused by geometric factors, mainly the displacement of Lu ions in the crystal lattice [2]. The magnetic properties arise from the 120° triangular arrangement of magnetic moments of the iron ion sublattice in the *ab* plane [3]. However, the main drawback of this material its difficulty in fabrication. This is caused by the fact that the hexagonal structure in the $LuFeO_3$ matrix and metastable and needs to be stabilized [4]. The metastable structure can be stabilized by either strain during thin film preparation or via doping. However, doping can also cause unexpected changes to either electrical or magnetic properties as well. Furthermore, the phase formation is complicated and the stability regions of the hexagonal phase are difficult to describe as they differ for each of the dopants while also being sensitive to the preparation method and even the calcination temperature [5]. Due to these reasons further insights and clarifications are still needed.

As such we provide insights into the stabilization of the hexagonal structure in Sc or Mn doped $LuFeO_3$ prepared using an aqueous sol-gel synthesis procedure. While also providing further clarification on the concentration ranges of the different structural phases present in the system. The crystal structure of the compounds was investigated by means of X-ray diffraction coupled with Rietveld refinement and Raman spectroscopy. Particle morphology was investigated by scanning electron microscopy. Lastly, we provide additional insight into the magnetic structure and its changes at low and room temperatures.

References

1. N.A. Hill, J. Phys. Chem. B. **104** (2000) 6694–6709.
2. S.M. Disseler, X. Luo, et. al., Rev. B. **92** (2015) 054435.
3. P. Suresh, K. Vijaya Laxmi, et. al., Phys. Rev. B. **97** (2018) 184419.
4. E. Magome, C. Moriyoshi, et. al., Jpn. J. Appl. Phys. **49** (2010) 09ME06.
5. A. Pakalniškis, D.O. Alikin, et. al., Materials (Basel). **15** (2022) 1048.

Inorganic and hybrid organic-inorganic materials exhibiting chiroptical activity

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Circularly Polarized Luminescence (CPL) is gaining increasing interest in materials chemistry and physics thanks to the broad range of possible biological [1] and technological applications,[2] including the design of CPL phosphors for specific chiroptical applications, such as in CPL-microscopy [3] and possibly in CPL security devices or inks.[4] In this contribution, we present the synthesis and the spectroscopic investigation of two classes of materials exhibiting CPL activity in the visible spectral region. The first class is fully inorganic and is constituted by the members of the $Tb_{1-x}Eu_xPO_4·0.67H_2O$ (with x = 0, 0.005, 0.01, 0.05, 0.1 and 1) solid solution,[5] whilst the second one is represented by chiral Tb(III)- and Eu(III)-based coordination compounds [6] (Fig. 1). These materials can be considered good candidates for advanced chiroptical applications.

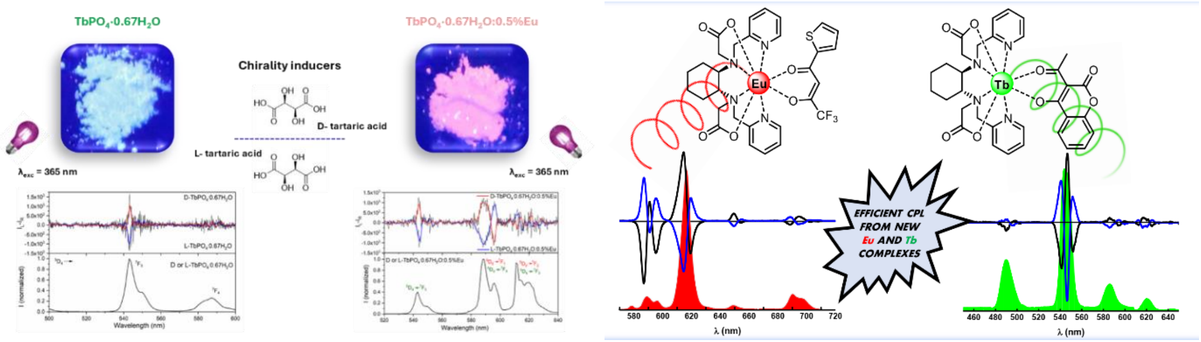

Fig. 1. Total and CP luminescence spectra of some materials discussed in this contribution.

References

1. Frawley, A. T.; Pal, R.; Parker, D. *Chem. Commun.* **2016**, *52* (91), 13349–13352
2. Zinna, F.; Pasini, M.; Galeotti, F.; Botta, C.; Di Bari, L.; Giovanella, U. *Adv. Funct. Mater.* **2017**, *27* (1), 1603719.
3. Stachelek, P.; MacKenzie, L.; Parker, D.; Pal, R. *Nat. Commun.* **2022**, *13* (1), 553.
4. MacKenzie, L. E.; Pal, R. *Nat. Rev. Chem.* **2021**, *5* (2), 109–124.
5. Ceccon, L.; Cavalli, E.; Ruggieri, S.; Bettinelli, M.; Piccinelli, F. submitted for publication.
6. Ruggieri, S.; Mizzoni, S.; Nardon, C.; Cavalli, E.; Sissa, C.; Anselmi, M.; Cozzi, P.G.; Gualandi, A.; Sanadar, M.; Melchior, A.; Zinna, F.; Willis, O.G.: Di Bari, L.; Piccinelli, F. *Inorg. Chem.* **2023**, 62, 8812-8822.

Zinc Aluminate Nd, Ce based material in form of core shell particles and sub-micrometer films for NIR Emitting applications

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Nanoarchitecture design of materials offers great opportunities to achieve unusual properties, but requires simple, scalable and reproducible fabrication techniques that ensure sufficient resolution and material quality[1]. This can be extremely challenging for complex structures that span multiple length scales, down to nanosized feature. We present a study showing advances in the fabrication of $ZnAl_2O_4$:Nd,Ce uniform-sized nanofibers via cost-efficient sol–gel route with nanoscale features and their peculiar properties interesting for **safer vitro bio-labelling applications**. From a broader perspective, this interdisciplinary work in chemistry, physic and bio- engineering areas can be applied in other material form such as sub-micron films. A simple and cost-effective screen-printing route assisted by molten salts has been developed to produce luminescent $ZnAl_2O_4$: Nd, Ce sub- micron films over poly and monocrystalline alumina substrates. The films are uniform and dense, and the use of sapphire substrate opens up new possibilities in optoelectronic and photonic devices due to their optical transparency in a wide wavelength range[2].

An adequate compositional engineering strategy as well as the Ce content play fundamental role in the fabrication of homogeneous $ZnAl_2O_4$-based material with the high optical performance. It has been demonstrated that the incorporation of Cerium together with Neodymium promotes NIR emission of the material[3]. In-depth analysis were done by XPS and XANES spectroscopy to quantify the Ce^{3+}/Ce^{4+}.The NIR luminescence under 357 nm is achieved by the incorporation of Cerium and its stabilization as Ce^{4+}.

The controlling of the crystallinity of the phase structure of the films is a mandatory requirement for a high- efficiency films. Certain texture was achieved over polycrystalline substrates, however predominant (hk0)-textured films were obtained over sapphire substrates. The preferential orientations degree has a role in the final luminescence response[4].

We believe that the proposed methodology to design $ZnAl_2O_4$-based material makes a crucial contribution to develop the efficient NIR emitters and may be applied to other aluminate-based systems.

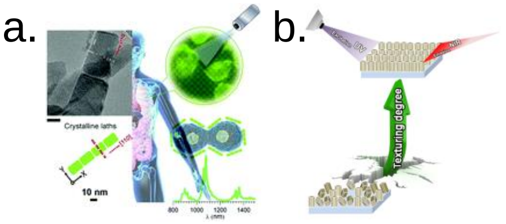

Fig. 1. (a) Nd- Ce co-doped ZnAl2O4 nanofibers show NIR emission under UV and IR excitation **(b)** Textured $ZnAl_2O_4$: Nd, Ce sub-micron films are obtained by a cost-efficient screen-printing technique assisted by molten salts.

References

1. R.E. Rojas-Hernandez, F. Rubio-marcos, J.F. Fernandez, I. Hussainova, Aluminate-Based Nanostructured Luminescent Materials :, Materials (Basel). (2021) 1–18.
2. R.E. Rojas-Hernandez, F. Rubio-Marcos, A. Serrano, I. Hussainova, J.F. Fernandez, Boosting phosphorescence efficiency by crystal anisotropy in SrAl2O4:Eu,Dy textured ceramic layers, J. Eur. Ceram. Soc. 40 (2020) 1677–1683. https://doi.org/10.1016/j.jeurceramsoc.2019.11.019.
3. R.E. Rojas-Hernandez, F. Rubio-Marcos, G. Gorni, C. Marini, M. Danilson, L. Pascual, R.U. Ichikawa, I. Hussainova, J.F. Fernandez, Enhancing NIR emission in ZnAl2O4:Nd,Ce nanofibers by co-doping with Ce and Nd: A promising biomarker material with low cytotoxicity, J. Mater. Chem. C. 9 (2021) 657–670. https://doi.org/10.1039/d0tc04752j.
4. R.E. Rojas-Hernandez, F. Rubio-Marcos, A. Serrano, S. Román-Sánchez, J.F. Fernandez, I. Hussainova, Highly textured zinc aluminate: Nd, Ce films over sapphire for NIR emitting applications, Ceram. Int. (2023). https://doi.org/10.1016/j.ceramint.2022.12.190.

Novel luminescent multi-component composites for anti-counterfeiting systems

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The study aimed to obtain *luminescent multi-component composites* that could emit in red and near-infrared range depending on the excitation used to illuminate them, possessing at least two levels of safety.

Various luminescent materials, having different natures and properties, mixed together, may work in synergy. Egyptian Blue (EB, $CaCuSi_4O_{10}$) and Han Blue (HB, $BaCuSi_4O_{10}$) have been chosen as blue pigments, able to convert efficiently red radiation into infrared one. Red phosphors such as $YPO_4:Eu^{3+}$, $YAG:Eu^{3+}$ and $Y_2O_2S:Eu^{3+},Mg^{2+},Ti^{4+}$ have been added to the blue pigments and dispersed in an aqueous solution, by using two different polyvinyl alcohol (PVA) or arabic gum (AG) as medium, or into a silica matrix.

The composite preparation included systematic studies to prepare a stable colloidal system and to investigate the role of parameters such as concentration, pH and the presence of any additives affecting its stability, the transparency and the optical properties. All counted parameters are important for following using of investigated composites as the security markers. The kind of interactions responsible for the stability of composite was also investigated. Based on the tests, the specific luminescent characteristics of the composites tested were selected to allow their application in the field of security and anti-counterfeiting.

Luminescence Thermometry with Lanthanoid Ions: An Approach to Gain a Better Understanding of Non-radiative Transitions

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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. 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 and Pukhov [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 want to 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 verified by careful experiments [8]. This is supposed to break with the paradigm that radiative and non-radiative decay channels are two different pathways but indeed are much more related than may be actually expected.

References

1. a) M. Bixon, J. Jortner, *J. Chem. Phys*. **48** (1968), 715–726; b) R. Englman, J. Jortner, *Mol. Phys.* **18** (1970), 145–164.
2. a) L. A. Riseberg, H. W. Moos, *Phys. Rev*. **174** (1968), 429–438; b) J. M. F van Dijk, M. F. H. Schuurmans, *J. Chem. Phys*. **78** (1983), 5317–5323.
3. a) R. Englman, B. Barnett, *J. Lumin.* **3** (1970), 37–54; b) C. W. Struck, W. H. Fonger, *J. Lumin.* **10**, (1975), 1–30.
4. Z. Burshtein, *Opt. Engin.* **49** (2010), 091005.
5. a) K. K. Pukhov, V. P. Sakun, *Phys. Stat. Sol. B* **95** (1979), 391–402. b) Y. V. Orlovskii, R. J. Reeves, R. C. Powell, T. T. Basiev, K. K. Pukhov, *Phys. Rev. B* **49** (1994), 3821–3830.
6. a) V. L. Ermolaev, E. B. Sveshnikova, *J. Lumin.* **20** (1979), 387–395; b) E. B. Sveshnikova, V. L. Ermolaev, *Opt. Spectrosc.* **111** (2011), 34–50.
7. a) M. Suta, A. Meijerink, *Adv. Theory Simul*. **3** (2020), 2000176; b) C. D. S. Brites, R. Marin, M. Suta, A. N. C. Neto, E. Ximendes, D. Jaque, L. D. Carlos, *Adv. Mater.* **35** (2023), 2302749.
8. a) R. G. Geitenbeek, H. de Wijn, A. Meijerink, *Phys. Rev. Appl.* **10** (2018), 064006; b) M. Suta, Ž. Antić, V. Đorđević, S. Kuzman, M. D. Dramićanin, A. Meijerink, *Nanomaterials* **10** (2020), 543; c) T. P. van Swieten J. M. Steenhoff, A. Vlasblom, R. de Berg, S. P. Mattern, F. T. Rabouw, M. Suta, A. Meijerink, *Light: Sci. Appl.* **11** (2022), 343; d) B. Bendel, D. P. Thuy, S. Weber, D. Wenzel, A. Hoffmann, L.-W. Sadem, S. Haibach, M. Suta, *submitted* (2024).

The Presence and the Future of Luminescence Thermometry

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Luminescence thermometry presents a significant challenge in achieving accurate and reproducible temperature measurements under varying environmental conditions. This complexity arises from several factors, including the sensitivity of luminescent materials to changes in their surroundings, potential photobleaching, and the influence of quenching effects, which can all impact the emission intensity and lifetime of the luminescent signal. Therefore, it is crucial to develop robust calibration protocols and compensate for environmental perturbations to enhance the reliability and precision of luminescence-based temperature sensing.

Continuous innovation in material science, calibration techniques, and signal processing methods is necessary to ensure that luminescence thermometry can be effectively utilized in diverse and dynamic application environments, from biological systems to industrial processes, whether at very low or high temperatures.

In the presentation, we will discuss the current status of luminescence thermometry and its relevance to different application areas. This will include comparing its limitations and advantages to other methodologies and its comparison to pyrometry. The latter is often considered in contradiction to luminescence techniques, especially in the high-temperature regime. Additionally, we will explore various approaches to luminescence thermometry and their applicability to different anticipated applications.

Figure 1 illustrates the unique temperature dependence of the luminescence of $Ca_3Sc_2Si_3O_{12}$:0.1%Pr phosphor (a) and the derived relative thermal sensitivities based on the ratio of selected emission intensities (b). Specifically interesting is the resistance of the Pr^{3+} 5d$\rightarrow$4f luminescence to thermal quenching and the growth of intensity of the bluish-green emission from the $^3P_0$ level above ~800 K.

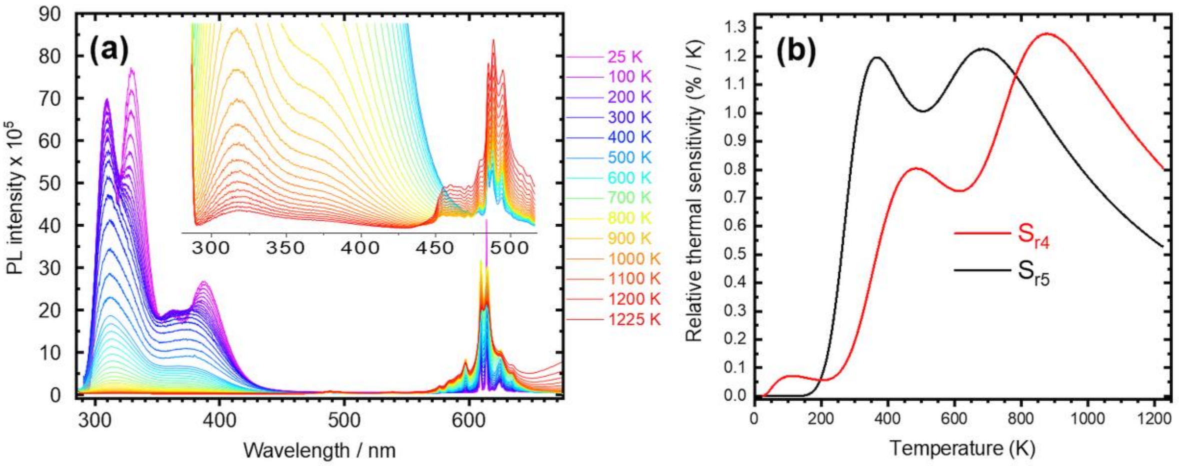

Fig. 1. Temperature dependence of luminescence of $Ca_3Sc_2Si_3O_{12}$:0.1%Pr phosphor (a) and the derived relative thermal sensitivities based on the ratio of selected emission intensities (b).

Acknowledgements:

We acknowledge the financial support of this research by the Polish National Science Centre (NCN) under the grant #UMO-2023/51/B/ST5/02341.

Oral presentation abstracts

Advancements and challenges in sintering of Cr^{4+}:YAG transparent ceramics

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Since the first successfully synthesized transparent Nd:YAG ceramics (Ikesue et al. 1995), the progress in transparent ceramic technology has significantly expanded the scope of applications for both continuous wave (CW) and pulsed lasers[1]. The most popular host for solid state lasers is Nd:YAG which occupies more than half of the laser crystals market. A large fraction of the laser market is occupied by passive Q-switched lasers which can operate in so called "giant pulse" generation mode. The crucial component of these lasers is phototropic material. Cr^{4+}:YAG remains the best choice for Q-switched lasers and suppresses all other alternatives (the exception of LiF crystals which are expensive and short lived). Global Cr^{4+}:YAG Crystals Market Size, Scope And Forecast Report highlight that the Cr^{4+}:YAG Crystals Market has witnessed swift and substantial growth in recent years, with projections indicating a continued significant expansion from 2023 to 2031. Despite the importance of Cr^{4+}:YAG ceramics, there is a limited number of published research articles. The reason for this is challenges which arise in Cr^{4+}:YAG transparent technology. One of the key components of YAG transparent ceramics technology is usage of TEOS sintering additive. Sintering of transparent YAG ceramics without TEOS sintering additives is one of the most perspective directions for further development of transparent ceramics. So far there are only a few papers that reported the sintering of Nd:YAG transparent ceramics without using TEOS sintering additives. Sintering of high quality Cr^{4+}:YAG transparent ceramics requires absence of TEOS sintering additives which is a challenge by itself[2]. Moreover, Cr^{4+}:YAG require presence of Ca^{2+} or/and Mg^{2+} charge compensation further complicates this task. This work focused on the influence of the single additives and their combinations on the sintering trajectory of tetravalent chromium - doped YAG ceramics[3].

Fig. 1: Photograph of the mirror polished Cr^{4+}:YAG ceramics

References
1. Chaika, M. A., et. all. . Eur. Ceram. Soc. 39, no. 11 (2019): 3344-3352.
2. Chaika, M. A., Ceram. Intern. 46, no. 14 (2020): 22781-22786.
3. Chaika, M. J. Eur. Ceram. Soc. 44, no. 13 (2024): 7432-7450.

Nanosized silicate-phosphate hydroxyapatite co-doped with Gd^{3+} and Eu^{3+} ions as a drug carrier

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In recent years, drug delivery systems have gained significant popularity. Direct administration of the active ingredient is often more suitable for bone tissue than oral dosages or infusions, as it minimizes unnecessary contact with other tissues and organs. Directly dosing anti-inflammatory drugs (such as ibuprofen or ketoprofen) to inflamed tissues not only reduces the liver's workload but also enhances drug performance by providing a more controlled and prolonged release (**Figure 1**).

Controlled drug release in bone tissue can be achieved through various methods and materials designed for sustained and targeted delivery of therapeutic agents. Here, the potential of bioactive apatite species ($Ca_{10}(PO_4)_6X_2$ where X = OH^-, F^-, or Cl^-) arises. Nanosized apatite, with its porous structure and excellent biocompatibility with bone tissue, shows great promise as a drug-loading matrix. Its unique structure allows ion exchange in multi-ion substitutions while maintaining beneficial bio-properties.

In this study, we aim to create multifunctional carriers for targeted drug delivery to damaged bone tissue, incorporating fluorescent tracking capabilities. The structure is modified to include silicate (SiO_4^{4-}) groups and co-doped with rare earth ions (RE^{3+}), specifically Eu^{3+} and Gd^{3+} ions. This combination is expected to enhance the bone treatment capacity due to the silicates and provide bio-imaging properties due to the rare earth dopants.

Various drug-loading approaches were applied and compared to identify the most effective method. Ketoprofen, a non-steroidal anti-inflammatory drug (NSAID) with analgesic and antipyretic effects, was used as the model drug. The drug loading capacity was analyzed using thermogravimetry. Additionally, the structure and morphology of the apatite matrix and the drug-loaded carrier were analyzed using techniques such as X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), and high-resolution transmission electron microscopy (HR-TEM). The drug release profile was assessed using UV-Vis spectroscopy.

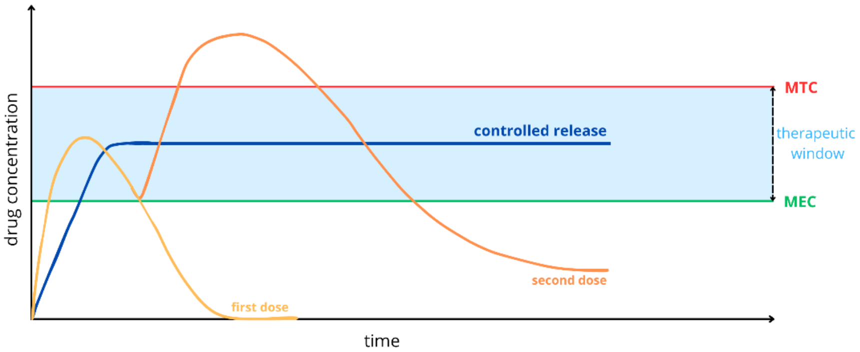

Fig. 1. Schematic comparison of the drug release profiles for oral dosage (first and second dose) and controlled release from the carrier. MEC stands for minimal effective concentration, MTC stands for maximum therapeutic concentration.

Persistent luminescence and trap properties of UV emitting materials based on RE-doped silicates

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For the last few decades, extensive research has been conducted on the materials that persist to emit optical radiation long after any charging stops. Most established persistent luminescence materials emit light in the visible part of the spectrum; however, there has been a growing interest in UV-emitting persistent phosphors in recent years. These materials have been tested for various applications, such as photocatalysis, sterilisation, and anti-counterfeiting, among others. Here, we report on RE-doped silicate materials that exhibit long-lasting UV afterglow after charging, not only with X-rays but also UV. Three materials were analysed in detail: UVA emitting $Sr_3MgSi_2O_8$: Ce^{3+} [1] and UVC emitting $Sr_2MgSi_2O_7$: Pr^{3+} [2] and $Ca_2Al_2SiO_7$: Pr^{3+} [3]. All samples with varied dopant concentrations were synthesised using solid-state reaction synthesis in an ambient atmosphere. A thorough investigation was conducted using photoluminescence (PL), electron paramagnetic resonance (EPR) and thermally stimulated luminescence (TSL) spectroscopy methods.

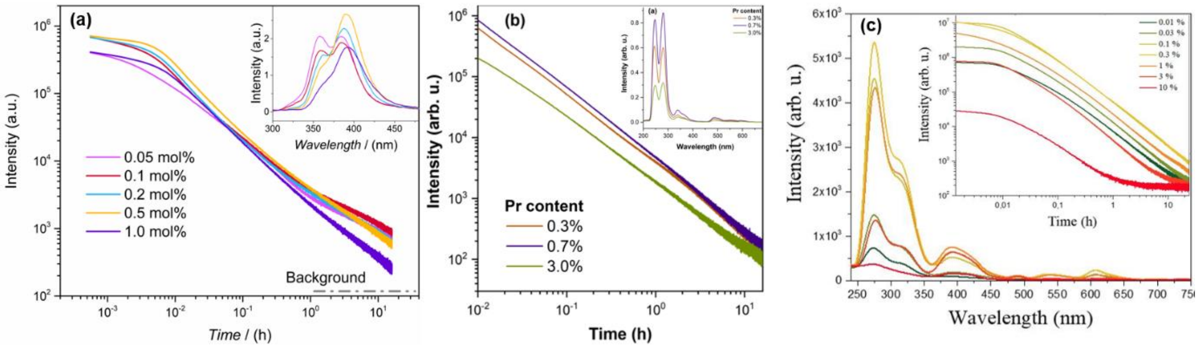

Fig. 1. Decay kinetics and persistent luminescence spectra of a) $Sr_3MgSi_2O_8$: Ce^{3+} b) $Sr_2MgSi_2O_7$: Pr^{3+} and c) $Ca_2Al_2SiO_7$: Pr^{3+}.

This research is funded by the Latvian Council of Science, project “Defect engineering of novel UV-C persistent phosphor materials”, project No. lzp-2021/1-0118.

References

1. G. Doke, G. Krieke, P. Rodionovs, D. Nilova, A. Antuzevics, Journal of Rare Earths (2024).
2. A. Antuzevics, G. Doke, G. Krieke, P. Rodionovs, D. Nilova, J. Cirulis, A. Fedotovs, U. Rogulis, Materials 16 (2023) 1776.
3. D. Nilova, A. Antuzevics, G. Krieke, G. Doke, I. Pudza, A. Kuzmin, J Lumin 263 (2023) 120105.

The hydrogenation behaviour of the Zintl phases Eu*Tt* (*Tt* = Si, Ge, Sn)

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Zintl phases exhibit a vast range of structure and bonding motifs upon hydrogenation, from “polyanionic hydrides” containing covalently bound hydrogen to ionic “interstitial hydrides”.[1] Within the CrB-type Zintl phases (space group no. 63, *Cmcm*) of the composition MTt (M = Ca, Sr, Ba; Tt = Si, Ge, Sn) several ternary hydrides $MTtH_x$ show features of interstitial as well as polyanionic hydrides.[2]

The CrB-type structure consists of planes of edge sharing *M* tetrahedra with rows of chalcogen like “zig-zag”-chains in between. Upon hydrogenation, the tetrahedral sites are filled with hydride ions up to a hydrogen content of $x = 1$. The filled tetrahedra in hydrogen poorer phases are unordered whereas richer phases show ordered supercells. Hydrogenation beyond fully occupied tetrahedra is achieved by a tilting of the chains, accompanied by new *Tt*-*Tt*-bonds and the termination of the resulting bands through covalently bound hydrogen. To distinguish between the three groups, the phases are referred to as *α*-, *β*- and *γ*-hydrides with rising hydrogen contents. The maximal hydrogen uptake increases with rising cation size as the chains are further apart (e.g.: $CaSiH_{4/3-y}$, $SrSiH_{5/3-y}$, $BaSiH_{2-y}$) and decreases toward heavier anions.[2]

Given the similar ionic radii between Sr and Eu one would expect the *γ*-hydride of EuSi to be analogous to $SrSiH_{5/3-y}$. However, for Eu*Tt* (*Tt* = Si, Ge, Sn) only one report of $EuSiH_{1.8}$ was published, with the hydrogen content being determined via carrier hot gas extraction.

Eu*Tt* (*Tt* = Si, Ge, Sn) were synthesized by induction heating, hydrogenated in autoclaves and analyzed with powder X-ray diffraction and Rietveld refinement. The X-ray powder diffraction data of hydrogenated EuSi suggests a structure isotypic to *γ*-$SrSiH_{5/3-y}$ in space group *Pnma* (a = 1444.82(9) pm, b = 395.52(2) pm, c = 2414.7(2) pm). An *in situ* neutron powder diffraction experiment was conducted on EuGe showing multiple hydrides upon hydrogenation and reversibility between phases.

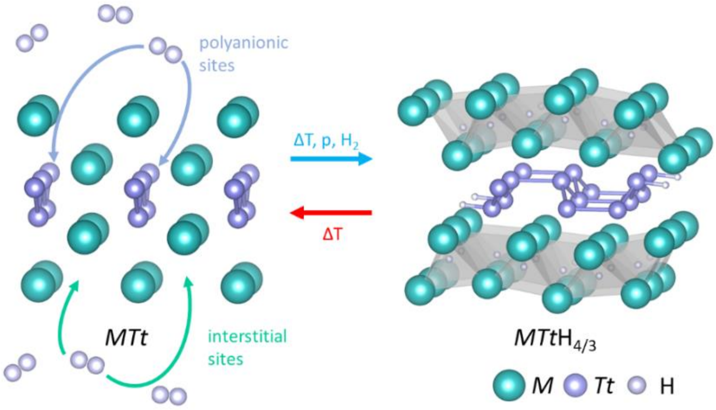

Fig. 1. Structural features of CrB-type *MTt* and the ternary hydride $MTtH_{4/3}$.

References
1. U. Häussermann *et al.*, Struct. Bond., **139** (2011) 143–162.
2. H. Auer *et al.*, Inorg. Chem., **56** (2017) 1061-1071.
3. M. Armbruster *et al.*, Z. Anorg. Allg. Chem., **635** (2009) 1758–1766.

Bimodal, Shape-Tunable, Eu^{3+}-Doped $GdPO_4$ Nanoparticles and Their Impact on Zooplankton Daphnia Magna

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Inorganic luminescent nanoparticles containing various lanthanide ions are extensively researched, particularly for applications in energetics, biomedicine, anti-counterfeiting, and more [1,2]. However, their synthesis often overlooks green chemistry principles, relying on environmentally harmful precursors and solvents. This typically results in nanoparticles with hydrophobic surfaces, limiting their potential applications, especially in bio-related fields.

Our research presents Eu^{3+}-doped $GdPO_4$ nanorods, nanoprisms and sub-microspheres synthesized via hydrothermal route, a method considered to adhere to green chemistry principles. Nanoparticles produced via this approach are hydrophilic, facilitating their easy redispersion in aqueous media, thus, showing promise for bio-related applications [3]. With magnetically active Gd^{3+} and optically active Eu^{3+} ions, these nanoparticles are potential candidates as agents in bioimaging. The presentation will include a comprehensive analysis of the structural, optical, and magnetic properties of $GdPO_4:Eu^{3+}$ nanoparticles, as well as results from bioaccumulation and toxicity studies on zooplankton *Daphnia magna* (Fig. 1).

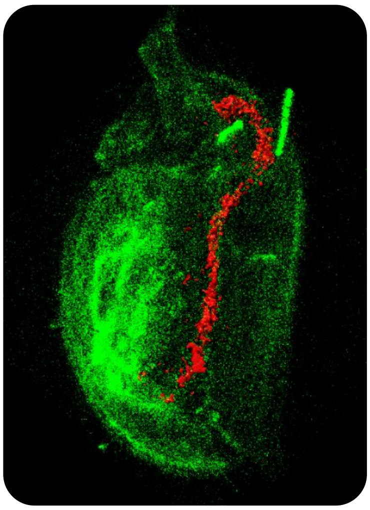

Fig. 1. Confocal microscopy image of a single *Daphnia magna* with $GdPO_4:15\%Eu^{3+}$ nanorods visible (red) in its digestive tract.

References

1. Z. Yi, Z. Luo, X. Qin, Q. Chen, X. Liu, Accounts Chem. Res., **53** (2020) 2692-2704.
2. G. Wang, Q. Peng, Y. Li, Accounts Chem. Res., **44** (2011) 322-332.
3. M. Janulevicius, V. Klimkevicius, A. Vanetsev, V. Plausinaitiene, S. Sakirzanovas, A. Katelnikovas, Mater. Today Commun., **23** (2020) 100934.

Study of the tetrad effect in adsorption systems

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Lanthanides are a group of metals containing fifteen f-electron elements of the sixth period with the increasing atomic numbers from 57 to 71, from lanthanum to lutetium. Chemical similarity of lanthanides results from the same electronic structure of the outer shells and slight differences in atomic and ionic radii. With the increase in the atomic number in the La-Lu series, the subsequent valence electrons are located in the 4f subshell and as f-electron elements they have the electronic configuration: 4f1-14 5d0.1 6s2, where lanthanum, gadolinium and lutetium have the 5d1 electrons. At present lanthanides have numerous applications, includ those electronic, electrical and ceramic industries, as phosphors, dyes, car catalysts, fuel cells, NiMH batteries and in medicine. Such a wide use of lanthanides is related to their uncontrolled presence in the environment and the need to eliminate them. Among the methods used for removing lanthanides from the aquatic environment, the adsorption method is very common. In the research, an attempt was made to analyze occurrence of the tetrad effect in the adsorption systems was analyzed on several adsorbents: zeolite A and mordenite as well as the clays: bentonite and red clay. The tetrad effect was first observed and described independently by Peppard, Fidelis and Siekierski. It involves dividing the entire series of lanthanides into four tetrads: La, Ce, Pr, Nd (I tetrad), Pm, Sm, Eu, Gd (II tetrad), Gd, Tb, Dy, Ho (III tetrad), Er, Tm , Yb, Lu (IV tetrad). The occurrence of the tetrad effect (concave or convex) in the course of the Kd partition constants in the adsorption systems enables prediction of the interaction nature (covalency) between the lanthanide ion and the ligand in the complexation reaction products. The lack of the tetrad effect proves that the interaction between the electrons of the ligands and the f-orbitals of lanthanide ions (Ln^{3+}) in their complexes is of Coulombic nature and the electron orbitals of these two forms do not overlap [1-3]. Therefore, determining the existence of the tetrad effect contributes to prediction of nature of substrates and products of the adsorption process.

References

1. M. Majdan, A. Gładysz-Płaska, S. Pikus, D. Sternik, O. Maryuk, E. Zięba, P. Sadowski, J. Molec. Struct., 702 (2004) 95-102.
2. A. Gładysz-Płaska, M. Majdan, S. Pikus, J. Colloid. Inter. Sci., 317 (2008) 409-423.
3. K. De Jesus et al., J. Mol. Liq., 333 (2021) 116006.

Structural and Electrochemical Investigation of Al-Eu Compositional Thin Film Libraries

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In this study, Al-Eu compositional thin film libraries were produced via thermal co-evaporation, covering a compositional range of 0.5 - 5.0 at.% Eu. The resulting samples were characterized using Scanning Electron Microscopy (SEM), Scanning Energy Dispersive X-ray Spectroscopy (SEDX), X-ray Diffraction (XRD), Atomic Force Microscopy (AFM), and contact angle measurements. Additional electrochemical measurements have been conducted. As shown in previous studies, rare-earth elements, significantly influence the structural and electrochemical properties of Al [1]. In the case of the Al-Eu system, three intermetallic compounds are known, alongside two eutectic points [2]. Until now there are no comprehensive studies on the influence of Eu on the electrochemical behavior of Al matrices over a broad compositional range. This study represents a step in identifying promising compositions and potential applications of Al-Eu thin films. The use of compositional thin film libraries allows to analyze broad compositional ranges in a short time frame. The findings so far show pronounced nanostructuring and the formation of intermetallic compounds within the thin film libraries as illustrated in **Figure 1**. Furthermore, contact angle measurements indicate significant deviations in the region of the first eutectic point. It also shows that Eu strongly effects the stability of the Al matrix with all electrochemical tests conducted so far resulting in the ablation of the films. To further investigate the electrical influences of Eu on the alloy Deep-Level Transient Spectroscopy (DLTS) was performed to analyze the energy levels of potential defects and to determine the temperature coefficient of the electrical resistivity [3].

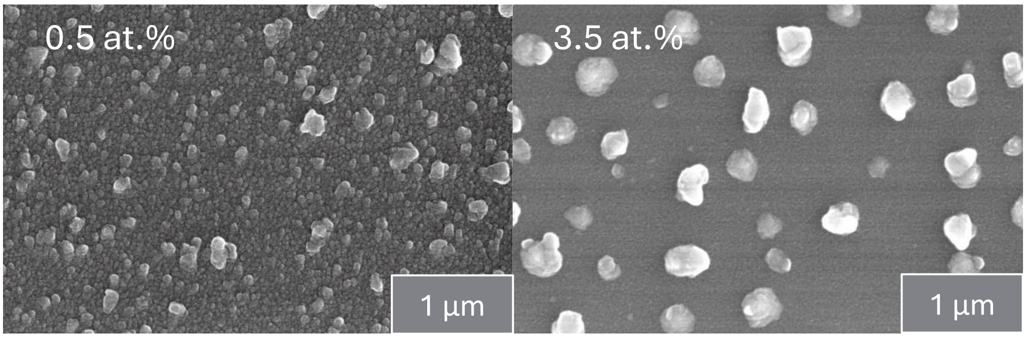

Fig. 1. SEM images of the co-evaporated AL-Eu thin film library, showing 0.5 at.% Eu on the left and 3.5 at.% Eu on the right.

References
1. A.I. Mardare, C.D. Grill, I. Pötzelberger, T. Etzelstorfer, J. Stangl, A.W. Hassel, J Solid State Electrochem **20** (2016) 1673-1681
2. H. Okamoto, JPE **12** (1991) 499-500.
3. J. Lauwaert, S. Khelifi, In Capacitance Spectroscopy of Semiconductors. Taylor and Francis, Oxfordshire UK, 2018, p. 61-84

Luminescent microstructures: laser 3D printing and luminescence study

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As more and more research on luminescent materials is being conducted, more and more potential applications seem to within reach. Luminescence is being applied in various photonic devices, such as waveguides, in QR codes and in solar concentrators. One of the most attractive applications of 3D printing is for the production of microlasers. Currently, luminescent materials such as YAG, are being produced by using the aging Czochralski [1,2,3] method. This method can efficiently produce monocrystals, but producing them in microscale and post-processing is still difficult. This study aims to show that 3D printing, along with calcination, can be used to replace the czochralski method in the production of luminescent materials some initial results of synthesis and experimentation on luminescent materials will also be provided and reviewed. Some promising results were also obtained in this study on the subject of YAG ($Y_3Al_5O_{12}$) synthesis inside a structurized polymer by utilising a femtosecond laser system.

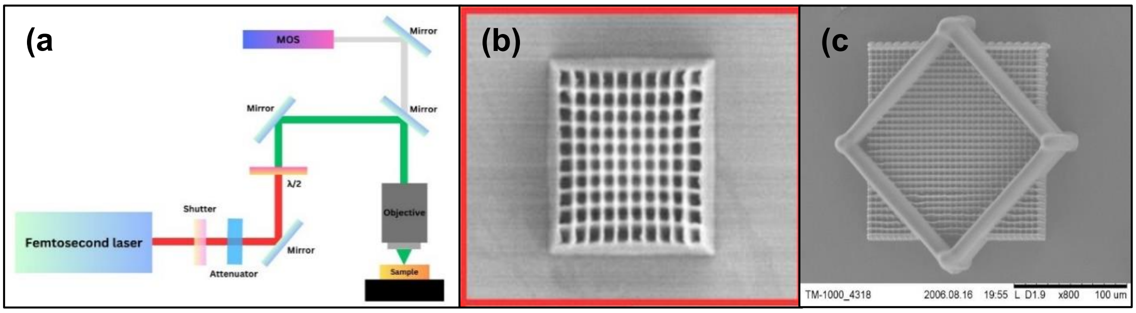

Figure 1. (a) Femtosecond laser system scheme used for the fabrication of microstructures. (b) SEM image of photonic crystal obtained from YAG precursor inside a polymer. (c) SEM image of a woodpile with a support structure made using SZ2080^{TM}.

YAG precursor 3D objects were produced using Laser Nanofactory machine (UAB Femtika) and SZ2080^{TM} microstructures using Pharos Yb:KGW femtosecond laser system. 517 nm wavelength laser was used for the fabrication of YAG precursor microstructures, while 515 nm wavelength was used for SZ2080^{TM}. In order to study and determine the most optimal production parameters for this materials, they were produced in 3D array of raster structures by changing laser power and fabrication speed. After fabrication polymerized YAG precursor samples were immersed in ethanol to dissolve the polymer and rinsed with NovecTM 7100 in order to reduce the surface tension that can cause deformation of the structures, while SZ2080^{TM} microstructures were immersed 4-methyl-2-pentanone to dissolve the polymer. While fully ideal structures post-calcination are yet to be obtained, this work is already showing some promising results.

References

1. Ikesue, A., Aung, Y. L., and Lupei, V., [Ceramic Lasers], Cambridge University Press (2013).
2. Ramirez, M. O., et al. , “Three-dimensional grain boundary spectroscopy in transparent high power ceramic laser materials,” Opt. Express 16, 5965–5973 (2008).
3. Uhrin, R. and Belt, R. F., “Manufacturing methods and technology engineering for growth of large diameter nd: Yag laser crystals,” Litton Systems, Inc. (1979-1983).

Weak Coordination in Silicate-Analogous Host Structures

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Silicates are the most abundant natural compound class and comprise an almost inexhaustible structural variety. On this basis, various substitution variants of silicates, such as nitridosilicates, have been developed. A rather young material class are borosulfates or "sulfatoborates", featuring corner-sharing boron and sulfur-centered oxo-tetrahedra (Fig. 1, left), which thus can also be considered as silicate-analogous materials [1]. Borosulfates show the weakest coordination strength towards doped rare-earth ions of all silicate-analogous host structures so far. Further, fluorooxoborates, featuring borate (BO_3F) tetrahedra are of also interest in this context [2]. We demonstrate that these compound classes exhibit coordination strengths similar to fluorides but involve condensed anions. In our contribution we will focus on the luminescence in such weakly coordination solid state host structures of Eu^{2+}, Eu^{3+}, Tb^{3+}, Ce^{3+} and Gd^{3+} – the latter leading to a potential application as Boltzmann thermometer [2-5]. The observed deep-UV luminescence of trivalent cerium and divalent europium (Fig. 1, centre and right) might be of interest for disinfection purposes [2,5].

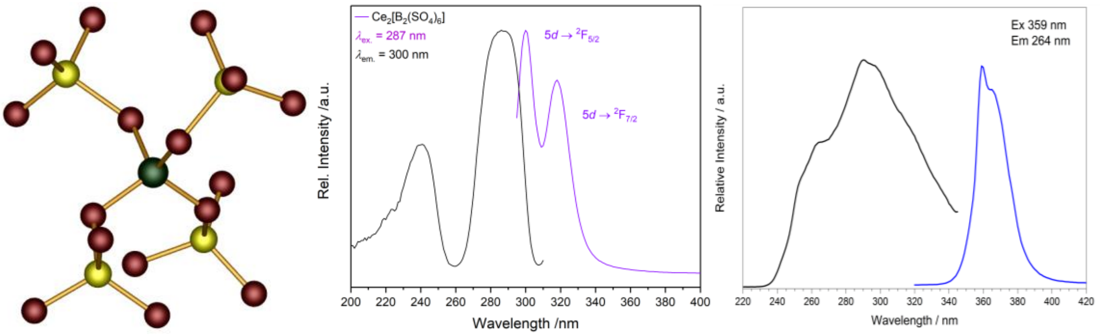

Fig. 1. Typical basic supertetrahedral building unit of borosulfates, i.e. $B(SO_4)_4$ (left), luminescence spectra of $Ce_2[B_2(SO_4)_6]$ (centre) and of $Ba[B_4O_6F_2]:Eu^{2+}$ (right).

References

1. J. Bruns, H. A. Höppe, M. Daub, H. Hillebrecht, H. Huppertz, Chem. Eur. J., **26** (2020), 7966−7980.
2. S. G. Jantz, M. J. Schäfer, L. van Wüllen, F. Pielnhofer, R. Weihrich, H. A. Höppe, Chem. Eur. J., **24** (2018), 443.
3. P. Netzsch, M. Hämmer, P. Gross, H. Bariss, T. Block, L. Heletta, R. Pöttgen, J. Bruns, H. Huppertz, H. A. Höppe, Dalton Trans., **48** (2019), 4387.
4. P. Netzsch, M. Hämmer, E. Turgunbajew, Th. P. van Swieten, A. Meijerink, H. A. Höppe, M. Suta, Adv. Opt. Mat. **10** (2022), 2200059.
5. H. Höppe, Rare-Earth Elements. DeGruyter, Berlin/Boston, 2024.

Synthesis and investigation of $LaScO_3$:Yb, Er – a new versatile ratiometric optical temperature sensor

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Modern research into luminescence concerns a wide variety of topics beyond just providing illumination, including lasers [1], anti-counterfeit measures [2], and sensors [3]. For these broader applications of luminescent materials, rare-earth elements are a near-irreplaceable tool. Options such as combining several lanthanides or using different matrices, as well as the many energy levels available due to f-shell electrons make lanthanide luminescence very versatile and create many options to investigate [4].

In this work, one such previously unexplored combination is investigated. The interlanthanide $LaScO_3$ was chosen as a matrix, due to its structural peculiarities and lack of innate absorption bands in the visible part of the spectrum. Er^{3+} and Yb^{3+} were selected as the dopants, as their applicability in ratiometric temperature measurements coming from Er^{3+} 520/549 nm peak ratio is well-established, with Yb^{3+} as an enabler of upconversion [5]. This also provided the advantage of enabling comparison of the influence of the matrix on the system as well as the temperature dependence to the same dopants in other matrices.

The results showed that the system was suitable for temperature sensing. Furthermore, beyond the traditional use of the 520/549 Er^{3+} luminescence peak ratio, it was shown that for certain temperature ranges, two other peaks could potentially be applied – specifically one located at 661 nm and another corresponding to an uncommon transition at 702 nm. Some unusual lattice parameter dependence of dopant concentration was also observed.

References

1. M. Galceran, M. C. Pujol et. al., J. Am. Ceram. Soc., **93, 11** (2010) 3764-3772
2. E. Paradisi, C. Mortalò et. al., ACS Appl. Nano Mater. **7, 7** (2024), 6893–6905
3. S. F. Collins, G. W. Baxter et. al., J. Appl. Phys. **84, 9** (1998) 4649–4654
4. V. K. Rai, Appl. Phys. B **88** (2007) 297-303
5. T. C. Huang, W. F. Hsieh, J. Fluoresc. **19** (2009), 511-516

2 inch diameter growth of Eu doped $BaCl_2$/KCl/NaCl eutectic scintillator for X-ray imaging applications

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[Introduction] Imaging detectors that detect radiation such as X-rays, gamma rays, α rays, and β rays are widely used in applications such as medical imaging, security, resource exploration, high energy physics, and astronomy. In the X-ray imaging applications, radiation imaging sensors were composed of photodetector arrays and indirect flat panel detector (FPD) coupled with a scintillator plate. Up to now, we reported phase-separated scintillator fibers (PSSFs) in eutectic materials for high resolution radiation imaging such Tb:GAP/α-Al_2O_3[1], Tb:$BaCl_2$/KCl/NaCl [2]. These eutectics consist of higher refractive index scintillator fibers of several μm in diameter surrounded by lower refractive index matrix material. Such eutectic structure works as an optical waveguide. As a result, high resolution X-ray imaging can be achieved[3]. However, the ms order decay time to Tb^{3+} 4f4f transition is too slow for applications such as X-CT that require decay time below several μs.

[Material and Method] Eutectic growth was performed by the vertical Bridgman method using a 2inch diameter carbon crucible at a growth rate of 0.01 mm/min. $BaCl_2$, NaCl, KCl, and $EuCl_2$ powders with 99.9% purity were mixed at the eutectic point of 1 mol.%:$EuCl_2$, 26.2 mol.%:$BaCl_2$, 33.2 mol.%:NaCl, 39.6 mol.%:KCl as the starting material.

[Results] A photograph of a polished 2 inch dia. wafer was shown in Fig.1. The scattered electron image (BEI) of transverse and vertical cross-section of the eutectic is shown in Fig.2. The phase separated eutectic structure is well aligned and the region with such fibrous eutectic structure had optical transparency in the wafer. n this eutectic, 395 nm emission ascribed to Eu^{2+} 4f5d transition was observed at the highest refractive index $BaCl_2$ phase. The obtained eutectics have scintillation decay time of around 400 ns, accelerated with increasing Eu concentration (Fig.3). In our presentation, relationship between growth condition, eutectic structure, light guiding and scintillation properties is discussed. Radiation imaging is also demonstrated.

Fig.1 Photograph of the polished wafer

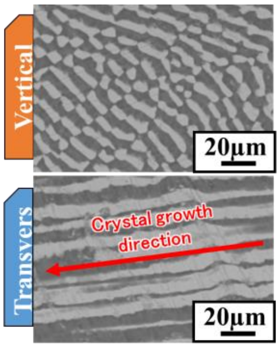

Fig.2 BEI of transverse and vertical cross-section of the eutectic r

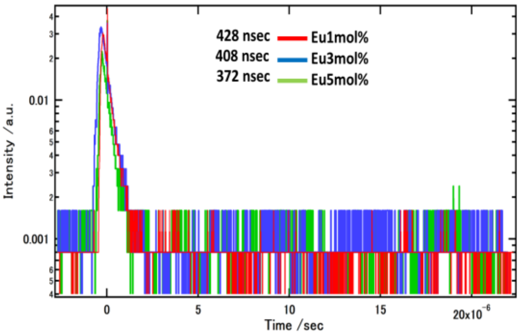

Fig.3 Scintillation decay curves under 662keV gamma-ray irradiation.

References
1. K. Kamada et al., Ieee Trans. Nucl. Sci., vol. 65, no. 8, pp. 2036–2040, 2018.
2. Y. Takizawa, K. Kamada et al 2022 Jpn. J. Appl. Phys. 61 SC1009
3. K. Kamada et al 2021 Jpn. J. Appl. Phys. 60 SBBK04

Energy transfer pathway between Cr^{3+} and Er^{3+} in $MgGa_2O_4$

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Phosphor-converted infrared light-emitting diodes (pc-LEDs) represent a significant advancement over conventional semiconductor LEDs based on InGaAs and GaAs, as well as traditional infrared sources like tungsten halogen lamps and laser diodes. They provide enhanced versatility, improved temperature stability, lower costs, and reduced energy consumption.[1] Consequently, there is an increasing demand for pc-LED light sources capable of emitting SWIR light. These developments hold great potential for applications in spectroscopy, optical coherence tomography, optical communication, and non-invasive medical imaging. Therefore, finding the most efficient phosphor is of utmost importance.

For practical applications, promising results have been achieved by applying phosphors containing Cr^{3+} and Ni^{2+} on top of blue LED chips,[2] utilizing the energy transfer pathway from Cr^{3+} ions to Ni^{2+}. In this study, we present an alternative approach that employs energy transfer from Cr^{3+} to Er^{3+}, resulting in narrower and prominent emission in the NIR-II range.

In this study, we present an investigation focused on the $MgGa_2O_4$ samples doped with varying concentration of Cr^{3+} and Er^{3+}. We examine the impact of chromium clusters present in the inverse spinel structure of $MgGa_2O_4$[3] and their efficiency in transferring energy to Er^{3+} ions. Our research integrates high-pressure measurements with temperature-dependent analyses and luminescence kinetic measurements. The objective is to clarify how the crystal field strength affects optical properties, investigate the mechanisms behind thermal quenching, and uncover the energy transfer pathways between Cr^{3+} and Er^{3+}.

References

1. V. Rajendran, H. Chang and R.-S. Liu, *Opt. Mater. X*, 2019, **1**, 100011.
2. C.-Y. Chang, M.-H. Huang, K.-C. Chen, W.-T. Huang, M. Kamiński, N. Majewska, T. Klimczuk, J.-H. Chen, D.-H. Cherng, K.-M. Lu, W. K. Pang, V. K. Peterson, S. Mahlik, G. Leniec and R.-S. Liu, *Chem. Mater.*, 2024, **36**, 3941–3948.
3. V. Rajendran, C.-Y. Chang, M.-H. Huang, K.-C. Chen, W.-T. Huang, M. Kamiński, T. Lesniewski, S. Mahlik, G. Leniec, K.-M. Lu, D.-H. Wei, H. Chang and R.-S. Liu, *Adv. Opt. Mater.*, 2024, **12**, 2302645.

Cation dependent Eu^{III} luminescence in carbacylamidophosphate based tetrakis-complexes

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Among the ligand systems satisfying the criteria of highly luminescent lanthanide complexes designing, there are carbacylamidophosphates (CAPh) - ligands having functional fragment -C(O)N(H)P(O)= [1]. Changing the substitutes near the chelating core in CAPhs molecules allows to influence on properties of lanthanides' complexes, including luminescence, thermal stability, solubility, stability upon storage, etc., which determines the perspective for practical use of the compounds.

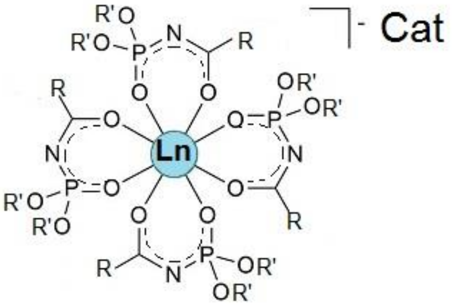

Fig. 1. General structural formula of Cat[LnL$_4$] complexes.

Among the most typical complexes of lanthanides with CAPhs there are tetrakis-complexes Cat[LnL$_4$] (Figure 1). The nature of the counter cation can be considered as an additional factor which allows alteration of the complex properties. Herein, we present structure and properties of a set of luminescent europium tetrakis-complexes based on four types of CAPh ligands (HL$^{1-4}$) (Figure 2) and different cations (Cs$^+$, NMe$_4^+$, NEt$_4^+$, and PPh$_4^+$). The influence of the CAPhs' substitutes and the cations on the thermal and luminescent properties of the Cat[EuL$^{1-4}_4$] is discussed.

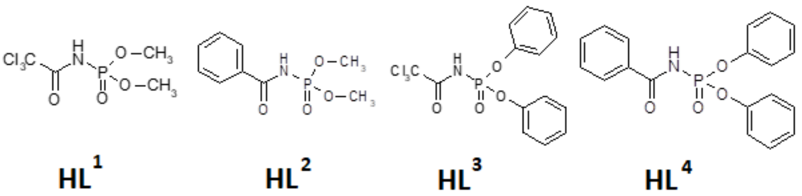

Fig. 2. Structural formulas of CAPhs used for synthesis of europium tetrakis-complexes.

References

1. V. Amirkhanov, V. Ovchynnikov, V. Trush, et al., in: Ligands: Synthesis, Characterization and Role in Biotechnology, Nova Science Publishers, New York, p. 199–2

Growth, scintillation properties, and pulse shape discrimination capability of Na-substituted CaI_2:Eu scintillator

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[Introduction] ^{48}Ca is a promising candidate for experimentally observing neutrinoless double beta decay (0νββ) events. Our team has successfully grown CaI_2 single crystals using the vertical Bridgman method; since 2016, the reported scintillation properties of CaI_2 include high light yield (>100,000 photons/MeV), outstanding energy resolution (3.2% FWHM at 662 keV) and outstanding pulse shape discrimination (PSD) capabilities [1,2,3]. However, its strong cleavage makes it difficult to process. In this study we focused on NaI, which has been reported to form a solid solution with CaI_2[4], and aimed to grow Na-substituted CaI_2 :Eu single crystals to modify the crystal structure of CaI_2, thereby optimizing both processing and scintillation characteristics.

[Material and Method] The starting materials were CaI_2 of 99.995% purity, NaI of 99.995% purity, and EuI_2 of 99.95% purity. The crystal growth was conducted by the Vertical Bridgman method. Scintillation and PSD properties were evaluated.

[Results] Fig.1(a) shows the photograph of the grown 10% Na-substituted CaI_2:Eu single crystal. The cleavage properties of 10% Na-substituted CaI_2:Eu were significantly reduced compared to CaI_2:Eu. Fig. 1(b) presents the pulse height spectra of the ^{137}Cs γ-ray source. Applying the PMT quantum efficiency correction to account for variations in the luminescence spectra, the light yield of about 86,000 photons/MeV for 10% Na-substituted CaI_2:Eu. Detailed result on crystal growth, luminescence, and scintillation properties across different composition will be presented in the conference.

(a) (b)

Fig.1 (a) Photograph of Bridgman-grown crystal, (b) Energy spectra of 10% Na-substituted CaI_2:Eu and NaI

References

1. K. Kamada, A. Yoshikawa, et al., Single crystal growth and scintillation properties of $Ca(Cl, Br, I)_2$ single crystal, Ceram. Int. 43 (2017) S423–S427.
2. T. Iida, A. Yoshikawa et al., High-light-yield calcium iodide (CaI_2) scintillator for astroparticle physics, Nucl. Instrum. Methods Phys. Res. A 958 (2020) 162629.
3. M. Yoshino, A. Yoshikawa et al., Comparative pulse shape discrimination study for $Ca(Br, I)_2$ scintillators using machine learning and conventional methods, Nucl. Instrum. Methods Phys. Res. A 1045 (2023) 167626.
4. H.J. Seifert, B. Muller, E. Stotzel, Thermochemical and Structural Study on Alkali-Metal Iodide and MgI_2, CaI_2 Systems, 289 Revue De Chimie Minerale, 17 (1980) 147-157.

Electronic waste recycling using a coordination chemistry approach

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The contemporary increase in electronic consumption contributes to the growing problem of e-waste accumulation. Neodymium magnets and nickel-hydrogen batteries/accumulators are key components of many electronic devices, and their improper disposal may lead to environmental degradation and the loss of valuable raw materials. Neodymium magnets can be recycled by either direct recycling routes, which allow for the magnets to be refurbished and re-used in the same form, or by pyrometallurgical [1], hydrometallurgical [2], and electrochemical [3] extraction processes, resulting in a recovery of converted battery components. Hydrometallurgical recovery is the most common method for refining and recovering rare earths from spent nickel-hydrogen batteries [4]. Other methods include thermal treatment [5], mechano-hydrometallurgical [6] recovery, extraction-precipitation [7], often without the exact characterization and separation of all of the e-waste components.

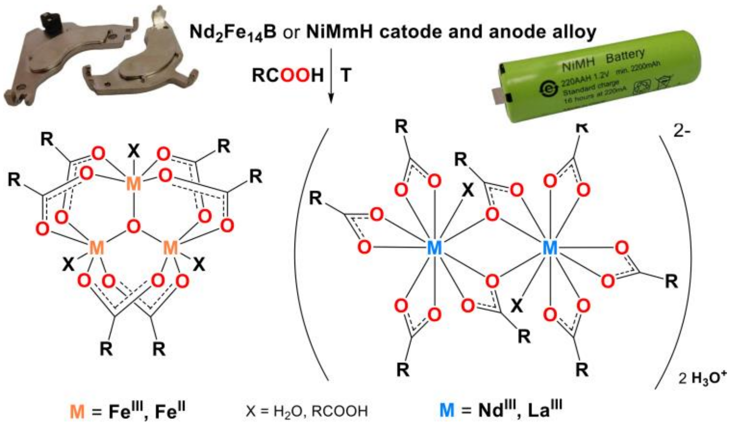

Fig. 1. Direct reaction of neodymium magnets or nickel-hydride batteries'/accumulators' anode alloys with organic acids.

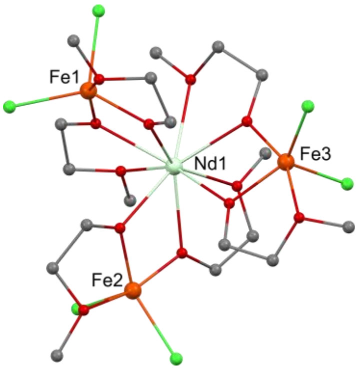

Fig. 2. Structure of $[NdFe_3(OR)_6Cl_6]$ obtained from neodymium magnets using $CuCl_2$ and 2-methoxyetanol.

The main concept of this project focuses on the transformation of electro waste such as **neodymium magnets** and spent nickel-hydride batteries into homometallic (*Figure 1.*) and heterometallic (*Figure 2.*) coordination compounds by the reaction with carboxylic acids (such as acetic or citric acid) or $CuCl_2$ in alcohol solution. Those complexes can be used as wood preservatives, potential magnetic materials, catalysts for simple organic reactions or molecular precursors for the synthesis of mixed metal oxide materials.

References

1. M. Firdaus, M. A. Rhamdhani, Y. Durandet, W. J. Rankin, K. McGregor, J. Sustain. Met., **2** (2016) 276-295.
2. C. Tunsu, In Waste Electrical and Electronic Equipment Recycling; Ed. F. Veglio, I. Birloaga, Elsevier, 2018, p. 175.
3. P. Venkatesan, Z. Sun, J. Sietsma, Y. Yang, Sep. Purif. Technol., **191** (2018), 384-391.
4. M. K. Jha, A. Kumari, R. Panda, J. R. Kumar, K. Yoo, J. Y. Lee, Hydrometallurgy, **165** (2016), 2-26.
5. S. M. Shin, D. J. Shin, G.-W. Jung, Y. H. Kim, J. P. Wang, Arch. Metall. Mater., **60** (2015), 1139-1143.
6. A. Porvali, S. Ojanen, B. P. Wilson, R. Serna-Guerrero, M. Lundström, J. Sustain. Met., **6** (2020), 78-90.
7. H. Zhi, S. Ni, X. Su, W. Xie, H. Zhang, X. Sun, J. Rare Earth., **40** (2022), 974-980.

Photochromic and radiochromic effect in $M_3MgSi_2O_8$:Eu^{2+} (M = Ca-Ba)

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The photochromic effect is a reversible change in the color of a material upon exposure to light, while the radiochromic effect is the phenomenon where a material's color changes upon exposure to ionizing radiation. Both photochromic and radiochromic materials find applications in various fields such as dosimetry for the detection of X-rays or UV light [1], rewritable data storage [2], anti-counterfeiting [3], displays [4] smart windows, textiles [5], and others. However, inorganic materials with significant absorbance changes are rare.

In this research, we investigate photochromic and radiochromic properties of $M_3MgSi_2O_8$: Eu^{2+} (M=Ca-Ba). The samples were prepared using solid-state synthesis in H_2/Ar atmosphere. In all $M_3MgSi_2O_8$: Eu^{2+} samples strong changes in absorbance are detected after irradiation with UV or X-rays. Photographs and diffuse reflectance spectra of $M_3MgSi_2O_8$ doped with 0.01% Eu^{2+} are shown in Fig. 1 a.

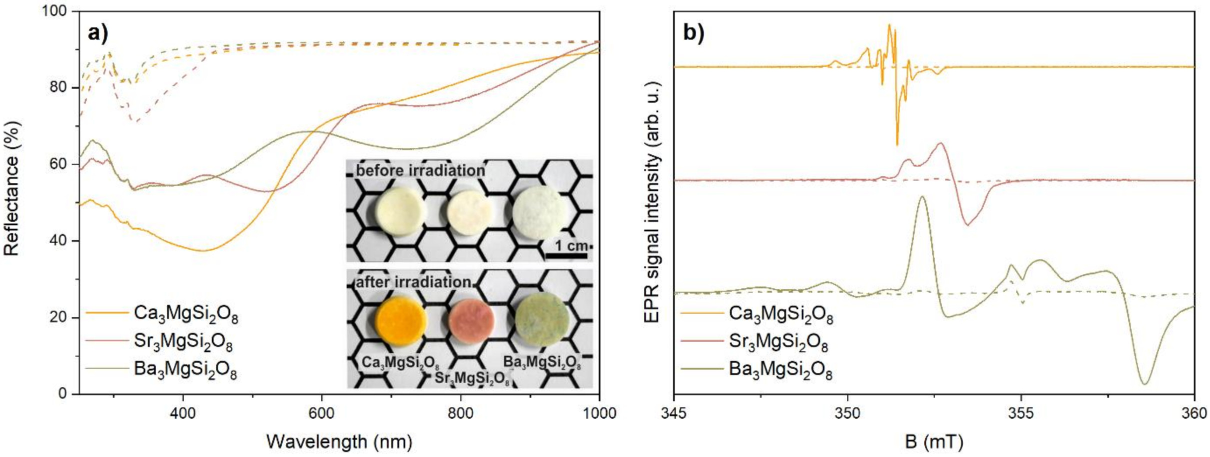

Fig. 1. a) Diffuse reflectance spectra and b) EPR spectra of $M_3MgSi_2O_8$ doped with 0.01% Eu^{2+} before (dashed lines) and after irradiation with 250 nm (solid lines). Inset: photographs of samples before and after irradiation.

The position of dominant absorbance bands depends on the chemical composition of the host matrix and gradually shifts to the red spectral region with the increase of ionic radius of alkaline earth ion. Sample-dependent EPR signals are detected after the irradiation (see Fig. 1.b), which can be related to electron-type paramagnetic defects. The origin of photochromic and radiochromic effect and the role of Eu^{2+} in charge transfer processes will be discussed.

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References

1. Z. Yang et al., Laser Photon Rev., 17, no. 5, (2023), p. 2200809.
2. Z. Yang et al., Adv. Opt. Mater., 9, no. 20, (2021), p. 2100669.
3. X. Zhou, S. Zhang, K. Han, J. Jin, Y. Sun, and Z. Xia, Adv. Opt. Mater., 12, no. 11, (2024), p. 2302429.
4. A. Alkayyali, Y. Iravantchi, J. Herskovitz, and A. P. Sample, Proc. ACM Hum. Comput. Interact., 6, (2022).
5. J. Du, Z. Yang, H. Lin, and Dirk Poelman, Responsive Materials, (2024), p. e20240004.

High-Precision Luminescence Thermometry Beyond 1000 °C with $Ca_3Sc_2Si_3O_{12}$:Pr Garnet

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Luminescence thermometry has become an emerging technique for remote temperature sensing in various fields, including materials science, health sciences and technologies, environmental monitoring among others [1]. A significant challenge in this area is achieving high relative thermal sensitivity across an extensive temperature range with constantly high signal-to-noise ratio, potentially exceeding 1000 degrees [2].

In this presentation, we will introduce Pr^{3+}-activated $Ca_3Sc_2Si_3O_{12}$, a compound specifically designed and developed for luminescence thermometry. By thoroughly analyzing its temperature-dependent steady-state and time-resolved luminescence, we will highlight the unique properties of Pr^{3+} ions that make this activator particularly suitable for temperature sensing over a wide range of temperatures between 25 K and 1225 K. We will demonstrate the crucial relevance of the host for the temperature-dependent luminescence properties of Pr^{3+}, detailing how this interplay influences the luminescence properties of the phosphor, which are essential for effective thermometry with a constantly retained relative thermal sensitivity over 0.5% K^{-1} over almost the entire range.

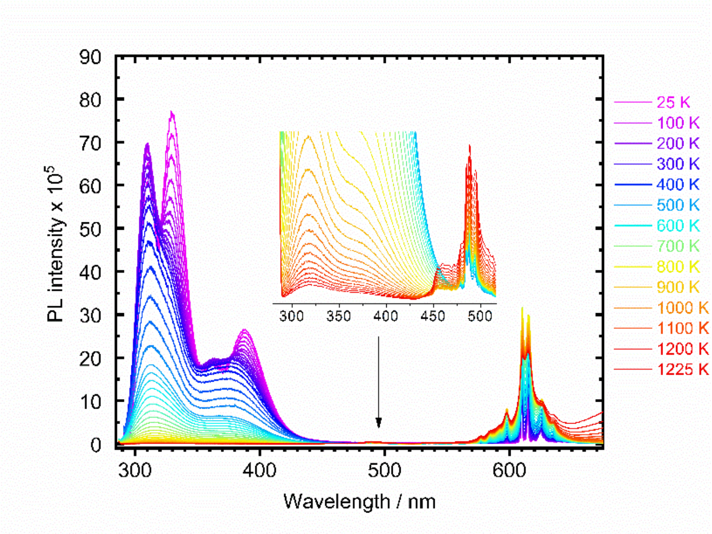

Fig. 1. Temperature-dependent photoluminescence spectra of $Ca_3Sc_2Si_3O_{12}$: 0.1 mol% Pr^{3+} upon excitation at 275 nm.

Acknowledgments
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References

1. C. D. S. Brites, R. Marin, M. Suta, A. N. Carneiro Neto, E. Ximendes, D. Jaque, L. D. Carlos, Adv. Mater. 35 (2023) 2302749 (1-45).
2. J. M. Herzog, D. Witkowski, D. A. Rothamer, Meas. Sci. Technol. 32 (2021) 054008 (1-14).

Compositional dependence of the spectroscopic properties of multicomponent phosphate glasses doped with rare earth ions

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Recent advances in the research field of materials chemistry contributed to the increase in interest in phosphate systems doped with rare earth ions (RE^{3+}) that have been studied for the following applications: light-emitting diodes LED, high-power laser systems, fibers, optical amplifiers, and solar cells [1-4]. It is well-known that glasses based on P_2O_5 are attractive optical materials due to their exceptional characteristics like high transparency in a broad spectral region, low melting point, and low refractive index [5,6]. However, the applications of phosphate glass systems may be limited due to the relatively low chemical durability associated with the hygroscopic properties of P_2O_5. Moreover, from the point of view of the spectroscopic properties, the phosphate glasses are characterized by relatively high phonon energy (~1200 cm^{-1}) compared to the energy of other oxide glasses, contributing to the lower luminescence intensity for rare earth ions in systems. For that reason, the main goal of most research remains to search for new chemical compositions of RE^{3+}-doped phosphate materials with optimal structural, thermal, and spectroscopic properties while having acceptable chemical durability.

This work comprehensively analyzed structure-property relationships for phosphate glasses doped with selected rare earth ions. The X-ray diffraction measurements (XRD) confirm the fully amorphous nature of the studied systems independently of glass compositions. The local structure was examined using infrared (IR) and Raman spectroscopy, and results obtained from both techniques clearly indicate that different structural phosphate groups are present in glass matrices. The Raman spectra and the phonon sideband measurements for glass samples containing Eu^{3+} ions were also used to determine the phonon energy of the glass host. Next, RE^{3+}-doped phosphate-based glasses with various glass compositions have been examined using luminescence spectroscopy. The near-infrared emission spectra and luminescence decay curves for glass systems doped with erbium, praseodymium, and thulium ions were registered and analyzed. The broad emission bands corresponding to $^4I_{13/2}$-$^4I_{15/2}$ (1.5 μm), $^1D_2$-$^1G_4$ (1.45 μm), and $^3F_4$-$^3H_6$ (1.8 μm) transitions of Er^{3+}, Pr^{3+} and Tm^{3+} ions were observed, respectively. It was noticed that the intensity of near-infrared emission bands significantly changes with various glass compositions. Additionally, the dependence of spectroscopic parameters such as full width at half maximum (FWHM) and measured luminescence lifetime (τ_m) was established and discussed. Our results confirm that composition influences the properties of phosphate-based glasses singly doped with RE^{3+} ions that can be suitable for near-infrared luminescence applications.

References
1. L. Han, J. Song, W. Liu, Z. Xiao, L. Zhang, A. Lu, Z. Xiao, W. You, Q. Zhang, J. Lumin., **227** (2020) 117559.
2. J.H. Campbell, T.I. Suratwala, J. Non-Cryst. Solids, **263&264** (2000) 318-341.
3. G.S. Li, C.M. Zhang, P.F. Zhu, C. Jiang, P. Song, K. Zhu, Ceram. Int., **42** (2016) 5558-5561.
4. G. Li, C. Zhang, P. Song, P. Zhu, K. Zhu, J. He, J. Alloys Compd., **662** (2016) 89-93.
5. V. Venkatramu, R. Vijaya, S.F. León-Luis, P. Babu, C.K. Jayasankar, V. Lavín, L.J. Dhareshwar, J. Alloys Compd., **509** (2011) 5084-5089.
6. K. Jha, A.K. Vishwakarma, M. Jayasimhadri, D. Haranath, J. Alloys Compd., **719** (2017) 116-124.

Thermodynamic and kinetic studies on REE ions recovery onto biochar of dead Posidonia oceanica leaves

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The widespread use of rare earth elements (REE) in cutting-edge technologies has led to an increase in their consumption and the urgency of finding sustainable solutions for their recovery[1].The European Community included REE in the list of critical raw materials, i.e. the list of materials whose recovery is of strategic interest[2]. Adsorption by using materials derived from biomass is considered one of the most promising recovery techniques being cost-effective and in line with the principles of environmental sustainability and of circular economy[3,4]. In the present contribution are reported the results of the adsorption study of three REE cations, namely La^{3+}, Nd^{3+} and Dy^{3+} onto a biochar coming from the pyrolysis of dead Posidonia oceanica (BCP), a marine plant whose leaves accumulate in abundance on the sicilian coast, and onto its chemically activated forms with KOH (BBCP) and with H_3PO_4 (ABCP). The biochars were characterized through elemental analysis, surface area and average pore size measurements, ATR-FTIR and XRF spectra, and potentiometric measurements for the pHpzc determinations.

At first, single batch adsorption experiments were carried out at different pH values below the pH of formation of low soluble hydrolytic species of REE (~ 6.5)[5]. Then, pH = 5.0 was chosen as the best pH in terms of REE recovery and kinetic and isotherm experiments were carried out at $I \rightarrow 0$ mol L^{-1} and T = 298.15 K. The adsorption study of ABCP, the best REE adsorbent among those investigated, was therefore extended to evaluate the effect of ionic medium ($NaNO_3$ 0.1 mol L^{-1}).

The recyclability of ABCP adsorbent was also evaluated through column experiments in which HNO_3 and EDTA 0.1 mol L^{-1} were chosen as extractant solutions. Inductively Coupled Plasma Optical Emission Spectroscopy was used to measure the REE concentration in the suspensions.

References:
[1] T.B. da Costa, M.G.C. da Silva, M.G.A. Vieira, J Rare Earths, 38(4), 339-355.
[2] European Commision,https://www.consilium.europa.eu/it/infographics/critical-raw-materials/ (accessed 14 March 2024), 2024.
[3] S. Cataldo, N. Muratore, F. Giannici, D. Bongiorno, V. Chiodo, S. Maisano, A. Pettignano, Environ. Sci. Pollut. Res., 2022, 29, 90231-90247.
[4] S. Cataldo, V. Chiodo, F. Crea, S. Maisano, D. Milea, A. Pettignano, J. Mol. Liq., 2018, 271, 481-489.
[5] R. Qadeer, J. Hanif, J. Carbon., 1995, 33, 215–220.

Influence of Ytterbium and potentiostatic anodization on the corrosion of co-evaporated Magnesium Thin-Films

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Magnesium is an attractive material in many applications due to its low density, high strength and good machinability. Nevertheless, its poor corrosion resistance limits its possible applications as a pure metal. Therefore, different alloying materials and protection strategies are often used to improve the corrosion resistance. Rare-earth elements show a significant potential in Mg alloys. However, there are only limited studies of the influence of Yb as an alloying element with Mg.

A thin film library of Mg-Yb with a compositional gradient was produced, using a self-developed co-evaporation system, similar to those described in an earlier paper from our research group [1]. For the mapping of the Mg-Yb library scanning energy-dispersive X-ray (SEDX) spectroscopy was used. In order to identify the composition along the library, various locations were measured by quantifying the EDX data (IDFix software, remX GmbH) obtained under irradiation with a 20 keV electron beam. Samples with an overall compositional gradient from 1 at% to 10 at% Yb were produced. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed for identifying the crystallography and investigating the surface morphology. Scanning droplet cell microscopy (SDCM) using a 3D-printed cell with a tip diameter of 2 mm was employed for the investigation of the corrosion properties of different alloys in phosphate-buffered saline (PBS) [2]. Electrochemical investigations of the alloys were done as well on the as-produced samples as on anodized samples. The anodization was performed potentiostatically for 5 min at 1 $V_{\text{vs. SHE}}$ in 1 M NaOH.

For testing the corrosion properties, potentiodynamic polarization curves were recorded and Tafel plots were investigated for the calculation of polarization resistance (R_P) and the corrosion rate (*cr*). Also, an immersion test with periodical electrochemical impedance spectroscopy (EIS) was used for the confirmation of the polarization resistance. Analysis of the electrolyte from the immersion tests was performed with inductively coupled plasma with optical emission spectroscopy (ICP-OES) to confirm the corrosion rate.

Figure 1 shows that the anodization of the alloys lowers the *cr* and increases the R_P in higher Yb contents, indicating an improved corrosion resistance. Also, the addition of Yb lowers the corrosion rate significantly as well in the as-produced as in the anodized alloys with an asymptotic behaviour in higher contents.

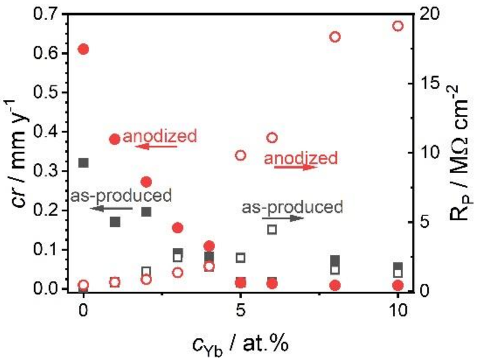

Fig. 1. Change of corrosion rate and polarization resistance with increasing Yb content.

References

1. I. Mardare, C.D. Grill, I. Pötzelberger, T. Etzelstorfer, J. Stangl, A.W. Hassel, , J. Solid State Electrochem. **20** (2016) 1673–1681.
2. J.P. Kollender, M. Voith, S. Schneiderbauer, A.I. Mardare, A.W. Hassel, J. Electroanal. Chem. **740** (2015) 53–60

Synthesis and Luminescence of Rare-Earth-Free Zn_2SiO_4 via Solid-State and Molten Salt Methods

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Deep ultraviolet (DUV) emitters, including UV-C and UV-B, are essential for a wide range of applications, from medicine to agriculture. Current UV light sources, primarily mercury and excimer lamps based on dielectric barrier discharges, suffer from relatively low efficiency and present several health and environmental hazards. Consequently, there is an urgent need to develop environmentally friendly alternatives to mercury-based UV sources. Rare earth-doped phosphors show promise but have limitations related to the availability of rare earth elements.

In this context, we synthesized rare-earth-free zinc silicate (Zn_2SiO_4) powders using two different methods: the traditional solid-state reaction and the molten salt route. We conducted comprehensive investigations into the structural and optical properties of the synthesized materials and performed detailed luminescence characterization using electron beam, X-rays, and synchrotron radiation excitations.

Our results indicate that the synthesis method significantly affects the crystal structure, morphology, and optical properties of zinc silicate powders. The molten salt method facilitated the formation of Zn_2SiO_4 at lower temperatures, resulting in rod-shaped particles, whereas the solid-state reaction required higher temperatures to achieve single-phase Zn_2SiO_4, yielding spherical particles. Cathodoluminescence studies at room temperature (RT) and 6 K revealed intense DUV emission peaking at 4.31 eV (287 nm), attributed to defects in the Zn_2SiO_4 structure. Additionally, RT experiments under X-ray excitation confirmed the presence of a UV-B emission band. Time-resolved spectroscopy studies at low temperatures under synchrotron radiation excitation near the material's fundamental absorption onset unveiled luminescence characteristics related to surface centers as well as $[SiO_4]^{4-}$ and $[ZnO_4]^{6-}$ clusters within Zn_2SiO_4 materials.

The identification of eco-friendly, rare-earth-free zinc silicate powders capable of UV-B emission presents promising opportunities across various technological fields. This research advances our understanding of rare-earth-free phosphors and opens up new avenues for the development of next-generation UV-B emitting devices for disinfection and sterilization.

Keywords: Rare-earth-free Zn_2SiO_4; Solid-state reaction; Molten-salt synthesis; UV-B emission; Cathodoluminescence; Synchrotron radiation

Lanthanide-doped nanomaterials with nonlinear optical and multimodal functionalities

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The main scientific aims of this presentation are engineering of multifunctional luminescent nanomaterials based on lanthanide-doped nanoparticles and others such as semiconducting quantum dots or magnetic nanoparticles, and the next step presenting their physicochemical properties, focussing mainly on linear and nonlinear optical features. An important objective is the characterization of the nonlinear optical properties of this emerging new class of hybrid materials, for potential applications in nanophotonics and biophotonics, using femtosecond laser techniques, including Z-scan and two-photon excited emission [1,2]. These novel nanostructures exhibit efficient ultraviolet, visible and/or infrared luminescence, which can be easily modulated depending on selected nanocomponents or additional co-doping ions. The implementation of selected strategies for enhancing the physicochemical properties of nanoparticles may lead to the design of novel hybrid nanomaterials that simultaneously exhibit properties of two distinct types of nanocrystals, have a biocompatible functionalized surface, or be useful in more than one sensing application. In order to be more specific, within the talk, nanostructures that might offer multifunctional features in a single nanomaterial including one- and two-photon induced luminescence bioimaging [3], merged two-photon induced luminescence and magnetic properties [4], theranostic capabilities [5] as well as providing simultaneous noncontact temperature and pressure sensing will be introduced [6].

References

1. J. K. Zareba, M. Nyk, M. Samoc, Adv. Opt. Mater., **9** (2021) 2100216.
2. K. C. Nawrot, M. Sharma, B. Cichy, A. Sharma, S. Delikanli, M. Samoc, H. V. Demir, M. Nyk, ACS Photonics, **9** (2022) 256.
3. M. A. Antoniak, U. Bazylinska, D. Wawrzynczyk, M. Cwierzona, S. Mackowski, D. Piatkowski, J. Kulbacka, M. Nyk, J. Mater. Chem. C, **8** (2020) 14796.
4. M. A. Antoniak, R. Pazik, U. Bazylinska, K. Wiwatowski, A. Tomaszewska, M. Wnuk, S. Mackowski, A. Lewinska, M. Nyk, Mater. Sci. Eng., C, **127** (2021) 112224.
5. M. Y. Tsang, P. Falat, M. A. Antoniak, R. Ziniuk, S. Zalewski, M. Samoc, M. Nyk, J. Qu, T.Y. Ohulchanskyy, D. Wawrzynczyk, Nanoscale, **14** (2022) 14770.
6. M. A. Antoniak, S. Zalewski, R. Oliva, A. Zak, R. Kudrawiec, M. Nyk, ACS Appl. Nano Mater., **3** (2020) 4209.

Luminescent properties of Laser Induced White Light source based on $Yb_3Al_5O_{12}$ nanocrystals

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Since the discovery of laser induced white emission (LIWE) in 2010 by Wang and Tanner, its understanding was greatly improved [1]. This phenomenon is based on the generation of strong emission covering entire visible and part of the nearinfrared region under focused laser beam in vacuum. LIWE is promising for use in artificial light sources, converters for solar panels, nanoheaters, etc [2]. In This work investigates a highly efficient LIWE source based on $Yb_3Al_5O_{12}$ nanocrystals (Fig. 1). We characterize the luminescent properties of the LIWE source through spectral analysis, rise and decay time measurements, and evaluate the stability of the luminescence under varying excitation light power densities. The findings are particularly relevant for specialized illumination applications demanding precise control over luminous properties.

Fig. 1: Photograph of the LIWE vacuum bulb at 975 nm excitation

References

1. Wang, J., & Tanner, P. A. (2010). J. Am. Chem. Soc., 132(3), 947-949.
2. Chaika, M., et. all. (2024). J. Phys. Chem. C., 128(20), 8351–8356.

The studies of rare-earths luminescence in sol-gel glass-ceramics containing fluoride crystals

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Trivalent rare-earth ions are promising optical dopants whose energy levels enable the generation of luminescence across broad spectral ranges from ultraviolet, through visible light up to infrared irradiation. Thus, such a tremendous spectrum of emitted wavelengths opens vast application possibilities for optical materials doped with RE^{3+}, which could be successfully utilized, e.g., as light sources, display devices, or amplifiers operating in the telecommunication windows [1-3].

Among the various classes of optical materials doped with RE^{3+} ions, many researches are devoted to the oxyfluoride glass-ceramics (OxGCs). Indeed, OxGCs are very attractive host materials because RE^{3+} ions could be effectively incorporated inside the low-phonon energy fluoride crystals, significantly promoting the generated luminescence. Regarding OxGCs preparation, the unquestionable ascendancy falls for the sol-gel technique because the individual chemical reactions (i.e., hydrolysis of the metal/semi-metal alkoxide and (poly)condensation) are usually performed at relatively low temperatures, reducing the risk of fluorides evaporation, which makes the possibility to obtain particularly enhanced emission of RE^{3+} [4]. On the other hand, the presence of high-vibrational OH groups inside the host – naturally created during aqueous sol-gel processing – could restrict the efficiency of RE^{3+} luminescence [5]. Therefore, the crystal size and amount of precipitated fluoride phase within the sol-gel host, as well as effectiveness in the densification of the host matrix, play a decisive role in overall luminescence originating from optically active RE^{3+} ions.

The main concept of this research was to prepare the series of sol-gel OxGCs doped with selected rare-earth ions, i.e., Pr^{3+} and Ho^{3+}, containing LaF_3 crystals. Our intention was to investigate the impact of heat-treatment conditions on the structure as well as emissions of RE^{3+} ions in fabricated OxGC materials. The ATR-IR spectroscopy, XRD technique as well as TEM microscopy were used to determine the structural changes within the silicate sol-gel host and the crystallization of LaF_3 phase. The luminescence properties of the synthesized oxyfluoride glass-ceramic materials were characterized based on the excitation and emission spectra, along with the decay analysis from the excited states of RE^{3+} ions.

References

1. I. Gupta, S. Singh, S. Bhagwan, D. Singh, Ceram. Int. **47** (2021) 19282-19303.
2. L.S. Archana, D.N. Rajendran, Mater. Today Proc. 41 (2021) 461-467.
3. D. Wei, H.J. Seo, Y. Liu, X. Yang, J. Lumin. **253** (2023) 119488.
4. P.P. Fedorov, A.A. Luginina, A.I. Popov, J. Fluor. Chem. **172** (2015) 22-50.
5. A.E. Danks, S.R. Hall, Z. Schnepp, Mater. Horiz. **3** (2016) 91-112.

Visible-to-UVC upconversion of new phosphates activated by praseodymium ions

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In recent decades, significant progress has been made in the study of new luminescent materials and a deeper understanding of the properties of existing ones. Additionally, advances in characterization techniques have improved our understanding of luminescence mechanisms. The optical phenomenon of upconversion of visible light to UV radiation has been especially intensively studied. This process involves the sequential absorption of at least two visible photons by a material to achieve an excited state in which one UV photon is emitted. Pr^{3+}-activated matrices, whose $^1S_0$ level lies significantly above the bottom edge of the 4f5d configuration, are ideal candidates for upconversion. Depending on the band gap, upconversion emission can be observed in the UVA (320~400 nm), UVB (280~320 nm), and UVC (100~280 nm) intervals. The UVC interval is the most interesting for research due to its strong ability to damage cellular DNA. This destructive property of UVC radiation is promising for applications in the disinfection of water, air, and surfaces.

Currently, upconversion UVC radiation of Pr^{3+} ions excited by visible light has been investigated in fluoride ($BaYF_5$), phosphate (YPO_4), oxyfluoride ($Y_7O_6F_9$) and silicate (Y_2SiO_5) matrices [1-4]. Since phosphates are the least susceptible to hydrolysis among the mentioned compounds, they are considered excellent carriers for UV-emitting phosphors in various applications.

In this work, we present the luminescent and upconversion properties of Pr^{3+}-doped $Ba_3La(PO_4)_3$ crystallites synthesized by the sol-gel method. Additionally, strategies to enhance upconversion intensity will be discussed. The potential applications of the new crystallites as UVC phosphors are also discussed and compared with YPO_4:Pr^{3+}.

ACKNOWLEDGEMENTS

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References

1. N. Rebrova, P. Zdeb, K. Lemański, B. Macalik, O. Bezkrovnyi, P. Dereń, Inorg. Chem., **63** (2024) 3028-3036.
2. Z. Zhu, Y. Wang, W. Zhang, T. Wu, X. Wang, Y. Yang, T. Wang, X. Xu, Opt. Lett., **47** (2022) 1879-1882.
3. Y. Sun, Y. Wang, C. Hu, X. Zhou, J. Hao, W. Li, H. Li, *Mater.* **15** (2022) 7680.
4. E. Cates, A. Wilkinson, J.-H. Kim, J. Lumin. **160** (2015) 202–209.

NIR-CPL/CD active Yb(III) complexes bearing both central and axial chirality

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A growing interest is rising about NIR emitting Ln(III) complexes [1] because of their potential uses for bioimaging applications.[2] NIR-CPL [3] could expand this potential from biological and medical applications [4] to the technological field.[5]

New NIR-CPL/CD active Yb(III) complexes (Fig. 1) were synthesized by combining two ligands involving different types of chirality: central and axial chirality.[6] CPL analysis showed how the axial chirality dominates, in this case, determining the sign of the spectra (Fig. 1). Central stereochemistry seems instead to draw the sign of NIR-CD. DFT calculations confirmed the experimental data.

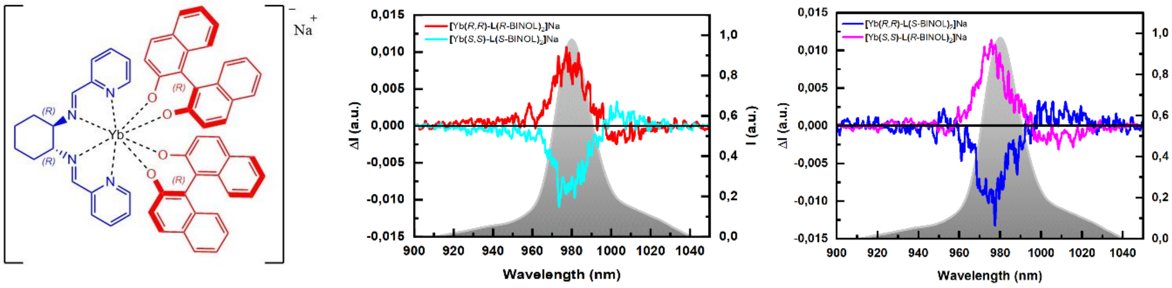

Fig. 1. Yb(III) complexes synthesised (the [Yb(*R*,*R*)-**L**(*R*-BINOL)$_2$]Na has been chosen as representative) (left); NIR-CPL spectra of the two enantiomeric couples of the investigated Yb(III) complexes (centre and right) .

References

1. E. Cavalli, C. Nardon, O.G. Willis, F. Zinna, L. Di Bari, S. Mizzoni, S. Ruggieri, S.C. Gaglio, M. Perduca, C. Zaccone, A. Romeo, F. Piccinelli, Chem. – Eur. J., **28** (2022) e202200574.
2. K.Y. Zhang, Q. Yu, H. Wei, S. Liu, Q. Zhao, W. Huang, Chem. Rev., **118** (2018) 1770-1839.
3. S. Mizzoni, A. Sickinger, S. Ruggieri, F. Riobé, L. Guy, O. Maury, B. Baguenard, A. Ledoux, Y. Guyot, S. Guy, M. Sanadar, A. Melchior, F. Piccinelli, New J. Chem., **48** (2024) 9627-9636.
4. P. Stachelek, L. MacKenzie, D. Parker, R. Pal, Nat. Commun., **13** (2022) 553.
5. F. Zinna, L. Arrico, L. Di Bari, Chem. Commun., **55** (2019) 6607-669.
6. S. Ruggieri, O.G. Willis, S. Mizzoni, E. Cavalli, M. Sanadar, A. Melchior, F. Zinna, L. Di Bari, G.D. Bisag, M. Fochi, L. Bernardi, F. Piccinelli, *submitted for publication*.

Excited-state absorption meets multiparametric thermometry: Merging strategies for enhanced thermal sensing

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Measuring temperature remotely is of utmost importance in the field of materials science, spurring the development of sensing techniques, with luminescence thermometry (LT) being particularly suitable for detecting thermal changes at the submicron scale[1]. In LT, temperature-induced changes in the spectroscopic properties of an ensemble of probes are harnessed to output a thermal readout. However, a recently raised inquiry in the literature is: *which property and/or strategy should be used in LT?* By exploring new strategies, we may push the field of LT toward unforeseen thresholds. Aware of this interplay, the use of excited-state absorption (ESA) thermometry for LT has recently drawn attention[2], however, employing sophisticated methods to treat ESA thermometric data remains an untrodden avenue. A promising algorithm for this purpose is multiple linear regression (MLR), which combines explanatory variables to forecast the outcome of a response variable[3]. In this context, proof-of-concept phosphors, i.e., $GdYO_3:Eu^{III}$(1-9at.%) and $GdYO_3:Eu^{III}$(9at.%),Al^{III}(3at.%) were synthesized by an adapted Pechini route at 1100 °C/5 h. X-ray diffraction (XRD) and Rietveld analysis revealed single-phase formation of $GdYO_3$ host in the absence of spurious phases. At room temperature, the 7%-Eu^{III} phosphor excelled among all samples, while the 9%-Eu^{III},3%-Al^{III} sample exhibited the best performance (relative emission intensity) among the Al^{III}-codoped samples. These samples are labeled 7Eu and 9EuAl, respectively. The emission spectra were recorded for both phosphors in the 77 – 500 K temperature range under 464 nm ($^5D_2 \leftarrow {}^7F_0$), 532 nm ($^5D_1 \leftarrow {}^7F_1$) and 586 nm ($^5D_0 \leftarrow {}^7F_1$) excitation. The ratio between the $^5D_0 \rightarrow {}^7F_2$ (612 nm) emission band under each excitation was used to evaluate thermal changes, yielding three distinct thermometric parameter ($\Delta_{J/J'}$): $\Delta_{1/2}$ (532/464), $\Delta_{0/2}$ (586/464), and $\Delta_{1/0}$ (586/532). Among these, $\Delta_{0/2}$ displayed the highest relative sensitivity (S_r), with values of 2.02% K^{-1} (7Eu) and 2.52% K^{-1} (9EuAl) near the cryogenic temperature of 77 K. The thermal resolution problem poses a meaningful query in LT. However, both thermometers displayed thermal uncertainties (δT) below 0.05 K near 77 K, with the highest uncertainty at around 0.15 K at 500 K. Although desirable, one may wonder about the sensitivity achievable by merging the three thermometric parameters. Using MLR, a five-fold gain in sensitivity was acquired (10.1% K^{-1} and 12.6% K^{-1} for 7Eu and 9EuAl, respectively). These values are among the highest reported for single-ion LT to date, and such S_r is combined with low uncertainty, which was maintained below 0.05 K for both samples via MLR. These findings highlight the potential of integrating ESA and MLR to advance the field of LT. Also, it demonstrates that enhanced performance can be achieved by combining materials design with data analysis. Therefore, this study sets the stage for using advanced methods to analyze ESA data, thereby unlocking the hidden potential of simple systems. The future of these algorithms in LT is promising, and new implementations are likely to drive exciting developments in this field.

References

1. E. Ximendes, R. Marin, L. D. Carlos, Light Sci. Appl. **237 (**2022) 01 – 13.
2. J. Stefánska, A. Bednarkiewicz, L. Marciniak, J. Mat. Chem. C **10** (2022) 5744 – 5782.
3. F. E. Maturi, C. D. S. Brites, E. C. Ximendes, C. Mills, B. Olsen, D. Jaque, S. J. L. Ribeiro, L. D. Carlos, Laser & Photonics Reviews **15** (2021) 2100301.

Study and quantification of divalent lanthanides in persistent phosphors

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Lanthanides are the work horses in a wide range of optical and luminescence applications. Some of them, like Eu, Sm, Tm and Yb, can rather easily be stabilized in a divalent state [1]. Others however, 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. In particular, certain 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+}. By means of X-ray absorption techniques, their presence can be detected once the persistent phosphor is charged. These materials thus also offer a unique opportunity to study the luminescence and absorption spectra of these uncommon Ln^{2+} ions. In this report we focus on the optical properties of metastable Nd^{2+}, Sm^{2+}, and Dy^{2+} codopants in aluminate-based persistent and storage phosphors [6]. They are investigated using low temperature diffuse reflectance and luminescence spectroscopy.

This study further confirms the role of these lanthanide co-dopants as electron trapping defects in persistent phosphors. At the same time, it 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 [3,4]. Finally, it also allows to quantify in a rather direct way the number of (co)dopant ions that change their valence state.

References

1. M. Suta, C. Wickleder, J. Lumin. **210** (2019) 210-238
2. M. Karbowiak, C. Rudowicz, J. Lumin. **199** (2018) 116-125
3. J.J. Joos, K. Korthout, L. Amidani, P. Glatzel, D. Poelman, P.F. Smet, Phys. Rev. Lett. **125** (2020) 033001
4. J. Kong, A. Meijerink, Adv. Opt. Mater. **11** (2023) 2203004
5. J. Ueda, T. Shinoda, S. Tanabe, Opt. Mater. Express **3** (2013) 787
6. D. Van der Heggen, J.J. Joos, P.F. Smet, submitted for publication.

Oxonitridosilicate phosphors for LEDs

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Trivalent nitrogen anions, N^{3-}, substituting for divalent oxygen anions, O^{2-}, induce an increase in the anionic formal charge which can be compensated according to two different principles. In the first case, a cross-substitution principle is applied which allows the same stoichiometry to be kept, and very possibly, the same structure, provided size conditions are obeyed. In other words, trivalent rare-earth elements, which form strong bonds with nitrogen, are ideal substitutes to ensure the charge balance by replacing divalent alkaline earth cation. In the second case, the anionic charge compensation is carried out in rare-earth ternary or higher order oxides, according to $2N^{3-}$ replacing $3O^{2-}$. A particularly favorable situation is encountered when the crystal structure has enough flexibility to accept the consequent anion deficiency. As nitrogen is less electronegative than oxygen - 3 versus 3.5 on Pauling's scale - another consequence of the N/O substitution is an increase in the covalent character which results in significant modifications in chemical and physical properties.

The N/O substitution effect on spectroscopic properties of Eu^{2+} and Ce^{3+} ions was investigated for the following phosphors: $MSiO_{3-x}N_{2x/3}:Eu^{2+}$ or Ce^{3+}(M=Ca, Sr), $Me_2SiO_{4-x}N_{2x/3}Ce^{3+}$ (M=Ca, Sr). The incorporation of nitrogen atoms into the host lattice has been confirmed by Energy Dispersive X-ray (EDX) and IR spectroscopies. The spectroscopic studies showed that the investigated phosphors emit at longer wavelengths compared to their oxygen counterparts. The usefulness of these phosphors for application in white LED technology will be discussed based on the quantum efficiency of the emissions, luminescence decay times, and thermal quenching of the Eu^{2+} and Ce^{3+} emissions. The thermoluminescent properties of the investigated phosphors will be shown.

References

1. Pasiński D. and Sokolnicki J. (2018) Dyes and Pigments, 159, 283–289.
2. Sokolnicki J. (2022) J. Alloy. Compd, 903. 16397–16405.

Potential of Aluminosilicate in White WLED Light Production

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White light-emitting diodes (WLEDs) are widely utilized and extremely significant as they greatly reduce global energy demand and contribute to the decrease in fossil fuel usage. These devices are characterized by high lighting efficiency, low energy consumption, reliability, and environmental friendliness. Lighting plays a crucial role in the daily life of every individual, with electric light sources accounting for up to 20% of the world's electricity production.

Despite many advantages, LED technology also has drawbacks. The LED lighting available on the market emits light with an unpleasantly "cold" color. Excessive exposure to blue light disrupts the human circadian cycle, including the production of the sleep hormone melatonin. Therefore, the search for artificial light that closely mimics the spectrum of sunlight is one of the most important and urgent challenges faced by advanced science and technology.

This lecture will show the potential of inorganic phosphor from the aluminosilicate family doped with selected rare earth metal ions and transition metal ions in the generation of white light WLEDs. Luminescence properties such as emission stability, quantum efficiency, emission decay time, and emission thermal stability will be discussed in detail.

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Nanosheets of Rare-Earth Chalcogenides

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Our group has been interested in the synthesis of magnetic lanthanide chalcogenides, as two-dimensional nanosheets. The ability to control phase, shape and size of nanomaterials is a common challenge in nanoparticle synthesis. The rare earths present particular challenges due to the hard-soft mismatch with soft S, Se and Te materials. We have investigated single-source precursors to synthesize $LnSe_2$ nanosheets,[1] and separate reagents for $LnTe_3$.[2]. We will discuss periodic trends in the synthesis, and the magnetic properties of these materials.

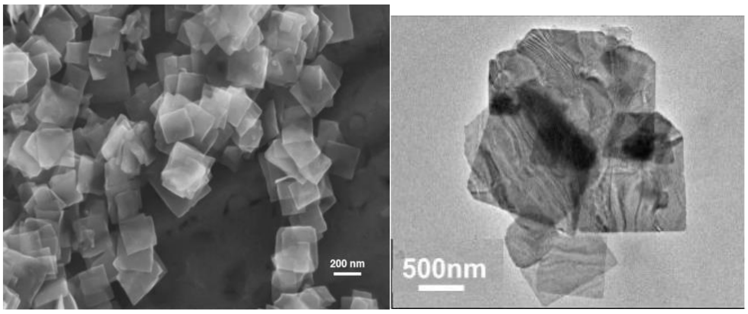

Fig. 1. Left, $SmSe_2$ nanosheets, right $NdTe_3$ nanosheets.

References

1. Atif, R.; Zarkov, A.; Asuigui, D. R. C.; Glaser, P.; Stewart, O., and **Stoll, S. L.**, “Single-Source Precursors for Lanthanide Diselenide Nanosheets”, *Chem. Mater.*, **2019**, *31(18)*, 7779-7789.
2. Swanson, J.; Jamal, S.; Hartman, T.; Stewart, O.; Glaser, P.; Biacchi, A.; Chen, Z.; Jensen, C.; Liu, K.; Henry, D.; Barbara, P.; Stoll, S. L., “Solution Synthesis of $NdTe_3$ Magnetic Nanosheets”, accepted. *Chem. Mat.*, **2024**.

Separation of Dy from acidic solutions using ionic liquids

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Dysprosium is one of the most important elements in the clean energy transition. With applications in wind power generation, electromobility and many others, securing its supply is a matter of strategic importance, as with many other elements of the REE Group. The need is all the more urgent as its global production is concentrated in a very small area of the world.

In this work, the possibility of realizing a process consisting of dissolution of dysprosium oxide in inorganic acids, liquid extraction into ionic liquid and electrodeposition of metallic dysprosium on a solid electrode was studied. Several ways were tested starting with both HCl and HNO3 using several ionic liquids:

- 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
- 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
- 1-butyl-3-methylimidazolium hexafluorophosphate
- 1-Butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide
- Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide
- Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide

While some ionic liquids have certain ability to extract dysprosium from acidic solutions itself (**Fig. 1**), extractants like tri-n-butyl-phosphate (TBP) were used to maximize the effectivity. The electrochemical step in form of current-modulated electrolysis was then applied to deposit Dy in the metallic state for further use.

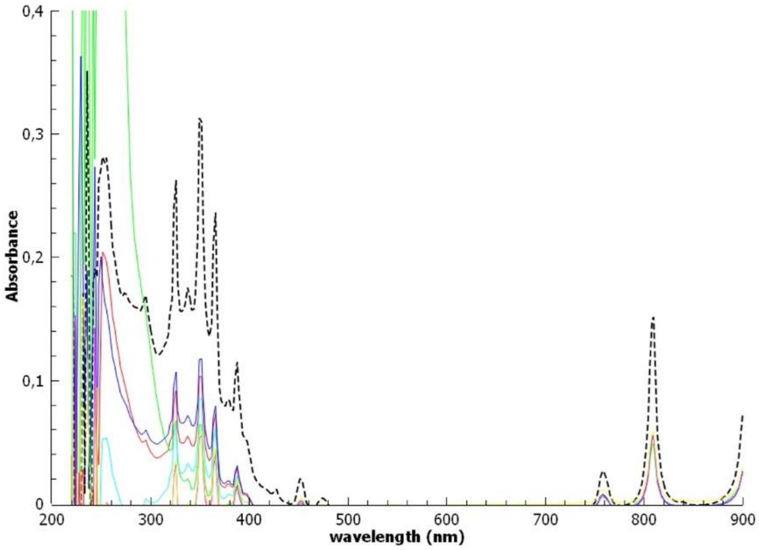

Fig. 1. UV-VIS spectra of acidic solution containing Dy before (dashed line) and after the l-l extraction into several ionic liquids

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On the nature of the Lu-based garnets highly sensitive luminescence thermometer

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Lutetium aluminum garnet (LuAG) is a well-known host material for scintillators, solid-state lasers, luminescence thermometry, LED lighting, or up-conversion. Various lanthanide ions were exploited in the field of optical temperature sensing or imaging. Pr^{3+} has been recently re-invented for luminescent thermometry when its 5d→4f emission was successfully used for improved sensitivity at a broad range of temperatures [1-3]. Also, the sensitivity of the Pr^{3+} interconfigurational transition to the host chemical composition and structure was successfully used to manage Pr-doped thermometer properties employing bandgap engineering [4,5].

In this research, Ga-modified LuAG:Pr has been investigated as a multimode optical thermal sensor in the temperature range of 13–700 K utilizing steady-state and luminescence kinetics parameters: decay lifetime and luminescence intensity ratio (LIR) of thermally coupled levels. The thermometric parameters for the whole series of the $Lu_3Al_{5-x}Ga_xO_{12}$:Pr (x = 0, 1, 2, 2.5, 3, 3.5, 4, 5) phosphor powders under the 4f→5d UV excitation are reported and systematically analyzed. When stimulated through the Pr^{3+} $^3H_4 \rightarrow {}^3P_2$ transition at 450 nm it exhibits luminescence characterized by significant temperature dependence. The thermometric performances were explored and compared in terms of thermal sensitivity and temperature resolution. Temperature sensing via 5d→4f emission kinetics reached S_r values in the 0.85-2.00 $\%K^{-1}$ range. The highest relative thermal sensitivity based on LIR peaks at 4.90 $\%K^{-1}$ for the $Lu_3AlGa_4O_{12}$:Pr composition and 5.26 $\%K^{-1}$ for LuAG within the temperature range of 30-600 K and 13-600 K, respectively. Accordingly, the temperature resolution δT *gives the best accuracy from around 0.1 K at cryo-temperatures up to 0.8 K at 600 K for both compositions.* These outcomes underscore the applicability of Pr^{3+} ions for luminescence thermometry, emphasizing the impact of the excitation wavelength on the thermal sensitivity. *The good* repeatability of LuAG-based thermometer was demonstrated by conducting thermal cycling experiments. Changing the excitation wavelength allows for the management of relative sensitivity and designing an optical thermometer with multiple sensing parameters.

Acknowledgements

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References

1. K. Fiaczyk, S. Omagari, A. Meijerink, E. Zych, *J. Lumin.,* **198** (2018) 163–170.
2. S. Wang, S. Ma, J. Wu, Z. Ye, X. Cheng, *Chem. Eng. J.* **393** (2020) 124564.
3. C.D.S. Brites, K. Fiaczyk, J.F.C.B. Ramalho, M. Sójka, L.D. Carlos, E. Zych, *Adv. Opt. Mater.*, **6(10)** (2018) 1701318 (1-10).
4. M. Sójka, J.F.C.B. Ramalho, C.D.S. Brites, K. Fiaczyk, L.D. Carlos, E. Zych, *Adv. Opt. Mater.*, **7** (2019) 1901102 (1–11).
5. P. Bolek, J. Zeler, C.D.S. Brites, J. Trojan-Piegza, L.D. Carlos, E. Zych, *Chem. Eng. J.*, **421(P1)** (2021) 129764.

Crystal Structure Design of High-Entropy Rare-Earth Aluminate Perovskites

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Four five-component high-entropy (HE) perovskite aluminates with different "average" rare earth (RE) cation radius (r_{ave}), namely $(Nd_{0.2}Sm_{0.2}Eu_{0.2}Er_{0.2}Y_{0.2})AlO_3$ (**I**), $(Pr_{0.2}Nd_{0.2}Sm_{0.2}Eu_{0.2}Gd_{0.2})AlO_3$ (**II**), $(La_{0.2}Pr_{0.2}Sm_{0.2}Eu_{0.2}Tb_{0.2})AlO_3$ (**III**) and $(La_{0.2}Pr_{0.2}Dy_{0.2}Yb_{0.2}Lu_{0.2})AlO_3$ (**IV**) were prepared by facile sol-gel citrate route. Corresponding series of the nanocrystalline powders were obtained from constituent RE oxides and $Al(NO_3)_3{\cdot}9H_2O$ by sol-gel technique following with subsequent heat treatment in air at 800 °C, 1000 °C, 1200 °C and 1500 °C. Phase composition, crystal structure and microcrystalline parameters of the powders after each stage of heat treatment were monitored by X-ray powder diffraction and SEM techniques. In the case of (**I**), (**II**) and (**III**) compositions with relatively weak dispersion of cation radii of constituent RE elements, single-phase products with orthorhombic *Pbnm* perovskite structure were obtained. In contrast, multiphase material was obtained in the case of material (**IV**) containing such RE elements as La, Pr, Dy, Yb and Lu, with differ considerably in they ionic radii. As the annealing temperature increases, the crystallite sizes of the perovskites (**II**) and (**III**) increase from 48–50 nm at 800 °C to 220–550 nm at 1500 °C, while the average microstresses values gradually decrease from 0.13–0.22 % to 0.017–0.019 %, respectively (Fig. 1). Lattice parameters of HE perovskites **I** (a = 5.2514 Å, b = 5.3011 Å, c = 7.4428 Å), **II** (a = 5.3012 Å, b = 5.2917 Å, c = 7.4805 Å) and **III** (a = 5.3074 Å, b = 5.2980 Å, c = 7.4876 Å) with the "average" RE^{3+} cation radii of 1.110 Å, 1.140 Å and 1.148 Å respectively follow well the empirical relations earlier established for the $RAlO_3$ rare-earth aluminate series [1], indicating that the crystal structure of HE perovskite materials are mainly governed by the geometrical factor.

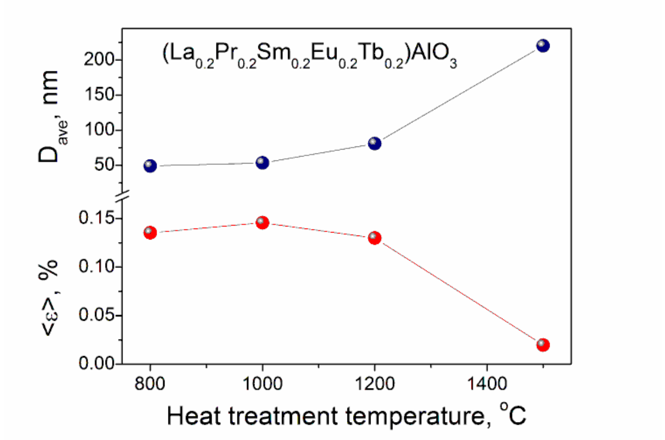

Fig. 1. Average crystallite size D_{ave} and microstress values <ε> of $(La_{0.2}Pr_{0.2}Sm_{0.2}Eu_{0.2}Tb_{0.2})AlO_3$ powders heat treated at different temperatures.

References

1. L. Vasylechko, A. Senyshyn, U. Bismayer, Perovskite-Type Aluminates and Gallates, In Handbook on the Physics and Chemistry of Rare Earths; Eds. K.A. Gschneidner Jr., J.-C.G. Bünzli, V.K. Pecharsky, Netherlands: North-Holland, 2009, Vol. 39, p. 113-295.

Towards Designing of Primary Optical Thermometers

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Temperature is one of the most frequently measured physical variables, and the global sensor market is largely the temperature sensor market. New and emerging technologies place increasing demands on precision, sensitivity, and often also speed and spatial resolution of measurement. Importantly, the measurements using optical methods are not disturbed in the presence of electromagnetic fields, and the measured object can even move fast. These are real, undisputable advantages over many other approaches to temperature sensing.

The last decade or two showed that luminescence thermometers may offer a wide operating range and some of them may work even well above 1000 K. In such thermometers, the physics behind is complex and usually different in specific fractions of their operating ranges. This complicates the issue of measurement accuracy in the long-term, and the calibration procedure has to be repeated quite frequently. The lack of well-defined physics which might be effectively used to define their calibration curves is a drawback that cannot be overlooked [1-2]. A different situation is when primary thermometers are considered. These are luminescence thermometer emissions of which change with temperature following a precisely defined physical equation due to unequivocal physical mechanism beyond .

In our project, we selected garnet and aluminate materials, activated with Pr^{3+}, Cr^{3+}/Eu^{2+}, respectively, considering their potential for primary luminescent thermometers. In Figure 1 the thermometric properties of LuGG:Pr^{3+} material are presented. It is shown that Boltzmann type thermometer based on Pr^{3+} ions with E_a~590 cm^{-1} covers 200-500 K temperature range of its readout with appropriate temperature resolution.

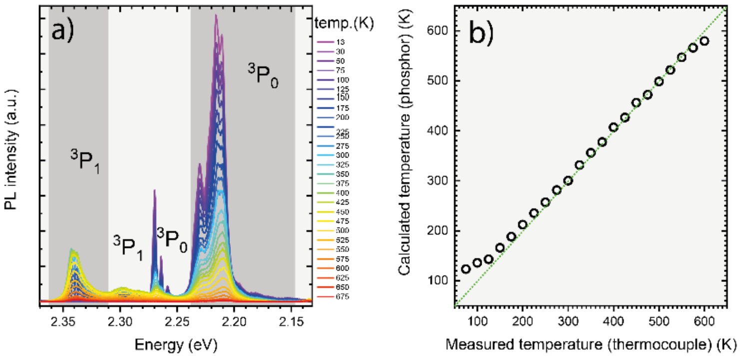

Figure 1. Temperature-dependent luminescence of the LuGG:Pr in the range of 15-675 K (a) and the result of the quality of the primary thermometer (b).

We will demonstrate how these materials can function as sensitive thermometers within the Boltzmann-defined temperature range, exhibiting valuable temperature readout parameters.

Acknowledgements

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References

1. C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millán, V. S. Amaral, F. Palacio, L. D. Carlos, Nanoscale 4 (2012) 4799.
2. C. D. S. Brites, S. Balabhadra, L. D. Carlos, Adv Opt Mater 7 (2019) 1.

Poster presentation abstracts

Dissolution Kinetics of Rare Earth Elements from Estonian Phosphate Rock during Processing with Hydrochloric Acid.

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Increasing demand for critical rare earth elements (REEs) due to the rapid expansion of smartphones, solar panels and permanent magnets has sparked the necessity of finding alternative sources [1]. Phosphate rock, the main sources of phosphorus for fertilizer production, is also considered a host mineral for REEs [2]. The waste-free recovery of REEs from phosphate ore has gained increasing prominence.

The study focuses on the effect of pH, particle size, and acid concentration on the leaching process of REEs from Estonian phosphate rock using hydrochloric acid. The particle size, acid concentration, dosage of acid, and pH of the solution directly impact the leaching rate of REEs. It was found that using an acid concentration of 0.8M and a reaction time of 60 minutes optimizes REEs leachability for the three studied particle sizes, achieving over 90% dissolution (Fig.1(a)).

The pH ranges from 1.6 to 1.9 and acid dosage of 3.0 (HCl/Ca mole ratio) showed the highest percentages of total REEs leaching across all acid concentrations and particle sizes (coarse: mean = 1735 µm, semi-fine: mean = 226.6 µm, and fine: mean = 66.1 µm).

The REEs leaching efficiency is controlled by the solubility limits of calcium (Ca) and phosphorus (P) in the system, and to simulate the kinetics of dissolution, the instant and saturation concentrations of Ca and P were employed. Calculated values show that when the initial acid concentration is increased, the dissolution rate constants (k) increase (Fig. 1(b)).

This novel study demonstrates the practical feasibility of HCl acid leaching for recovering REEs from phosphate rock, highlighting its potential as a sustainable solution to meet the rising demand for these critical elements.

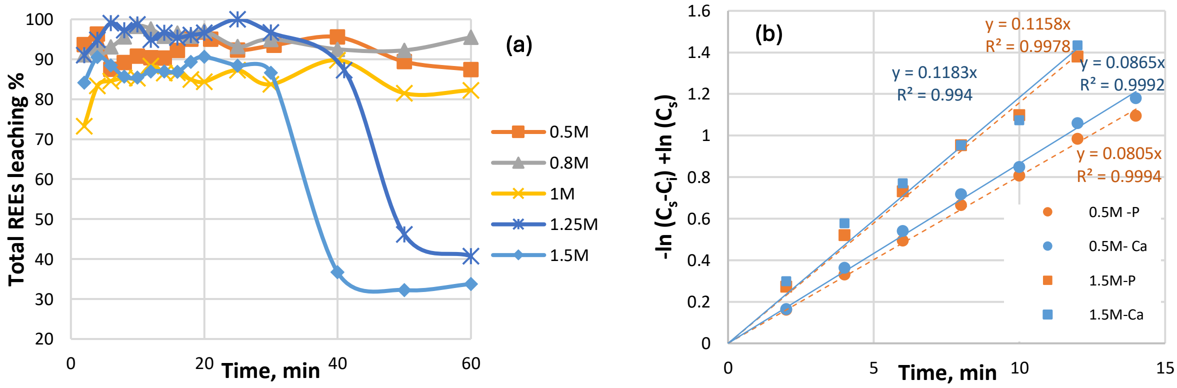

Fig. 1. (a) Total REEs leachability percentage from semi fine particle at different initial concentrations of HCl as a function of time; (b) Plot of calculated values for -ln (C_s-C_i) + ln C_s) as a function of time for calcium and phosphorus concentration at 0.5 M and 1.5 M initial acid concentrations.

References

1. Ragonnaud, G. *Securing Europe's Supply of Critical Raw Materials*; 2023.
2. Dushyantha, N.; Batapola, N.; Ilankoon, I. M. S. K.; Rohitha, S.; Premasiri, R.; Abeysinghe, B.; et al. The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy and global production. *Ore Geology Reviews*. Elsevier B.V. July 1, 2020. doi:10.1016/j.oregeorev.2020.103521.

Could Phosphogypsum Waste Be a Source of Rare-Earth Elements?

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The company "Lifosa" located in Kėdainiai (Lithuania) specializes in the production of phosphorus fertilizers (diammonium phosphate, monocalcium phosphate, monoammonium phosphate). The company itself synthesizes phosphoric acid from apatites, which it uses in the further process of fertilizer production. During the synthesis of phosphoric acid, a by-product phosphogypsum is formed. A huge amount of phosphogypsum waste were generated on the territory of the factory - about 45 million tons. So, next to Kėdainiai several kilometres long "phosphogypsum mountains" with a height of up to 80 m are deposited (see Fig. 1).

Fig. 1. Phosphogypsum mountains located on the territory of AB "Lifosa" factory.

The chemical composition phosphogypsum may vary depending on the origin of the phosphate raw material used in the technological process – apatite [1-3]. The results of analysis of different apatite ores showed the presence of different amount of rare-earth elements [4]. It was also determined, that the content and distribution of rare-earth elements in apatites are linked to the environment of phosphogenesis [5].

The phosphogypsum waste, originating from various locations within the factory dump in Kėdainiai (Lithuania), was subjected to physico-chemical characterization using a range of methods. The results of XRD analysis showed that the main crystalline phase phosphogypsum waste is gypsum ($CaSO_4{\cdot}2H_2O$), with no evidence of the presence of other crystalline phases. The results of the determination of metals in phosphogypsum using EDX, AAS and XRF analysis methods showed, that the amount of other metals is vanishingly small or below the detection limit of the analysis method. It was also demonstrated in this work, that the phosphogypsum waste could be successfully used as precursor for the synthesis of high quality bioceramic calcium hydroxyapatite.

References

[1] P.M. Rutherford et al., Waste Manag. Res. 13 (1995) 407-423.
[2] E. Saadaoui et al., Int. J. Env. Stud. 74 (2017) 558-567.
[3] M. Pliaka, G. Gaidajis, J. Env. Sci. Health. 57 (2022) 746-763.
[4] R. Frietsch, J.A. Perdahl, Ore Geol. Rev. 9 (1995) 489-510.
[5] S. Decree et al., Sedimentol. 71 (2024) 713-744

Influence of synthesis parameters on spectroscopic properties and microstructure of persistent Eu^{3+} -doped $ZnGa_2O_4$ phosphors

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In recent years, the efforts in investigating new persistent luminescence (PersL) nano phosphors for *in-vivo* imaging applications have been increasing. The main focus was on Cr^{3+} doped materials due to their red PersL in the first biological window (BW1, 700-950 nm). However, PersL in other wavelength ranges, i.e., in the second biological window (BW2, 1000-1350 nm), is desirable for in-vivo imaging for the low radiation absorption by biological tissues. The addition of rare earth ions as further dopants, together with Cr^{3+} ions, is beneficial to generate simultaneous emission in both the BW1 and BW2 regions, as in $Y_3Al_2Ga_3O_{12}:Cr^{3+},Er^{3+}$ [1], $Gd_3Sc_2Ga_3O_{12}:Cr^{3+},Yb^{3+}$ [2] and $ZnGa_2O_4:Cr^{3+},Yb^{3+}$ [3].

In particular, $ZnGa_2O_4$ (ZGO) spinels are very interesting PersL materials for which the best parameters have been reported in the past few years. However, the effect of the experimental preparation conditions on the incorporation of rare earth ions in the spinel crystal structure and on the microstructure is still a significant challenge to consider carefully. To this aim, we underline that the Eu^{3+} ion is a very useful luminescent probe that can help to elucidate the local environment around the lanthanide dopant.

In the present study, Eu^{3+} ion-activated $ZnGa_2O_4$ (ZGO:Eu) spinels were synthesized by a hydrothermal method [4] at pH levels ranging from 6 to 10 with Eu^{3+} ion concentrations of 1%, 2%, 3% and 5% (in mol) concerning the (Zn+Eu) content. The spinel structure was confirmed by X-ray powder diffraction analysis, and the luminescent properties were tested using photo- and PersL spectroscopy in the visible range. In particular, the effect of starting pH on the photoluminescence properties has been carefully studied, thanks to the sensitivity of Eu^{3+} to the crystalline environment. In addition, Raman spectroscopy was utilized to identify structural changes resulting from differences in the synthesis parameters and Eu^{3+} concentration. Furthermore, defect formation and PersL properties were analyzed based on thermoluminescence data.

References

1. J. Xu, et al., Inorg. Chem. 57 (2018) 5194.
2. J. Xu, et al., J. Am. Ceram. Soc. 100 (2017) 4033..
3. V. Castaing et al., Phys.Chem.Chem.Phys. 21 (2019) 19458.
4. A. Gerus, et al., Mater. Res. Bull., 168 (2023) 112473.

Upconverting Nanocomplexes Loaded Mesenchymal Stem Cells for Two-Step Photodynamic Therapy

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Breast cancer continues to be the most frequently diagnosed malignancy and the second leading cause of cancer-related fatalities among women [1]. Despite significant medical and scientific advances, standard cancer treatment methods often do not ensure successful treatment due to complications associated with cancer progression. Photodynamic cancer therapy (PDT) could be a promising treatment option. However, the photodrugs currently used in PDT, such as chlorin e_6 (Ce_6), are activated by visible light, which has low penetration into tissues, so this treatment is mainly effective for superficial tumors only.

Nanotechnology offers great promise in overcoming the drawbacks of PDT and extending its application. Among many nanomaterials rare-earth-doped upconverting nanoparticles (RENPs) and their complex with photodrug chlorin e_6 (RENPs-Ce_6) are especially promising. Due to the unique properties of RENPs they can be excited with near-infrared radiation resulting in emission in the visible part of the spectrum. As a result, the photodrug Ce_6 attached to the RENPs is excited and can generate singlet oxygen, which causes cell damage and leads to cell death [2]. However, it has been shown that less than 1% of intravenously injected nanoparticles reach the tumour [3]. To improve selectivity, we used mesenchymal stem cells (MSCs) as our therapeutic nanocomplex carriers because MSCs have oncotropic properties and tend to migrate towards cancer cells upon chemokine stimulation. We have shown that RENPs-Ce_6 complex is biocompatible and accumulates in MSCs. Also, we have demonstrated that MSCs can migrate with RENPs-Ce_6 complex towards breast cancer cells. Furthermore, we have carried out two-step photodynamic effect studies and shown that irradiation with near-infrared light has a phototoxic effect on RENPs-Ce_6 complex loaded cells. Overall, our results showed that the combination of RENPs-Ce_6 and MSCs can increase the efficiency of photodynamic therapy.

Acknowledgment

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References

1. F. Martino, M. Lupi, E. Giraudo, L. Lanzetti. Cell. Mol. Life Sci. 80, 244 (2023).
2. A. Skripka, V. Karabanovas, G. Jarockyte, R. Marin, V. Tam, M. Cerruti, R. Rotomskis, F. Vetrone. Adv. Funct. Mater. 29, 1807105 (2019).
3. Q. Dai, S. Wilhelm, D. Ding, A. M. Syed, S. Sindhwani, Y. Zhang, Y. Y. Chen, P. MacMillan, W.C.W Chan. ACS Nano 12, 8423–8435 (2018).

High-Entropy Oxides: Game-Changers in CO_2 Hydrogenation Photocatalysis

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Herein, we investigate the potential of nanostructured high–entropy oxides (HEOs) for photocatalytic CO_2 hydrogenation, a process with significant implications for environmental sustainability and energy production. Several cerium–oxide–based rare–earth HEOs with fluorite structures were prepared for UV–light driven photocatalytic CO_2 hydrogenation towards valuable fuels and petrochemical precursors[1]. The cationic composition profoundly influences the selectivity and activity of the HEOs, where the $Ce_{0.2}Zr_{0.2}La_{0.2}Nd_{0.2}Sm_{0.2}O_{2-\delta}$ catalyst showed outstanding CO_2 activation (14.4 $mol_{CO}\ kg_{cat}^{-1}\ h^{-1}$ and 1.27 $mol_{CH3OH}\ kg_{cat}^{-1} h^{-1}$) and high methanol and CO selectivity (7.84 % CH_3OH and 89.26% CO) at ambient conditions with 4–times better performance in comparison to pristine CeO_2. Systematic tests showed the effect of a high–entropy system compared to mid–entropy oxides. XPS, *in–situ* DRIFTS as well as DFT calculation elucidate the synergistic impact of Ce, Zr, La, Nd, and Sm, resulting in an optimal Ce^{3+}/Ce^{4+} ratio. The observed formate–routed mechanism and a surface with high affinity to CO_2 reduction offer insights into the photocatalytic enhancement. While our findings lay a solid foundation, further research is needed to optimize these catalysts and expand their applications.

References

1. D. Tatar et al. *ACS Appl. Mater. Interfaces* 2024, 16, 29946–29962

Europium Oxide-Modified Reduced Graphene Oxide Composite for Serotonin Detection

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The development of rapid and sensitive devices for the detection of neurotransmitters is crucial for clinical applications and the management of various diseases. Conditions such as Parkinson's, Alzheimer's disease, autism, schizophrenia, depression, and anxiety present significant healthcare challenges, making early diagnostics and personalized therapy essential. Serotonin (SER) has been shown to play crucial roles in various complex behaviors, including mood regulation, appetite, sleep, cognition, perception, motor activity, temperature control, pain management, sexual behaviour, and hormone secretion [1]. Among these conditions, depression has a particularly high impact on social life, ranking as the fourth leading cause of human disability. Depression is characterized by high recurrence rates, chronicity, and life-threatening conditions. Serotonin could be considered a biomarker for this condition because its levels in blood plasma and serum correlate with depression symptoms [1]. The normal human serotonin level ranges from 0.6 to 2 μM [2]. Sufficiently balanced SER is vital for both physical and psychological well-being. Thus, the precise determination of SER, as well as the development of sensitive and selective platforms for the detection of SER, has become an important issue in clinical diagnosis, especially at a very low concentration.

Traditionally, high-performance liquid chromatography, gas chromatography-mass spectrometry, and chemiluminescence immunosensor techniques have been employed for the detection of serotonin [3]. However, these methods often suffer from drawbacks such as poor selectivity, time-consuming procedures, and high costs. Recently, electrochemical techniques have emerged as a promising alternative, offering advantages such as low cost, ease of operation, good sensitivity, and excellent selectivity. In this context, the fabrication of electrochemical sensors has garnered significant interest in the research and industrial development field. Moreover, the use of metal oxides, particularly the lanthanide series, has shown exciting potential in various applications, including luminescence, supercapacitors, and photodegradation [4]. These materials have the ability to enhance the performance of electrochemical sensors, making them a suitable choice for the detection of serotonin [5].

The aim of the research was to study and develop electrochemical sensors based on europium oxide-modified reduced graphene oxide composite for SER detection. For this purpose, during the wet-synthesis procedure, GO was modified with the Eu_2O_3. The obtained rGO-based samples were characterized using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Furthermore, the proposed research will explore the development of an electrochemical sensor for the rapid and sensitive detection of serotonin. The sensor will be evaluated for its selectivity, sensitivity, and reproducibility. The introduction of innovative synthetic modifications offers the prospect of creating advanced materials based on graphene, which could be utilized across a wide range of sectors. This development is expected to positively impact on the advancement of sensing technologies, facilitating improved functionalities and heightened performance capabilities.

References

1. J. Moncrieff, R. E. Cooper, T. Stockmann, et al., Mol. Psychiatry, **28** (2023) 3243–3256.
2. A. Cernat, G. Ştefan, M. Tertis, C. Cristea, I. Simon, Bioelectrochemistry. **136** (2020) 107620.
3. S. Sharma, N. Singh, V. Tomar, R. Chandra, Biosensors and Bioelectronics, **107** (2018) 76-93.
4. G. Tessitore, G.A. Mandl, S.L. Maurizio, M. Kaur, J.A. Capobianco, RSC Advances **13(26)** (2023) 17787-17811
5. U. Rajaji, S. Manavalan, S.-M. Chen, M. Govindasamy, T.-W. Chen, T. Maiyalagan, Composites Part B: Engineering, **161** (2019) 29-36.

Zirconium phthalocyanine and reduced graphite oxide composite materials for photocatalytic purification of waste water

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Mechanism of axial coordination of central zirconium atom of phthalocyanines through carbonic acids and, in general, oxygen-containing groups is well known and described in the literature, also in our works [1-5]. We tried to use this mechanism for coordination during reaction, where central metal atom of Zr(IV) phthalocyanine was used for direct interaction with lateral active oxygen containing groups of graphite oxide (–OH, –COH, –COOH, –C=O) and also epoxy groups of surface of graphite oxide sheets for obtaining composite material. We compared the efficiency of standard reflux heating method and solvothermal method for producing this material, and also different solvents (dimethyl sulfoxide (DMSO) and 1,2,4-thichlorobenzene (TCB)) which are routinely used for synthesis of out-of-plane substituted IV group of periodic table metals phthalocyanines. Solvothermal method using DMSO proved to be much more effective, and gives ability to obtain stable composite and partial exfoliation of graphite oxide, coupled with the creation of highly porous material with a large specific surface area of about 700 m^2/cm^3. This in turn influences the optical properties of the composite and, what is especially important for biomedical applications, the generation of reactive oxygen species in a significant degree. Three model dyes were used to assess the photooxidation of organic substances: Methyl Blue, Rhodamine B, and Brilliant Green. High photoreduction coefficients were obtained for all dyes (50-70% at IR light exposure below 10 min.). The obtained material has high potential for creating, for example, purification filters for hospital wastewater in accordance with the GMP standard.

References

1. M.-E. Ragoussi et al., Angewandte Chemie Int. Ed. **51** (2012) 6421-6425
2. J. P. Mensing et al., J. Mater. Chem. **22** (2012) 17094-17099
3. J. Zhu et al., Carbon **49** (2011) 1900-1905
4. H. Hosseini et al., Biosensors and Bioelectronics, **52** (2014) 136-142
5. L.A. Tomachynski, et al., Inorganica Chimica Acta **361** (2008) 2569-2581

Lanthanide-Doped Gd-Ge-Si Alloys: Microstructure, Magnetic Properties, and Magnetocaloric Performance

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This study investigates the effects of f-block lanthanide doping on Gd-Ge-Si magnetocaloric alloys. Bulk samples of $Gd_{75}Ge_{15}Si_5X_5$ alloys, where X = Ce, Pr, or Nd were fabricated using the arc-melting method under a protective argon atmosphere. Microstructural analysis via SEM and EDX revealed a characteristic two-phase microstructure in Ce and Pr-doped alloys, while the Nd-doped alloy exhibited a three-phase microstructure. Magnetic properties were examined using VSM, with magnetization versus temperature measurements conducted from 50 K to 400 K. Additionally, AC magnetic susceptibility was measured both at 0 T and up to 1 T external magnetic fields. These measurements facilitated the evaluation of Curie temperatures, which increased to near room temperature with lanthanide doping, as shown in Fig. 1. Magnetization curves near the phase transformation temperature were than used to calculate magnetic entropy changes and assess the Relative Cooling Power (RCP) [1]. Interestingly, the addition of lanthanides changes the nature of the phase transformation from first to second order. Notably, the lanthanide-doped alloys demonstrated significantly higher RCP across various magnetic fields compared to the undoped Gd-Ge-Si alloy. Presented findings suggest that lanthanide doping is an effective strategy for enhancing the magnetocaloric properties of Gd-Ge-Si alloys, potentially advancing their applicability for room-temperature magnetic refrigeration technologies.

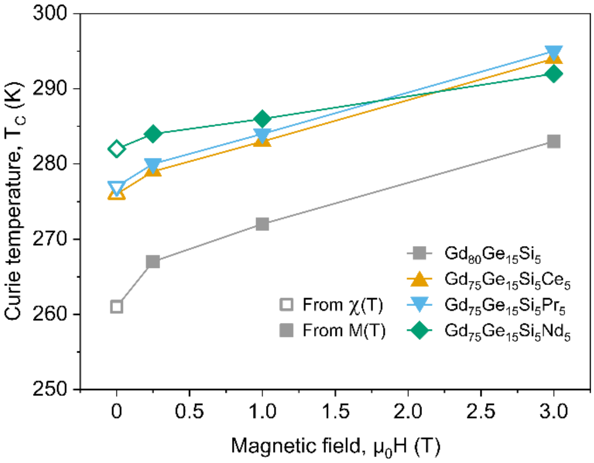

Fig. 1. Curie temperature as a function of applied magnetic field for $Gd_{75}Ge_{15}Si_5X_5$ alloys, where X = Ce, Pr, or Nd, determined from the M(T) and $\chi(T)$ measurements.

References
1. V. Franco, J.S. Blázquez, B. Ingale et al., Annu. Rev. Mater. Res., **42** (2021) 305-342.

Charge Compensation and Persistent Luminescence: $CaWO_4:Eu^{3+}$

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In non-destructive medical diagnostics, *pure $CaWO_4$* had a glorious past as an X-ray *intensifying screen phosphor* (to convert X-rays to light) instantly after the discovery of X-rays in 1895. Far later in the 1970s, the digital recording era led to a new $BaF(Cl,Br,I):Eu^{2+}$ *photostimulated luminescence (PSL)* phosphor. The demise of $CaWO_4$ was hastened by the *afterglow* of the $CaWO_4$ blue emission. Yet, the $CaWO_4$ mishap gave rise to new applications of $CaWO_4$ but now hosting eg Tb^{3+}/Eu^{3+}. A major overhaul of the $CaWO_4$ composition was needed for their use as *persistent luminescence* (*PersLum*) phosphors, though. Owing to the mismatch between the dopant R^{3+} and host $[WO_4]^{2-}$, *charge compensation* (*CC*) with Na^+ was applied to create pure $(Na^+,Ca^{2+},R^{3+})WO_4$ materials to match the $CaWO_4$ structure. This charge manipulation created concurrently the *structural defects* needed to obtain PersLum.

This contribution gives a step-by-step account of the *rebirth of the $CaWO_4$* screen phosphor as a *Eu^{3+},Na^+ co-doped* $CaWO_4$ PersLum phosphor. The co-doped materials were prepared using the coprecipitation method @ 300 K with optional annealing @ up to 1300 K for 3 h. The XRPD patterns (**Fig**) show marked improvement in crystallinity but no impurities appear due to annealing or increasing Eu^{3+} concentration (below 10 mol-%). The Eu (L_{III}) XANES spectra confirmed the absence of Eu^{2+} indicating a successful circumvent of the *Vegard's 1st rule* requesting the *same host (Ca^{2+}) and dopant (Eu^{3+}) charges*. Changing both the charge and size may still be risky, though. The EDX results (**Fig**) gave extremely clear support to the coprecipitation method with equal intensity of the Na^+ and Eu^{3+} EDX signals @ 1.1 keV. Identical experimental and calculated XRPD patterns indicate also the success of the coprecipitation. However, method relies on the right choice of the M^+, Ca^{2+} and Eu^{3+} with *alike ionic radii*.

The emission spectra of Eu^{3+} show isolated groups of sharp lines due to the $^5D_{0,1}\rightarrow{}^7F_J$ transitions typical to Eu^{3+}. No bogus emission lines/bands due to eg W^{VI} were observed. In contrast, the excitation spectra exhibit the charge transfer (Eu^{3+}) as well the W^{VI} $5d^6$ band in addition to much weaker sharp $4f^6\rightarrow4f^6$ lines but indicating W^{VI} to Eu^{3+} energy transfer.

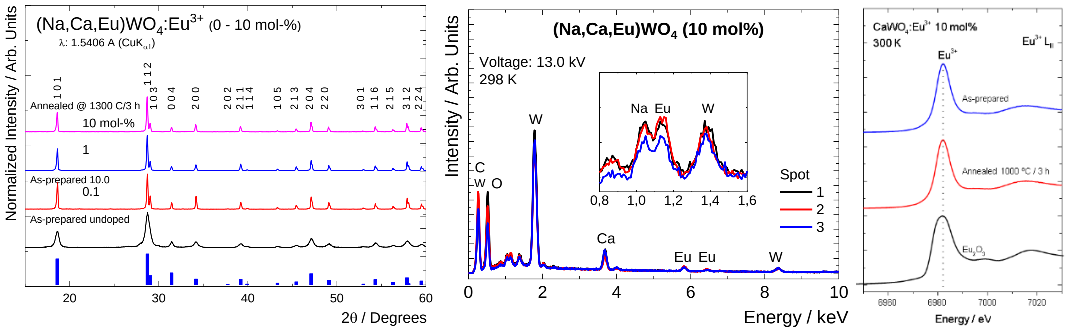

Fig (from left to right)**:** Experimental and calculated XRPD patterns, EDX spectra, and Eu (L_{III}) XANES spectra for the $(Na,Ca,Eu)WO_4$ powders coprecipitated @ 300 K.

Defects and Persistent Luminescence of Tb^{3+} Doped $Ca_2Ga_2GeO_{7+\delta}$

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Persistent luminescence (*PersLum*) of Tb^{3+} doped *$Ca_2Ga_2GeO_7$* (CGGO) is amid the few cases with an *original host lattice* - not materials well-known for ages – with new potential or biases. The (ancient) hosts may be suitable or not to the requirements set on the PersLum materials. The most significant property is the *capability to store energy* for a long time. Whatever are the efficiencies of the initial – excitation – or the final steps – emission, the *storage step is the most important* one which in the end decides the materials' performance.

The study of the Tb^{3+} doped CGGO starts *from scratch* and offers an unprecedented possibility to observe the details which really mater. Preparation of the CGGO materials requires high temperatures suggesting oxidation of Tb^{3+} to Tb^{IV}. However, the CGGO body colors are not brown/yellow which are the preeminent signs of *Tb^{IV} contamination*. This manifests as a sharp rise in *absorption at @ 525 nm but not observed* either. The CGGO host (**Fig**) suggests Ga^{3+} as a doping site for Tb^{3+} but Ga^{3+} (CN: 6) is much smaller ie 0.62 Å *vs* Tb^{3+} 0.923 Å - out of the±15 % tolerance limit. *Instead, Tb^{3+} may well reside at the (single) Ca^{2+} site* with 1.0 Å radius - only 8 % smaller than Tb^{3+}.

The Ca^{2+} *vs* Tb^{3+} charge mismatch offers a *trapping site for electrons*: *larger* Tb^{3+} in a *smaller* Ca^{2+} site has a *weak excess positive charge*. The trap depths can be estimated from the glow curves' of thermoluminescence (TL) band energies. An excess positive charge in a host lattice requires *charge compensation* since all materials must be *neutral*. The preparation (or post-annealing) in air offers the possibility to level the charge balance by *introducing interstitial oxide ion (O_{int})*. Thus the new correct formula is *$Ca_2Ga_2GeO_{7+\delta}$*.

After trap identification, *whereto the O^{2-} ion* is attached, ie *is there any space* for it in the CGGO crystal lattice? Despite the too common belief, the *structures of real materials are far from the rock salt (NaCl) structure* with nicely repeating 3D …Na-Cl-Na-Cl… chains. This is also the case with CGGO where the O^{2-} ions are bonded to the Tb^{3+} ions @ the Ca^{2+} sites. After many long hours of annealing @ high temperatures, the *interstitial O^{2-} seek the energetically most favorable* configuration and Tb^{3+}-O^{2-}-Tb^{3+} (ie Tb_{Ca}) chains are formed with *very short Tb^{3+}-Tb^{3+} distances*. When these distances are calculated, they appear to be quite exactly twice the Tb^{3+}-O^{2-} distances in eg Tb_2O_3.

Summa summarum, it is shown that there are both positive and negative trapping centers yielding short Tb^{3+}-Tb^{3+} distances. This facilitates a very *strong energy transfer* between these Tb^{3+} ions *via* O_{int}. This results in efficient *cross-relaxation processes* between the two Tb^{3+} ions *quenching the blue $^5D_3$ emission* of Tb^{3+} – easily observed in the PersLum spectra.

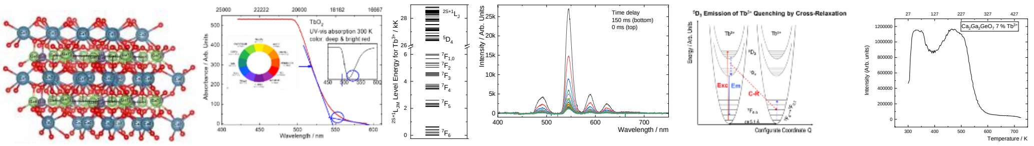

Fig (from left to right)**:** Crystal structure of $Ca_2Ga_2GeO_{7+\delta}$, UV-vis absorption of Tb^{IV}, part of the Tb^{3+} $4f^8$ low energy level structure, persistent luminescence spectra @ 300 K, cross-relaxation processes between the two Tb^{3+} ions leading to quenching of the blue $^5D_3$ emission of Tb^{3+}, and thermoluminescence (TL) glow curve of Tb^{3+} doped $Ca_2Ga_2GeO_{7+\delta}$.

Praseodymium Doped Garnets as New Generation Scintillators

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In order to convert high-energy radiation, such as gamma or X-rays, into visible light scintillating materials are needed. Over the years many different candidates to fit the requirements have been examined. However, compounds with garnet structures have attracted a particularly large amount of attention due to their radiation hardness. Praseodymium doped lutetium and gadolinium aluminum garnets have high density, high thermal stability, rather efficient luminescence processes, and thus high quantum efficiency which are needed for a good scintillator [1]. However, further optimization and improvement are still required especially a reduced decay time. The decay profile of the luminescence is important because the shorter it is the more signals can be measured within a defined timeframe, resulting in a better resolved and higher quality image, for example in CT or PET devices. One way to improve materials properties is to doping the aforementioned compounds with different elements. As such, by doping we could potentially be able to improve key aforementioned parameters: emission intensity, quantum efficiency and decay times [2,3]. One of the useful elements is boron. Primarily, it is applied as a flux, while boron has a suitable neutron capture cross section and can also help absorb gamma radiation [4]. However, garnets can be doped with larger amounts of other elements. In this case, we replaced some of the aluminum with scandium. Lutetium aluminum garnets and gadolinium aluminum garnets doped with Pr^{3+} and B^{3+} were obtained as a result.

In the present work, the effect of boron on the various characteristic of the LuAG and GdAG doped by praseodymium is investigated. Garnets doped with different amounts of boron were synthesized by the aqueous sol-gel method. The phase purity of the samples was analyzed by means of X-ray diffraction (XRD). The morphology of the compounds was evaluated by using scanning electron microscopy (SEM). Photoluminescence properties such as emission and excitation spectra, decay curves, quantum efficiency and temperature dependency of the emission and excitation spectra have been investigated. Radioluminescence was also measured in order to determine the scintillation properties of the samples [5]. The positive impact of boron addition into the garnet structure on the luminescence properties will be discussed in detail.

ACKNOWLEDGEMENTS:

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References

1. I.P. Machado, V.C. Teixeira, C.C.S. Pedroso, et. al. J. Alloys Compd. **777** (2019) 638-645.
2. C. Foster, Y. Wu, M. Koschan, et. al. J. Cryst. Growth **486** (2018) 126-129.
3. D. S. McGregor. Annu. Rev. Mater. Res. **48** (2018) 254-277.
4. G. Inkrataite, M. Kemere, A. Sarakovskis, R. Skaudzius. J. Alloys Compd. **875** (2021) 160002.
5. G. Inkrataite, J.N. Keil, A. Kizalaite, T. Jüstel, R. Skaudžius, Ceram. Int. (2024).

Quinolones as sensitizers of visible emitting lanthanide(III) ions

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This work presents a detailed study of lanthanide ions (Eu^{3+}, Gd^{3+}) with nalidixic acid and flumequine ligands as binary complexes and as ternary complexes with phenanthroline (phen) and triphenylphosphine oxide (tppo) as co-ligands.

When it comes to forming complexes with lanthanides, the choice of ligands plays a crucial role. Both flumequine and nalidixic acid because of their structures (Fig. 1) coordinate with metal ions in a bidentate fashion, utilizing the oxygen atoms from both their carbonyl (quinolone) and carboxylic groups. This not only allows to formation of stable complexes but also enhances the spectroscopic properties of lanthanide by displacing water molecules from the inner coordination sphere which might cause unwanted nonradiative quenching of luminescence. Both chosen ligands belong to a first generation quinolone antibiotics which makes them perfect ligands. Their anti-microbial properties have been thoroughly tested which expands the possibility of use their compounds in the biological and biolabeling areas and as ligands they are readily available at very reasonable cost. Introducing to the complexes co-ligands is aimed at increasing the luminescence properties of complexes.

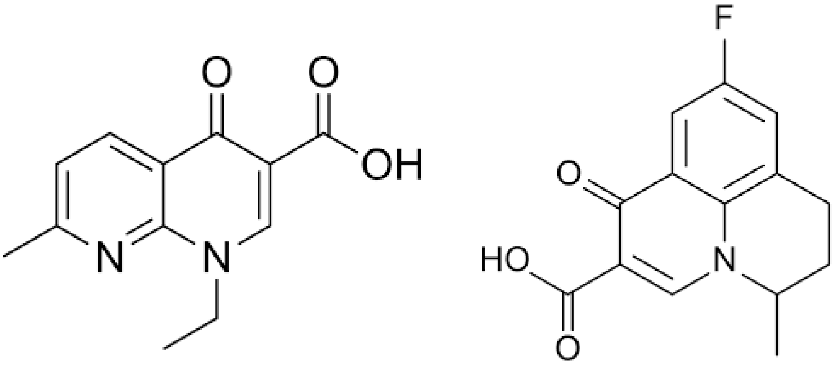

Fig. 1. Formula of nalidixic acid (left) and flumequine (right).

In order to characterize the structure of the compounds, carbon analysis, thermogravimetry and infrared spectroscopy (FTIR) were used. The strong red luminescence arises from the $^5D_0 \rightarrow {}^7F_2$ transition which indicates efficient energy transfer from ligand to metal ion. Furthermore, decay times, the overall and intrinsic quantum yields were used to determine a contribution of the radiative and non-radiative paths to the excited state deactivation and to estimate the efficiency of ligand-to-metal energy transfer. Luminescent properties indicate a high application potential of the tested compounds, especially when introduced into polymeric materials such as films or beads.

Synthesis and Optical Properties of Eu^{3+}, Sm^{3+}, and Ce^{3+}-Doped $Na_7Mg_{13}La(PO_4)_{12}$ Phosphors

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Phosphate materials containing PO_4^{3-} units form isolated, linear, cyclic, and branched anionic substructures, leading to the formation of orthophosphates, polyphosphates, cyclophosphates, and ultraphosphates, respectively [1]. Such diverse condensation possibilities between PO_4^{3-} units yield many different compounds with rich structural chemistry [2]. Over the last few decades, rare-earth-doped luminescent materials based on phosphate hosts have been extensively studied because of their excellent physical and chemical stability, high quantum yields, and high luminescence intensity at elevated temperatures. Such materials can be used as phosphors for white light-emitting diodes (wLEDs) [3], fluorescent lamps [4], up-converting phosphors, lasers, optical thermometers, photodynamic therapy, luminescent security pigments [5], etc.

In this study, the Eu^{3+}, Sm^{3+}, and Ce^{3+} concentration-dependent and temperature-dependent steady-state and kinetic PL properties of $Na_7Mg_{13}La(PO_4)_{12}:Ln^{3+}$ phosphors were investigated in detail. Some of these phosphors exhibited no concentration quenching, quantum yields close to 100%, and excellent thermal stability.

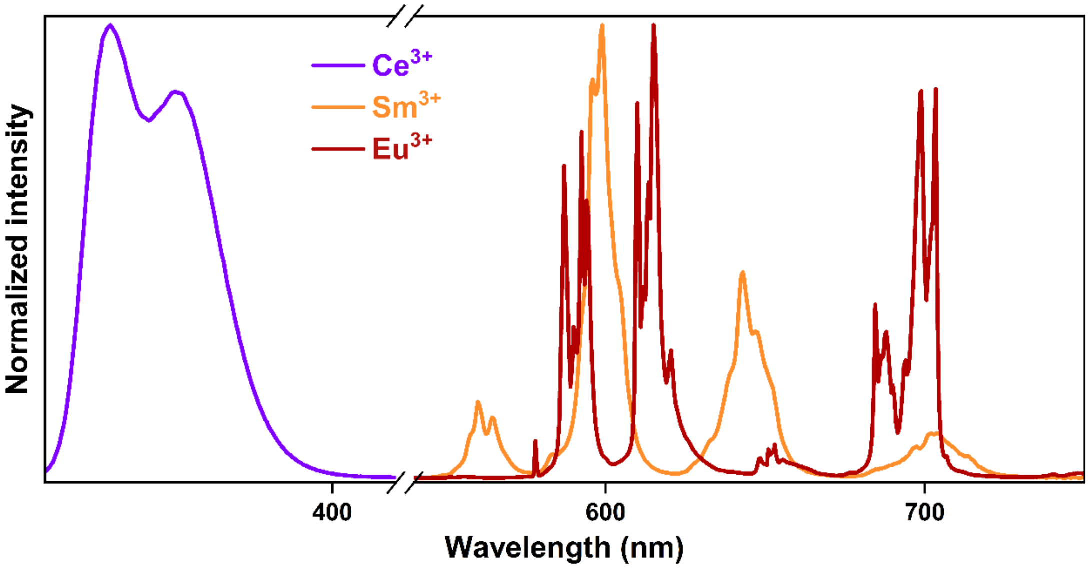

Fig. 1. Emission spectra of $Na_7Mg_{13}La(PO_4)_{12}$ doped with Ce^{3+} (λ_{ex} = 300 nm), Sm^{3+} (λ_{ex} = 402 nm), and Eu^{3+} (λ_{ex} = 393 nm) phosphors.

References
1. D.E.C. Corbridge, Bull. Soc. Fr. Mineral. Cristallogr., **94** (1971) 271-299A.
2. G. Han, et al. J. Am. Chem. Soc., **143** (2021) 18216-18232.
3. M. Derbel, A. Mbarek, G. Chadeyron, J. Photochem. Photobiol., A, **409** (2021) 113146.
4. F. Xiao, S. Xie, R. Yi, S. Peng, C. Xie, J. Lumin., **219** (2020) 116943
5. Z. Li, Z. Lyu, D. Sun, S. Shen, H. You, Mater. Today Chem., **26** (2022) 101116

Surface Functionalization of UCNPs for Excellent Colloidal Stability and Cellular Uptake

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Nanoparticle surface modification is crucial for enhancing the stability of optically active nanoparticles in aqueous colloids and improving their biocompatibility and functionality. Modified particles may exhibit improved cellular uptake, prolonged circulation in the bloodstream, and enhanced membrane permeation [1]. However, materials used for modifying nanoparticles for biomedical applications must meet specific requirements: they should be non-toxic and exhibit good adhesion properties to firmly attach to the particle surface.

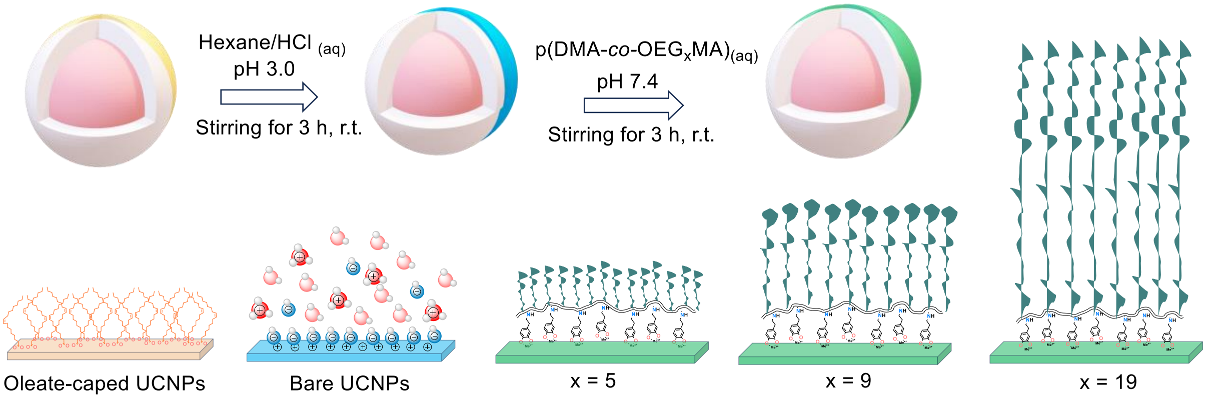

Fig. 1. Schematic representation of UCNP surface modifications employing brush-type copolymers with different length of oligoethylene glycol substituents

Upconverting nanoparticles with a core-shell architecture and the general formula $NaGdF_4:Yb^{3+},Er^{3+}@NaGdF_4:Yb^{3+},Nd^{3+}$ were synthesized in our laboratory using a protocol described in our recent publication [2]. The surfaces of the UCNPs were modified using custom-made brush-type copolymers with general formula of p(DMA$_m$-*co*-OEG$_x$MA), containing oligoethylene glycol substituents of different lengths ($x = 5, 9, 19$). The modified particles exhibited long-term stability in aqueous media (DI water at pH 6.2) and biological media (DMEM supplemented with 10% FBS). Subsequently, the modified UCNPs were transferred to the laboratories of the National Cancer Institute (Lithuania) for detailed accumulation studies in cancer cells with varying tumorigenicity (prostate C4-2, breast MDA-MB-231) and skin mesenchymal stem cells (S-MSCs). The latest results indicate that the upconverting nanoparticles are biocompatible and exhibit relatively high accumulation in cancer or mesenchymal cells and could be employed as biocompatible nanoprobes for bioimaging.

References

1. G. Sanita, B. Carrese, A. Lamberti. Front. Mol. Biosci. **7** (2020) 587012.
2. E. Ezerskyte, A. Morkvenas, J. Venius, S. Sakirzanovas, V. Karabanovas, A. Katelnikovas, V. Klimkevicius, ACS Appl. Nano Mater. **7** (2024) 6185–6195.

Synthesis and Characterization of Layered Double Hydroxides (LDH) Replacing the M^{2+}/M^{3+} Ions with Zinc, Copper and Lanthanum

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Recently, layered double hydroxides (LDHs) have attracted substantial attention due to their wide range of important application areas, e.g., catalysis, photochemistry, biomedical science and the environment. LDHs can be fabricated through different synthesis methods. The most common preparation techniques are co-precipitation [1] and recently developed sol-gel method [2]. In this study these two synthetic techniques have been applied for the preparation of Mg-Al LDHs replacing the M^{2+}/M^{3+} ions with zinc, copper and lanthanum.

New layered double hydroxides (LDHs) of $Mg_{2-x}Zn_xAl_1(OH)_y$, $Mg_{2-x}Cu_xAl_1(OH)_y$, and $Mg_2Al_{1-x}La_x(OH)_y$ have been synthesized by two methods. The level of substitution of magnesium by zinc or copper and aluminium by lanthanum has been investigated applying different synthesis methods. As previously mentioned, two synthesis methods, namely co-precipitation and sol-gel, have been developed for the preparation of metal-substituted LDHs with desired chemical composition.

Thermal analysis (thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) was used to study the decomposition mechanisms of the starting materials and end products. TG/DSC measurements was performed with Simultaneous Thermal analyser STA6000 from PerkinElmer. Fourier transform infrared spectroscopy (FTIR) was used to control the presence of different functional groups in the synthesized compounds. The data were recorded on PerkinElmer Frontier FT-IR spectrometer. X-ray powder diffraction (XRD) studies were used to identify crystalline phases that are formed during different stages of synthesis. For phase identification XRD data were collected on Rigaku MiniFlex II diffractometer. The morphological features have been investigated using scanning electron microscope (SEM) Hitachi FE-SEM SU-70. Antibacterial properties of the coatings were tested using the inhibition zone method.

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References

1. Theiss, F.L.; Ayoko, G.A.; Frost, R.L. Synthesis of layered double hydroxides containing Mg^{2+}, Zn^{2+}, Ca^{2+} and Al^{3+} layer cations by co-precipitation methods-A review. Appl. Surf. Sci. 2016, 383, 200–213.
2. Sokol, D.; Salak, A.N.; Ferreira, M.G.S.; Beganskiene, A.; Kareiva, A. Bi-substituted Mg_3Al-CO_3 layered double hydroxides. J. Sol-Gel Sci. Technol. 2018, 85, 221–230.

Impact of High-Temperature Heat Treatment on the Functional Properties of Gd-Doped Ni-Mn-Ga Magnetic Shape Memory Alloy

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Ni-Mn-Ga Heusler alloys are a class of magnetic shape memory alloys (MSMAs) known for their multifunctional properties that stem from their unique ability to undergo reversible martensitic transitions [1-2]. In this study, we investigated the fabrication and properties of Gd-doped $Ni_{50}Mn_{25}Ga_{20}Gd_5$ polycrystalline MSMA, synthesized using the arc-melting method. Two distinct heat treatments were performed: one at 1173 K, typical for Ni-Mn-Ga alloys [3], and another at a higher temperature of 1430 K, close to the melting point. Both as-cast and heat-treated alloys exhibited a two-phase microstructure. The reversible martensitic transition was absent in the as-cast sample (Fig. 1(a)), barely noticeable in alloy annealed at 1173 K (Fig. 1(b)), but became evident near room temperature (280 K) in sample annealed at 1430 K (Fig. 1(c)), as confirmed by Vibrating Sample Magnetometry (VSM) investigation. Additionally, the Curie temperature of the second phase was observed at low temperatures (around 100 K) in alloys heat-treated at 1173 K, a phenomenon absent in samples heat-treated at 1430 K. Notably, the observed phase transition temperature increased significantly compared to the undoped Ni-Mn-Ga alloy. Nanoindentation tests revealed that Gd-doped Ni-Mn-Ga alloys possess superior mechanical properties and reduced brittleness compared to their undoped material. These findings suggest that rare earth element doping, specifically with Gd, necessitates higher heat treatment temperatures to achieve desired functional properties in magnetic shape memory alloys. Moreover, Gd doping enhances mechanical properties and reduces brittleness while also shifting the reversible phase transformation closer to room temperature.

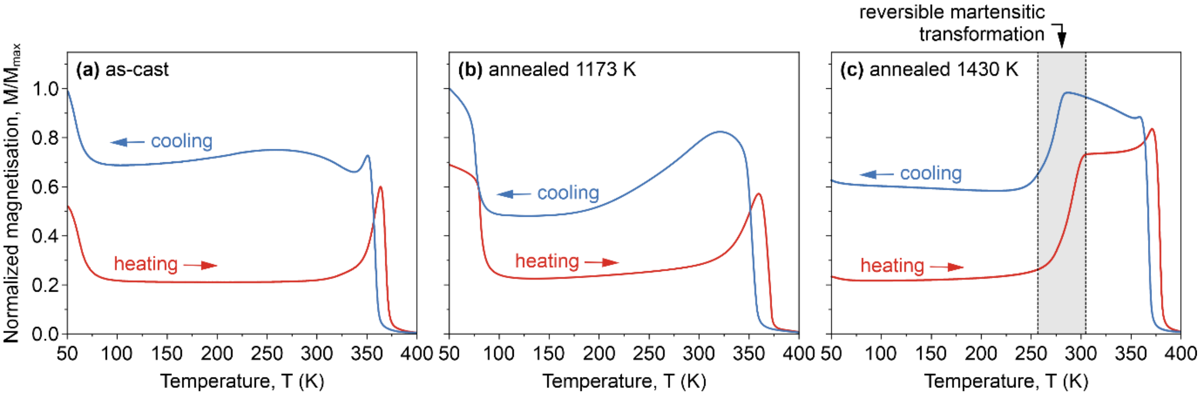

Fig. 1. Temperature-dependent magnetization curves recorded at 10 mT during heating and cooling of the $Ni_{50}Mn_{25}Ga_{20}Gd_5$ polycrystalline MSMA in **(a)** as-cast state and after heat-treatment at **(b)** 1173 K and **(c)** 1430 K.

References
1. M. Zelený, L. Straka, A. Sozinov, O. Heczko, Sci. Rep., **8** (2018) 1-8.
2. E. Faran, D. Shilo, Exp. Tech., **40** (2016) 1005-1031
3. M. Kök, Y. Aydogdu, Thermochim. Acta., **548** (2012) 51-55.

Thermoluminescence application in architecture studies of the Gothic cathedral in Opole

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Our previous investigations of the Gothic churches in Silesia have demonstrated the strong relationships between thermoluminescence intensities and the size of the material grains. In the studies presented now, we elaborate new method of preparing the materials for thermoluminescence measurements independent of the material's grain size. The bricks from six places of the Cathedral were taken to the study. The bricks for the testing were taken from internal walls. The XRD, EM, and Atomic emission spectroscopy methods were used to characterize the compositions, structure, and size of the grains in bricks studied. Thermoluminescence measurements were made using X-ray excitation within the 25-400 °C temperature range. The intensities of TL and integrated TL under the TL curves within the limited temperature range (from 80 to 120 °C) were calculated. Now determined TL intensities were correlated with earlier reported by us [1] relationships of TL intensities versus the date of the construction of four churches in Silesia from 1229 to 1555 year. Based on those relationships we defined the construction dates of the respective parts of the Cathedral in Opole and the dates of different parts of the Cathedral transformations during the renovations of the object.

References

1. A. Legendziewicz, J. Legendziewicz, The Thermoluminescence Studies of the Gothic Chuch in Świebodzin from Silesia in Poland. Optical Materials: (2024), doi: https://doi.org/10.1016/j.omx.2024.100308.

Synthesis of Biphasic Calcium Phosphate Granules from Gypsum Under Static and Rotating Conditions

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The rising demand for bone implants, driven by an aging population, is prompting exploration of synthetic substitutes that could mimic the structure of human bone, which contains calcium phosphate (CP) nanocrystals, mainly nonstoichiometric hydroxyapatite (HAp) and magnesium whitlockite (WH), embedded in a collagen matrix [1], [2]. Recent research advancements have shown that biphasic calcium phosphates (BCP) have superior biological properties over conventional single-phase CP-based materials in the context of implantology [3]. BCP materials not only retain the osteoinductive, osteoconductive, and biodegradable properties characteristic of monophasic CP but also offer the advantage of tunable biodegradability and mechanical properties by altering the ratios of their constituent CP phases[4].

In this study BCP granules, consisting of various amounts of magnesium whitlockite and carbonated hydroxyapatite phases, were synthesized via a low-temperature dissolution-precipitation process under static and rotating conditions using gypsum as a precursor. The phase compositions of the synthesized granules were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and inductively coupled plasma optical emission spectrometry (ICP-OES). Additionally, scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) analysis were employed to assess the surface properties of the granules.

References

1. N. Reznikov, M. Bilton, L. Lari. M.M. Stevens, R. Kroger, Science, 2018, 360.
2. H. Cheng, R. Chabok, X. Guan, A. Chawla, Y. Li, A. Khademhosseini, H.L. Jang, Acta Biomater 2018; 69:342.
3. J.M. Bouler, P. Pilet, O. Gauthier, E. Veron, Acta Biomater 2017; 53: 1-12.
4. A. Giuliani, M.L. Gatto, L. Gobbi, F.G. Mangano, C. Mangano, Int J Environ Res Public Health 2020; 17: 1-16.

Influence of phosphates on the tetrad effect in the adsorption systems with red clay or zeolites

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Lanthanides are a family of elements without which it is difficult to imagine modern civilization. However, apart from numerous benefits, they also cause a lot of trouble. Nuclear industry wastewater contains not only uranium and thorium but also lanthanide ions, including their radioactive isotopes, which get into groundwater and air. Therefore, it is important to develop effective methods of their cleaning [1].

The adsorption process of Ln(III) ions on zeolite A as well as Ln(III) and phosphate(V) ions on red clay modified with sodium chloride (Na-clay) or hexadecyltrimethylammonium bromide (HDTMA-clay) was investigated. An attempt was made to compare the sorption of Ln(III) ions throughout the series of lanthanides and the influence of phosphate(V) ions on the amount of sorption. Moreover, the presence of the double-double effect was examined. The sorption of lanthanides on red clay was found to be enhanced in the presence of phosphates(V). Occurrence of a tetrad effect in the course of logKd values (distribution ratio of Ln between the aqueous and solid phases) in a series of lanthanides was observed. Higher sorption values were obtained for the Na-clay sorption system (Fig. 1).

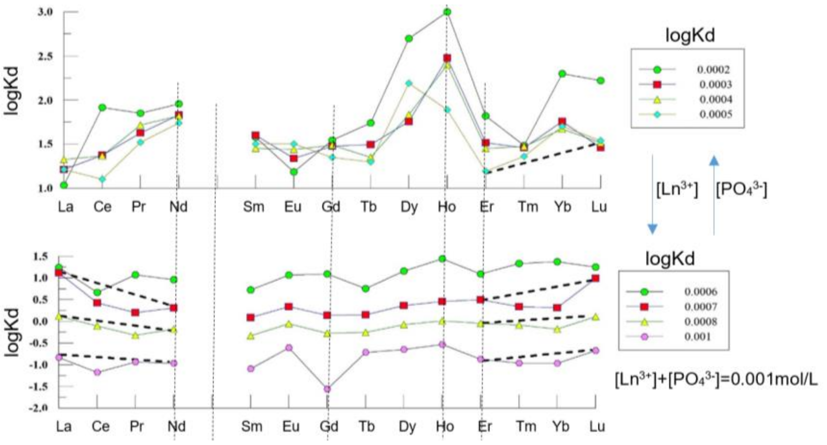

Fig. 1. Course of changes in the lanthanide partition coefficient in the Ln-acetate buffer-Na_2HPO_4-Na-clay system (pH 4.7).

There is no clear tetrad effect in the III tetrad (Gd-Ho), due to the probable change in the coordination number of lanthanides in both phases. In tetrads I (La-Nd) and IV (Er-Lu), the effect is “convex” for the lower lanthanide concentration and “concave” for the higher one. The reason may be that the system is dominated by phosphate complexes at a lower Ln concentration and by acetate complexes at a higher Ln concentration.

The occurrence of the double-double effect according to the Fidelis-Siekierski theory [2] is the result of a change in the covalency of metal-ligand bond in the lanthanide complexes occurring in the substrates and products of the reaction. The "convex" tetrad effect is observed when the covalency of the metal-ligand bond is greater in the products than in the reaction substrates, while in the case of the "concave" tetrad effect, the opposite situation occurs.

References

1. K. De Jesus et al., J. Mol. Liq., **333** (2021) 116006.
2. I. Fidelis, Double-double effect and its contribution to the lanthanide chemistry. Institute of Nuclear Research, Warsaw, 1973.

Photoluminescence of RE-doped bioactive glass

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Bioactive glass is described as inorganic material, non-toxic to cells, biocompatible, not causing inflammation, and able to form a hydroxyapatite surface layer when immersed in a simulated body fluids similar to the blood plasma. Lanthanide-doped glasses have been studied recently to prove that they might be useful in medical applications. One of their main feature is the photoluminescent property that be used for cell labeling, following crystallization processes in glass, tracking delivery and release of drugs, or radiation dosimetry.

The studies focused on the luminescent properties of the SiO_2–CaO and SiO_2–CaO–P_2O_5 glass powders doped with europium or thulium and ytterbium ions. The glasses were prepared by the sol–gel method and characterized to determine their morphology, structure, and composition. The main interest was to study the *in vitro* the degradation behavior of the glass and to follow the changes using emission spectroscopy. The nanosized and mostly amorphous samples were immersed in a phosphate-buffered saline for four weeks to investigate their bioactivity. After the incubation, a formation on the sample's surface of apatite layer was evidenced. Changes in the ion concentration in the buffer confirmed the dissolution and subsequent mineralization of the glass. The ability of energy up-conversion in the Tm^{3+}/Yb^{3+}-co-doped system has been proven. For all samples, a decrease in luminescence intensity after prolonged soaking in the buffer was observed, and the emission decay curves showed consequent lifetime shortening.

In situ investigations on H/O exchange reactions in yttrium hydride oxide YHO

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Recently, rare-earth heteroanionic hydrides, especially hydride oxides, have received increasing attention for their optical properties as thin film materials.[1] Many of their representatives exhibit photochromism in thin films, meaning they reversibly change color upon illumination by UV and/or visible light.[2] Oxygen-rich yttrium hydride oxide thin films are of particular interest due to their extraordinary air stability and color-neutral photochromic effect under moderate illumination intensities, making them promising candidates for applications such as smart windows.[3]

We have developed a synthetic procedure to produce bulk samples of orthorhombic YHO, which crystallizes in a distorted ordering variant of the CaF_2-structure type, known as the anti-LiMgN structure type.[4] During our investigation of this substance's air stability through *in situ* X-ray and neutron diffraction experiments, we observed that its decomposition to yttrium sesquioxide (Y_2O_3) proceeds via an intermediate phase with a different crystal structure (**Fig. 1**). We hypothesize that this intermediate phase, occurring between YHO and Y_2O_3, is an oxygen-rich yttrium hydride oxide $Y(H_{1-2x}O_x)O$, which could resemble the photochromic phase observed in thin films. This phase can be isolated as a single phase, and its oxygen content can be modified by quenching samples after different annealing times in air.

In this contribution, we present the results of *in situ* reaction tracking using X-ray and neutron diffraction, the structural identification of the intermediate phase, and investigations into the photochromism of these substances.

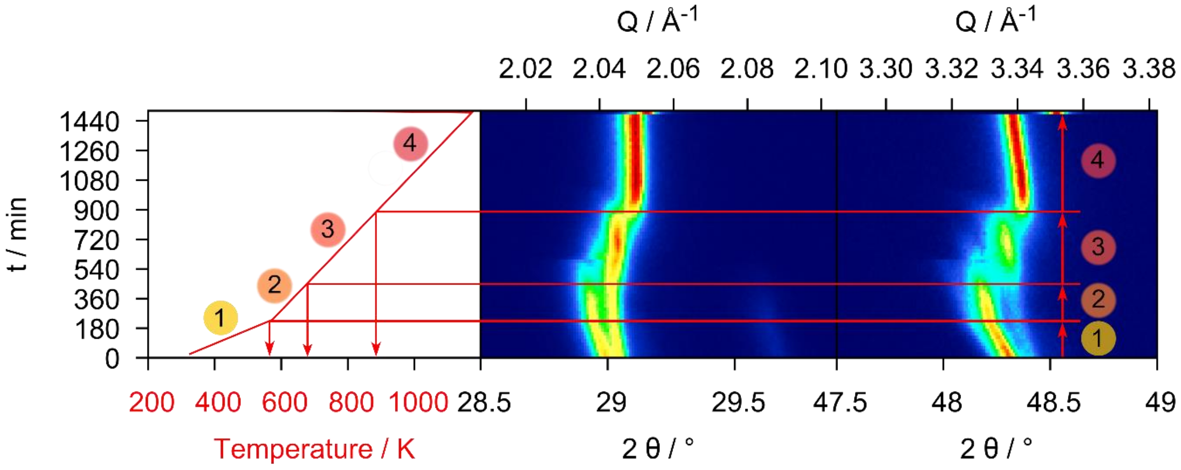

Fig. 1. False-color plot (red: high intensity, blue: low intensity) of the *in situ* X-ray diffraction experiment observing the decomposition of orthorhombic YHO in air (λ: Cu-$K_{\bar{\alpha}}$, 21 min per measurement) showing only two small angular sections of the measured diffraction patterns. The formation of an intermediate phase (step 3) that can clearly be distinguished from orthorhombic YHO (steps 1 and 2) and bixbyite-type Y_2O_3 (step 4) can be observed.

References
[1] H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli, K. R. Poeppelmeier, *Nat. Commun.* **2018**, *9*, 1, 772.
[2] F. Nafezarefi, H. Schreuders, B. Dam, S. Cornelius, *Appl. Phys. Lett.* **2017**, *111*, 10.
[3] T. Mongstad, C. Platzer-Björkman, J. P. Maehlen, L.P. Moji, Y. Pivak, B. Dam, E. S. Marstein, B. C. Hauback, S: Z. Karazhanov, *Sol Energy Mater. Sol. Cells* **2011,** *95*, 12, 3596.
[4] N. Zapp, H. Auer, H. Kohlmann, *Inorg. Chem.* **2019**, *58*, 21, 14635.

Novel Gain Media for UV-B Up-Conversion Laser

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The search for UV-up-conversion materials is of great scientific and technological interest due to the wide range of applications and potential to increase efficiency in various optoelectronic devices. Studies have shown that inorganic wide band gap materials doped with Gd^{3+} ions can achieve UV/Vis-up-conversion under near-infrared (NIR) excitation.[1] In addition, the use of Gd^{3+} in conjunction with other dopants such as Pr^{3+} has been shown to lead to efficient photon conversion and intense UV-B emission around 311 nm, branding these materials also as potential candidates for applications such as photochemistry and biomedicine.[2] Up-conversion from the blue spectral range has a significantly higher quantum yield than a process using NIR radiation.[3] It is therefore important to re-examine the efficiency and adjustability of up-conversion from the blue spectral range in more detail.

In this study, the phosphors were synthesized using solid-state synthesis and examined with regard to their optical properties. Particular attention was paid to the energy transfer between Pr^{3+} and Gd^{3+}.

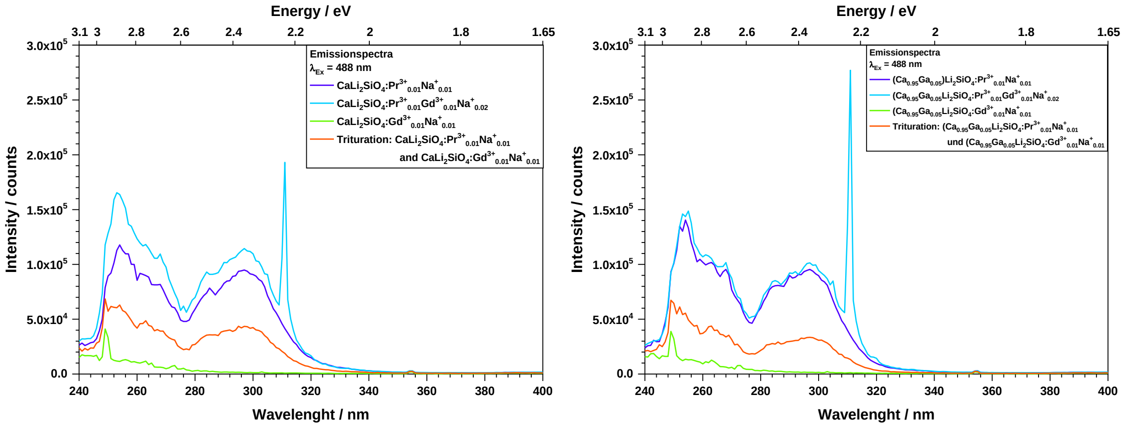

Fig. 1. Up-conversion emission spectra of $CaLi_2SiO_4$ doped with Pr^{3+}, with Gd^{3+}, or with both of them. All materials are also doped by Na^+ for the sake of charge compensation. Spectra were recorded upon excitation of 488 nm Laser (75 mW).

References

[1] V. Mahalingam, R. Naccache, F. Vetrone, J.A. Capobianco, Chemistry (Weinheim an der Bergstrasse, Germany) 15 (2009) 9660–9663.
[2] L. Rößmann, F. Schröder, T. Jüstel, Journal of Luminescence 263 (2023) 120033.
[3] F. Schröder, P. Pues, D. Enseling, T. Jüstel, Luminescence the journal of biological and chemical luminescence 38 (2023) 702–708.

Laser induced white emission and photocurrent of GaN nanoceramics

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The broadband white light emission (LIWE) generated by NIR laser has been studied since 2010, starting with Wang and Tanner's investigation of fully concentrated lanthanide oxides under vacuum conditions [1]. Due to its warm white light, LIWE has potential applications in general lighting. Various properties and factors such as the threshold nature, dependence on laser power, dependence on pressure, and changes in photoconductivity during LIWE generation have been investigated. Recently, it was discovered that this phenomenon can be used alternatively for optical memory.

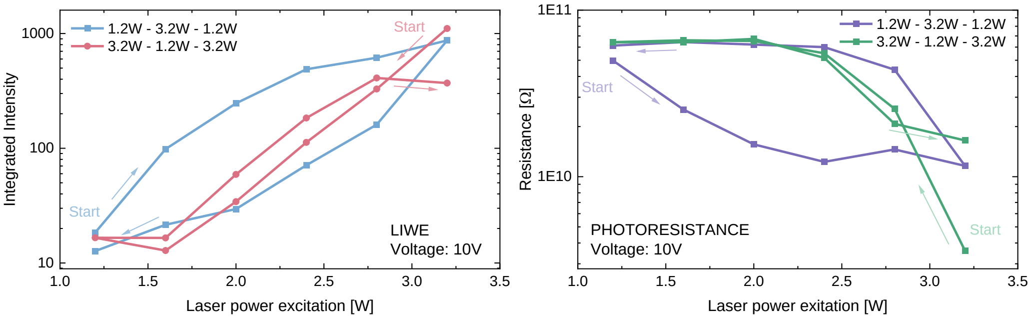

Fig. 1. The laser power dependence of integrated intensity of LIWE (a) and the maximum of photoresistance (b) measured in two consecutive measurement cycles: from the 1.2 W and from 3.2 W for GaN nanoceramic.

The GaN nanoceramics with an average grain sizes of 12 nm were synthesized using the modified Pechini and the ammonothermal methods. The nanoceramics were prepared using a low temperature high pressure technique. The optical characterization involved absorption and emission spectra induced by CW 975 nm laser diode are reported. LIWE measurements are characterized by the emission threshold and the intensity dependence on the laser power. The laser induced photocurrent (LIPC) measurements have also confirmed the threshold behavior [2]. Both LIWE and LIPC measurements conducted in forward and backward cycles have showed the hysteresis loop in the forward cycle case.

Acknowledgements

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References

1. J. Wang, P.A. Tanner, J. Am. Chem. Soc. **132,** 3 (2008) 947-949
2. M. Stefanski, P.Głuchowski, W. Strek, Ceram. Int. **46**, 18 (2020) 29060-2906

Luminescence and electron-hole trapping centers of phosphates and sulfates activated by transition and rare-earth ions.

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The study of the optical properties of doped phosphates and sulfates is linked to their practical applications as scintillators, dosimeters, and phosphors used in the manufacture of LED chips, as well as phosphorescent materials in the red and infrared spectral ranges for visualization.

The main issue for the implementation of these practical applications of doped phosphates and sulfates is the mechanism of emission, the accumulation of intrinsic and impurity electron-hole trapping centers, and their recombination decay with energy transfer from the matrix to the emitters, i.e. impurities.

In our work, it was shown that the energy of external exposure in the form of UV and X-ray irradiation exceeding the band gap of the matrix should be accumulated in the form of the formation of intrinsic and impurity trapping centers. The electron-hole pairs created by the irradiation should localize in the matrix within the dopants and anions, forming electronic states. The electronic state of the trapping centers, located in the forbidden zone at the bottom of the conduction band, corresponds to induced or combined emission states consisting of the electronic states of the dopants and anionic complexes. For example, in $Ca_2P_2O_7 - Mn$ and $CaSO_4 - Dy$, the combined electronic emission state corresponds to the intrinsic electronic states of $(P_2O_7)^{5-}$, SO_4^{3-} and the dopant electronic states of Mn^+ and Dy^{2+}, which are formed by the capture of free electrons of impurities and anions. The electronic combined states are stable at a temperature of 77 K. The hole component of the electron trapping centers is localized above the valence band in the form of $(P_2O_7)^{3-}$ and SO_4^- near the ground state of the dopants Mn^{2+} and Dy^{3+}, where anionic complexes were excited. During heating, electrons from the electronic states of $SO_4^{3-}, (P_2O_7)^{5-}$, $Mn^+,\ Dy^{2+}$ become ionized and move to the conduction, band in the temperature range of 220 – 330 K. Delocalized electrons recombine with holes near the dopants Mn^{2+} and Dy^{3+}. The energy released during the electron-hole recombination is transferred to the dopants Mn^{2+} and Dy^{3+}. Thus, the energy received from the external influence of the matrix during the decay of the radiative states is transferred to impurities. It has been experimentally found that in this temperature range, the intensity of the combined radiative state decreases, and the intensity of the main intracenter emission increases.

In such elementary processes, energy transfer from the matrix to the emitters occurs in dosimeters, scintillators, and phosphors.

Next-Generation X-Ray Imaging Scintillators: Challenges and Opportunities in Ce^{3+}-Doped $(Lu_{1-x}Tb_x)_3Al_2Ga_3O_{12}$ Garnet Crystals

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[Introduction] Scintillators play a critical role in X-ray imaging across various fields such as nondestructive testing and medical diagnostics. X-ray imaging heavily depends on sensitivity, which is influenced by factors such as light output and density. Garnet-structured compounds are promising candidates for scintillation applications, attributable to their high optical transparency, density, and flexibility offered by cation substitution. Our recent research focused on the development of Ce^{3+}-doped $(Gd,Y,Tb)_3(Al,Ga)_5O_{12}$ garnet scintillators showed amplified scintillation efficiency via synergistic Tb^{3+}-to-Ce^{3+} energy transfer (ET) processes [1]. However, such a study was limited to Tb^{3+} concentrations of up to 15%, even though the concentration of Tb^{3+} is crucial for ET between Ce^{3+} and Tb^{3+}. Bartosiewicz et al. previously found that a higher Tb^{3+} concentration, ≥ 50%, allows for more efficient $Tb^{3+} \rightarrow Ce^{3+}$ ET [2]. In this study, we grew Ce^{3+}-doped $(Lu,Tb)_3Al_2Ga_3O_{12}$ (LuTAGG:Ce) crystals with varying Tb^{3+} concentrations, extending up to 75%. The optical and scintillation properties were systematically investigated to understand the effects of Tb^{3+} concentration on the material's performance. The insights from this study are invaluable for optimizing compositions to enhance luminescence characteristics via synergistic codoping engineering.

[Materials and Methods] CeO_2, Tb_4O_7, Lu_2O_3, Al_2O_3 and Ga_2O_3 powders (99.99%) were mixed in the stoichiometric ratio. LuTAGG:Ce crystals were grown from the melt by the micro-pulling-down (μ-PD) method under the Ar+2%O_2 atmosphere [3].

[Results] The as-grown crystals are depicted in Fig. 1a. The regular morphology and high level of transparency indicate successful crystallization. The photoluminescence spectra (Fig. 1b), excited into Tb^{3+} absorption band, exhibit a gradual increase in the intensity of the Ce^{3+} $5d_1$-4f emission band, spanning from 450 nm to 750 nm. This enhancement in Ce^{3+} emission intensity is attributed to the improved ET process from Tb^{3+} to Ce^{3+}. The PL results are complemented by a detailed investigation of decay kinetics and scintillation properties.

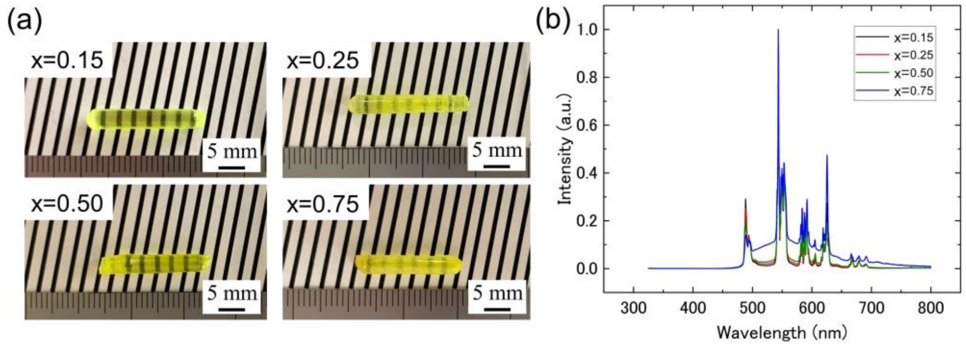

Fig. 1. (a) Photograph and (b) PL emission spectra of $(Lu_{1-x}Tb_x)_3Al_2Ga_3O_{12}$:Ce.

References

1. K. Omuro, A. Yoshikawa et al., J. Lumin., **273** (2024) 120663.
2. K. Bartosiewicz et al., J. Lumin., **188** (2017) 60-66.
3. A. Yoshikawa, et al., Opt. Mater., **30** (2007) 6-10.

On the Photoluminescence of Pr(III) Substituted Pyrophosphate Polymorphs

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Among the trivalent lanthanides, praseodymium is regularly exploited for its unique optical properties arising from a combination of intra- and interconfigurational transitions that stretch from the ultraviolet to the infrared range. Phosphates as wide band gap materials provide the necessary optical properties to realize deep UV emitting phosphors upon doping by a suitable activator. Calcium pyrophosphate ($Ca_2P_2O_7$) with its three crystallographically distinguished modifications presents a potentially interesting host material exhibiting excellent biocompatibility [1,2]. Therefore, in this study two of the three praseodymium doped polymorphs, viz. α-$Ca_2P_2O_7$ and β-$Ca_2P_2O_7$, are investigated with regard to their optical properties. The luminescent characteristics of the samples were studied dependent on the activator concentration and temperature. Finally, the interplay of the activator cation and the host structure was eluciated using the obtained optical and structural data.

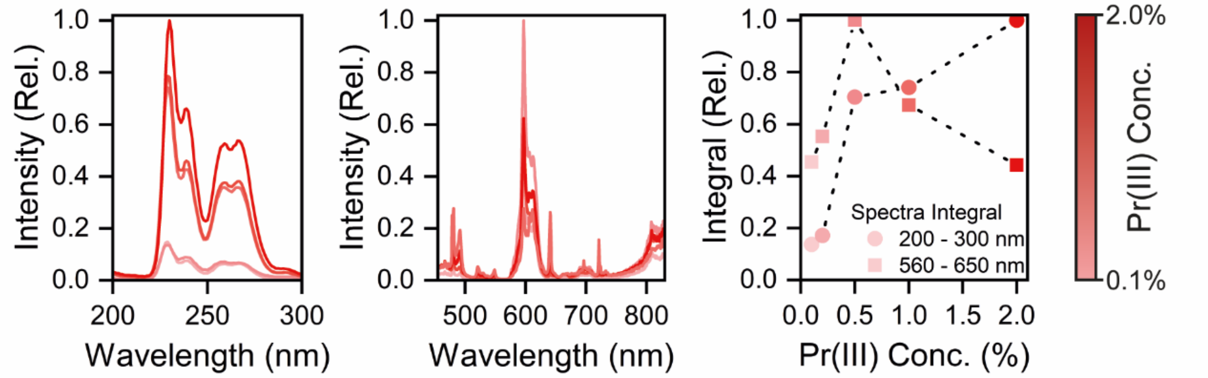

Fig. 1: Optical properties of a α-$Ca_2P_2O_7$:Pr doping series (Pr^{3+} conc.: 0.1 – 2.0 %). Emission spectra upon 160 nm VUV-excitation (left), emission spectra in the visible range upon 443 nm excitation (middle), and the respective emission integrals (right).

References

1. W. Habraken, P. Habibovic, M. Epple, M. Bohner, Mater. Today **19** (2016) 69
2. E.G. Komarova, M.B. Sedelnikova, A.M. Kondranova, S.O. Kazantsev, Y.P. Sharkeev, J. Phys.: Conf. Ser. **1281** (2019) 12037

Microorganisms as Promising Biotechnological Candidates for Rare Earth Elements Recovery

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In recent years there has been a notable increase in the demand for Rare Earth Elements due to their numerous and diversified industrial applications, consequently this has given rise to their greater exploitation and therefore to the generation of various wastes containing REEs. Considering the difficulty of sourcing REEs, research efforts are focusing on developing environmentally friendly recovery and recycling methods. Microorganisms, such as bacteria, algae, fungi, yeast and microalgae play a crucial role in the natural cycling of REEs and seems to be promising biotechnological candidates for their recovery [1]. Moreover, it has been found that the stability constants of rare earth metal ion complexes with ligands from organic acids such as citric acid, oxalic acid, gluconic acid and EDTA (Ethylenediaminetetraacetic acid) acid increase with increasing atomic number of rare earth elements [2]. Due to the microbial activity of producing organic acid, this study presents a preliminary investigation on the possibility to employ microorganisms, as single strain or consortium, for identify efficient bioleaching methods for REEs recovery by using the metabolites produced by microbial strains.

References

1. M. Vítová, D. Mezricky, World Journal of Microbiology and Biotechnology (2024) 40:189
2. L. Shen, H. Zhou, Q. Shi, X. Meng, Y. Zhao, G. Qiu, X. Zhang, H. Yu, X. He, H. He, H. Zhao, Hydrometallurgy 216 (2023) 106019

Structural, phonon, and optical properties of inorganic perovskites tuned by aliovalent doping

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Perovskite halides, $CsPbX_3$, which include chlorides, bromides, and iodides, are commonly used as nanocrystalline optoelectronic materials because of their effective tunable luminescence and easy fabrication procedures [1]. Perovskite halides have been the subject of much investigation as luminous materials because of their host emission, which is the result of excited carriers interacting with a deformed lead halide framework [1,2]. Their optical properties may be further tuned by doping, however aliovalent doping using RE ions is the most promising due to the creation of defects and the appearance of new energy transfer pathways.

The main aim of our studies is a deep characterization of the structural, phonon, and optical properties of microcrystalline perovskite materials doped with Nd and Yb ions [3-5], synthesized by a simple solid-state reaction method. We will show that phonon and optical properties are affected by a sequence of reversible structural phase transitions above the room temperature. We will also characterize the application potential of the obtained materials as luminescent thermometers and the layers for the production of solar cells.

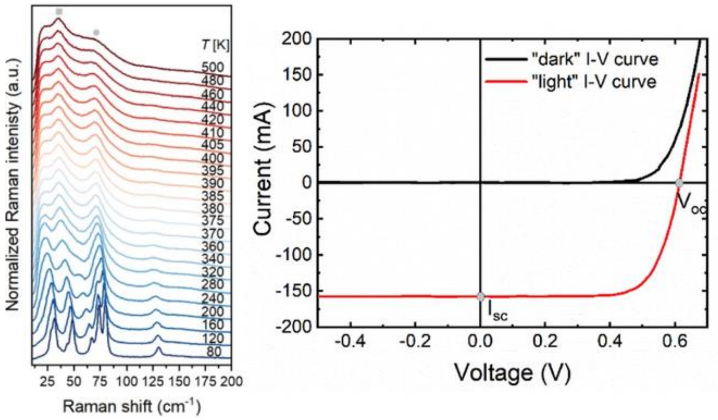

Fig. 1. Thermal evolution of Raman spectra obtained for $CsPbBr_3$:Yb^{3+} (left) and *I*-*V* characteristics for the solar cell with $CsPbBr_3$:Yb^{3+} thin layer in dark and under illumination. Figures are licensed under CC BY 4.0 [5].

References

1. R.J. Sutton, G.E. Eperon, L. Miranda, E.S. Parrott, B.A. Kamino, J.B. Patel, M.T. Hörantner, M.B. Johnston, A.A. Haghighirad, D.T. Moore, H.J. Snaith, Adv. Energy Mater., **6** (2016), 1502458.
2. I. Chung, J.H. Song, J. Im, J. Androulakis, C.D. Malliakas, H. Li, A.J. Freeman, J.T. Kenney, M.G. Kanatzidis, J. Am. Chem. Soc., **134** (2012) 8579–8587.
3. M. Stefanski, B. Bondzior, A. Basinski, M. Ptak, B. Lou C.G. Ma, Inorg. Chem. Front., **11** (2024), 2626–2633.
4. M. Stefanski, V. Boiko, M. Ptak, W. Strek, J. Alloys Compd. **905** (2022) 164216.
5. M. Stefanski, B. Bondzior, T. Gzyl, E. Zielony, M. Betke, A. Sieradzki, M. Ptak, Adv. Opt. Mater., **11** (2023) 2301672.

New Insight in the Sol-Gel Synthesis of Lanthanide Substituted Garnets

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Yttrium aluminium garnet (YAG) is a unique garnet that has a wide range of applications due to it is outstanding chemical, physical and optical properties. Lanthanide-doped and co-doped YAG still are very interesting compounds from theoretical point of view to study the enhancement of luminescence properties. On the other hand, such investigations are very perspective from possible new optical applications of garnet crystal structure compounds [1-6].

In the presented work, ten samples of lanthanide substituted garnets ($Y_{1.5}La_{1.35}Ce_{0.15}Ga_3Al_2O_{12}$, La = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) were prepared using sol-gel synthesis method which allows to obtain final product with high purity and homogeneity at relatively low-temperature [6]. The obtained precursor gel samples were ground in an agate mortar and heated at 800 ℃ for 5 h with a heating rate of 5℃/min. Finally, all the samples were additionally annealed at 1000 ℃ for 5 h.

The phase and chemical compositions of the obtained garnets were studied by powder X-ray diffraction analysis and FTIR spectroscopy. The surface morphology of all specimens was analysed by scanning electron microscope (SEM) and particle sizes were calculated with Image-J. It was demonstrated that the formation of single-phase $Y_{1.5}La_{1.35}Ce_{0.15}Ga_3Al_2O_{12}$ garnets occurs independent on the selected lanthanide element. The FTIR results were in a good agreement with XRD analysis data. From the results of SEM studies, it was found that the surface of most of the synthesized compounds is porous and consists of spherical or irregularly shaped nano- or micro-sized particles. The luminescence properties of these novel garnet crystal structure compounds are under investigation.

References

1. E. Cavalli et al. YAG:Pr3+ transparent ceramics for applications in photonics: synthesis and characterization. Mater. Res. Expr. 1 (2014) 045903.
2. J. Drabik, L. Marciniak. The influence of Eu3+ concentration on the spectroscopic properties of YAG:Ti, Eu3+ nanocrystalline luminescent thermometer. J. Lumin. 208 (2019) 213-217.
3. Z.H. Xu et al. Yb3+/Mn2+ co-doped Y3Al5O12 phosphors for optical thermometric application. Opt. Mater. 124 (2022) 111949.
4. H. Ali et al. Tuning the photoluminescence spectral properties of Ce and Sm co-doped YAG ceramic for optical applications. J. Korean Ceram. Soc. 59 (2022) 679-685.
5. V. Dormenev et al. Scintillation Properties of Garnets and Oxyorthosilicates With Different Dopants. IEEE Transac. Nucl. Sci. 70 (2023) 1392-1397.
6. D. Vistorskaja et al. Novel lanthanide-doped $Y_{3-x}Na_xAl_{5-y}V_yO_{12}$ Garnets: Synthesis, Structural and Optical properties. Opt. Mater.:X. 22 (2024) 100300.

Synthesis of Nickel-Rhenium-Phosphorous Catalysts and their Application for Oxygen Evolution Reaction

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The current challenge is the design and development of low-cost, high-activity catalysts for the water splitting process, with the aim of producing pure hydrogen. This hydrogen can then be applied for hydrogen/oxygen (H_2/O_2) fuel cells and in other areas. In this study, we present a straightforward approach to synthesise an efficient nickel-rhenium-phosphorous (NiReP) catalyst for the production of hydrogen through water splitting using the electroless metal deposition technique. The morphology, structure, and composition of the NiReP catalysts have been examined using a range of analytical techniques, including scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma optical emission spectroscopy (ICP-OES). The activity of the catalysts has been investigated for hydrogen evolution (HER) and oxygen evolution (OER) reactions in 1 M KOH using linear sweep voltammetry (LSVs) and chrono-techniques. The data on the HER and OER in an alkaline medium on the NiReP catalysts with varied Ni and Re amounts are compared and discussed based on electrochemical data.

Acknowledgment

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Luminescent Properties of Eu^{2+}-doped $Sr_5(PO_4)_3Cl$ Synthesized in Air Atmosphere

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Optical materials with adjustable luminescence attract a lot of attention due to their broad application possibilities. As one of the most common and highly efficient activators, an Eu^{2+} ion possesses broadband absorption in the UV to blue regions, as well as multicolor emission. Most commonly Eu^{2+}-doped materials are synthesized in reducing atmosphere; nevertheless, some specific inorganic matrices allow for the stabilization of Eu^{2+} oxidation state in air atmosphere. Self-reduction phenomenon is known for the materials such as borates, silicates, and phosphates. One of the suitable hosts is strontium chlorapatite ($Sr_5(PO_4)_3Cl$). This matrix is able to adopt a variety of isovalent and aliovalent ions including lanthanides.

In this study, Eu^{2+}-doped $Sr_5(PO_4)_3Cl$ powders with various Eu content were synthesized by molten salt method in air atmosphere using Eu^{3+}-doped strontium phosphate ($Sr_3(PO_4)_2$) as a starting material. The optimization of synthesis parameters was performed in terms of temperature, time, precursor-to-flux ratio and Eu content. The self-reduction of Eu^{3+} to Eu^{2+} occurred during the phase transformation from $Sr_3(PO_4)_2$ to $Sr_5(PO_4)_3Cl$. The presence of Eu^{2+} ions was clearly visible from the optical properties of the synthesized materials. Luminescent properties were investigated by means of photoluminescence measurements. Excitation spectra, emission spectra and decay curves of the samples were studied. Temperature-dependent photoluminescence measurements were performed as well.

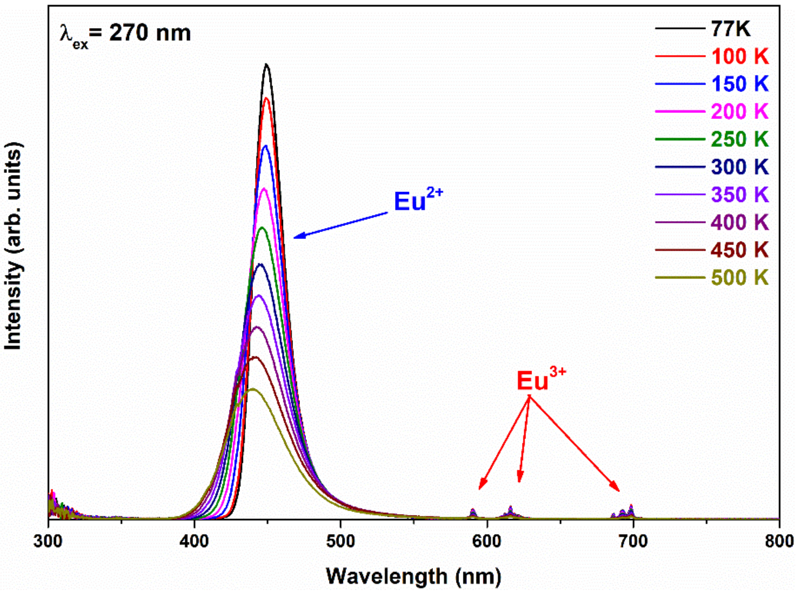

Fig. 1. Temperature-dependent emission spectra of $Sr_5(PO_4)_3Cl$:Eu powder.

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Broad Luminescence Generated by IR Laser Excitation from $CsPbBr_3:Yb^{3+}$ Perovskite Ceramics

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Interest in lead halide perovskites has been increasing in recent years due to their unique optical properties, such as precise control of absorption and emission color, either by size or composition. The name "perovskite" was first given by Gustav Rose in 1839 after Russian mineralogist Lev Perovski to the mineral $CaTiO_3$. However, it is now used as a general term for several groups of materials that present, among others, the general formula $APbX_3$, where A can be either an organic or an inorganic cation exhibiting a network of corner-shared PbX_6 octahedra, and crystalizing in either cubic, orthorhombic, or tetragonal phases [1], while X can be substituted by oxygen or halide elements, such as Br. Here, we demonstrate the generation of broadband emission in the visible and infrared ranges induced by a concentrated beam of infrared radiation from $CsPbBr_3$ ceramics doped with Yb^{3+} ions. The sample was obtained by the conventional solid-state reaction method, and XRD measurements confirmed the phase purity of the material crystallizing in the orthorhombic system. Spectroscopic measurements required further sample preparation in the form of ceramics using a high-pressure press. The research showed that as the excitation power increases, the emission intensity does not increase linearly from the beginning of the experiment. Irradiation of the material results in the accumulation of the delivered energy. Absorption of a sufficient number of photons triggers avalanche emission. It was found that the most intense luminescence is produced in a vacuum. Changes in conductivity were also observed, where the excitation was able to lower the resistivity of the material and it was highly dependent on the excitation power. The mechanism responsible for the generation of the observed phenomenon involving intervalence charge transfer (IVCT) transitions has been postulated.

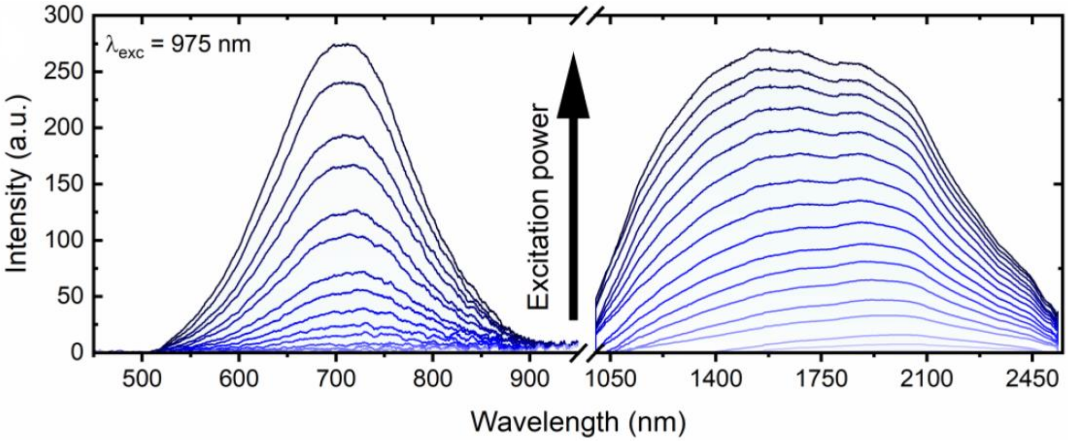

Fig. 1. Laser-induced emission spectra of $CsPbBr_3$:10%Yb^{3+} recorded in the VIS and NIR ranges.

References

1. Q.A. Akkerman, L. Manna, ACS Energy Lett., **5** (2020) 604-610.

Acknowledgement

The authors acknowledge the support from grant no. NCN-2021/43/D/ST5/01865 funded by National Science Center, Poland.

The limiting factors of quantum-cutting efficiency of ytterbium-doped lead halide perovskites: dimeric and monomeric ytterbium species

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Ytterbium-doped cesium lead halide perovskites exhibit unusual down-conversion with quantum efficiencies exceeding 100% [1-2]. This phenomenon has been attributed to the quantum-cutting (QC) when a perovskite exciton (~500 nm) is converted into two Yb^{3+} excitations (~1000 nm). However, the mechanism of energy transfer from the perovskite to the Yb^{3+} ions is still debated, and it is still unclear what processes limit the conversion efficiency.

In this work, Yb-doped $CsPbX_3$ (X: Cl^-, Br^-, or both) perovskite samples prepared by different techniques were investigated. Electron paramagnetic resonance (EPR) measurements were applied to study ytterbium incorporation into the perovskite matrix and ultrafast time-resolved fluorescence together with microscopic studies – to evaluate the QC efficiency limiting factors.

We demonstrate that two types of ytterbium species are formed, depending on the concentration of Yb^{3+}. The photoluminescence (PL) of Yb^{3+} shows a biexponential decay at low concentrations, attributed to the presence of monomeric and dimeric Yb^{3+} species. The fast decay component is attributed to monomeric Yb^{3+} ions, which do not perform QC and have low PL yield. This component disappears when the concentration of Yb increases to about 5% and PL of dimeric species dominates. The PL decay becomes faster again when the ytterbium concentration exceeds about 10%, due to migration limited excitation quenching. These two processes are important QC efficiency limiting factors.

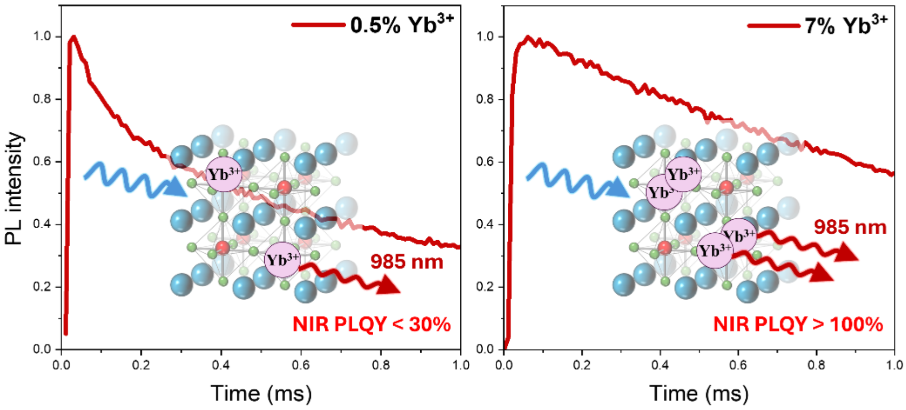

Fig. 1. NIR PL kinetics of Yb-doped $CsPbX_3$ perovskites with different Yb^{3+} concentrations.

References
1. Milstein, T.J., et al., Nano Lett. 18 (2018) 3792.
2. Ishii, A. & Miyasaka, T., JCP 153 (2020) 194704.

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Laser induced white emission as a tool for pressure sensing

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Laser-induced white emission (LIWE) occurs when a material is excited with a focused infrared laser and is characterized by the emission of warm white light [1]. Emission have a broadband character and cover visible range. It increased with a simultaneous decreasing f-f transitions. In particular the effect of excitation power density and concentration of dopants ions were investigated. The intensity of white emission was characterized by exponential dependence on excitation power density [2]. Therefore, it can be used as a new source of indoor lighting. Light parameters are similar to sunlight.

It was also observed that for $La_{1-x}AlO_3$:xNd nanocrystals, the intensity ratio of broadband emission and f-f upconversion transitions of neodymium ions is dependent on the concentration of neodymium ions, as well as being strongly pressure-dependent.

The significant sensitivity of luminescence to pressure indicates that the effect could be useful as optical sensors for measuring vacuum.

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References

1. J. M. Gonçalves et al. ECS J. Solid State Sci. Technol. 12 (2023) 056002
2. J. M. Gonçalves et al., Dalton Trans., 52 (2023) 2073-2079

Controlling oxygen vacancies in CeO_{2-x} for CO_2 reduction

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Ceria (CeO_2) is a semiconductor oxide of the most abundant of the rare earth elements. It can exhibit considerable amounts of oxygen vacancies while retaining its fluorite crystal structure, allowing for increased oxygen storage capacity, band gap tuning and enhanced CO_2 adsorption [1]. Several studies have shown that these oxygen vacancies in CeO_2 can act as an active site in catalysis, for instance for the dissociation reaction of CO_2 [2]. Such reactions could integrate CO_2 in a circular, net zero emission economy [3-4].

We have applied both wet chemical and dry thermal methods to introduce oxygen vacancies in ceria nanoparticle synthesis and thin film deposition. Various characterization methods have been explored to quantify the amount of oxygen vacancies, among them XRD (x-ray diffraction), Raman spectroscopy, UV-VIS spectroscopy, XPS (x-ray photon spectroscopy) and TPR (temperature programmed reduction). While most techniques allowed a qualitative indication of the presence of oxygen vacancies, TPR provided the most quantitative assessment.

Further, we studied the reverse water-gas shift reaction using plasmon assisted photocatalysis with CeO_{2-x} as the support material (Au/CeO_{2-x}). In this emerging technology, broad sunlight absorption is made possible through supported gold plasmonic nanoparticles, allowing for CO_2 reduction without external heating [5-6]. The impact of pre-introduced oxygen vacancies in the ceria support was found to be overruled by the reducing conditions during the catalytic conversion. Nonetheless, preliminary results indicate a substantial contribution of oxygen vacancies in the CO_2 dissociation reaction.

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References

1. Montini, T.; Melchionna, M.; Monai, M.; Fornasiero, P., Chemical Reviews 2016, 116 (10), 5987-6041.
2. Ashford, B.; Wang, Y.; Poh, C.-K.; Chen, L.; Tu, X., Applied Catalysis B: Environmental **2020,** *276*, 119110.
3. Al-Mamoori, A.; Krishnamurthy, A.; Rownaghi, A. A.; Rezaei, F., Energy Technology 2017, 5 (6), 834-849.
4. Artz, J.; Müller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternberg, A.; Bardow, A.; Leitner, W., Chemical Reviews 2018, 118 (2), 434-504.
5. Volders, J.; Elen, K.; Raes, A.; Ninakanti, R.; Kelchtermans, A.-S.; Sastre, F.; Hardy, A.; Cool, P.; Verbruggen, S. W.; Buskens, P.; Van Bael, M. K., Nanomaterials 2022, 12 (23), 4153.
6. Schuurmans, J. H. A.; Masson, T. M.; Zondag, S. D. A.; Buskens, P.; Noël, T., ChemSusChem 2024, 17 (4), e202301405.

The Sol-Gel Synthesis and Characterization of Novel Garnet-Type Luminescent Materials

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In recent years, inorganic luminescent materials have been considered as key and technologically important components of many lighting and display systems, determining the successful functionality of devices [1]. Garnet structure compounds are recognized as one of the best phosphor host materials. Yttrium aluminium garnet (YAG) stands out due to its good stability, wide optical transparency spectrum range, and the ability to incorporate large amounts of Ln^{3+} ions without concentration quenching. For these reasons, YAG:Ln is widely used in the field of fluorescence, including lasers, light-emitting diodes, and scintillators [2-4]. Therefore, the aim of this work was to synthesize novel garnet-type phosphors by the sol-gel synthesis method, to characterize their structural and morphological features, as well as to study their optical properties. The obtained products were investigated using XRD, FTIR, and SEM methods. Also, the emission and excitation spectra were recorded, the colour coordinates, the decay times and quantum efficiencies were determined.

Figure 1 shows the XRD patterns of the $Y_{2.97-x}K_xTb_{0.03}Al_5O_{12}$ samples. The monophasic $Y_{2.97-x}K_xTb_{0.03}Al_5O_{12}$ garnets can be successfully obtained, when the amount of potassium is in the range of $0.3 \leq x \leq 0.75$.

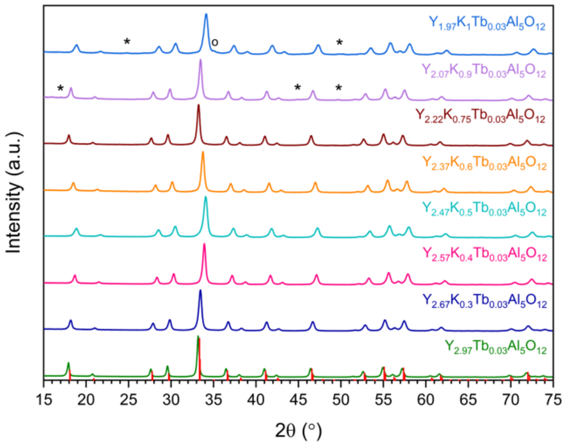

Fig. 1. XRD diffraction patterns of $Y_{2.97-x}K_xTb_{0.03}Al_5O_{12}$ samples. The crystalline phases are marked: vertical red lines - $Y_3Al_5O_{12}$, * – $YAlO_3$, o – Al_2O_3

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References

1. S. Ye, F. Xiao, Y.X. Pan, Y. Y. Ma, Q. Y. Zhang, Mat. Sci. Eng. R., **71** (2010) 1-34.
2. A. Jain, P. Sengar, G. A. Hirata, J. Phys. D. Appl. Phys., **51** (2018) 303002 1-62.
3. J. C. A. Santos, E. P. Silva, N. R. S. Souza, Y. G. S. Alves, D. V. Sampaio, C. Kucera, L. G. Jacobsohn, J. Ballato, R. S. Silva, Ceram. Int., **45** (2019) 3797-3802.
4. M. Borlaf, M. Frankowska, W. W. Kubiak, T. Graule, Mater. Res. Bull., **100** (2018) 413-419.

Visible-to-UVC Upconversion in Pr^{3+}-Doped Phosphors: A Step Towards Innovative UVC Light Sources

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Antibiotic resistance is escalating into a significant global health problem, mostly due to the excessive and improper use of antibiotics in both medical and agricultural. Therefore, preventing bacterial infections through effective disinfection of air, water, and surfaces is essential. Since the 1930s [1], ultraviolet C (UVC) lamps, which emit radiation in the 220-280 nm range, have served as a potent disinfection method. These high-energy photons are absorbed by microbial DNA, causing the formation of pyrimidine dimers between adjacent thymine bases, which prevents bacteria from reproducing. Because UVC radiation does not naturally reach the Earth's surface, microbes have not developed resistance to it, preserving its effectiveness as a disinfection strategy.

In this study, we synthesized and analyzed visible-to-UVC upconversion [2] material composed of an inorganic host doped with praseodymium ions (Pr^{3+}). When excited by vacuum ultraviolet (VUV) or visible light, these materials exhibited broad and intense emission in the 240–300 nm range. This UVC luminescence is attributed to the $4f^15d^1 \rightarrow 4f^2$ transitions of Pr^{3+} ions [3]. We investigated the upconversion mechanisms by examining the luminescence intensity dependence on pumping power and decay kinetics. We also discussed the correlation between the host structure and optical properties in the UVC range.

These materials are promising candidates for mercury-free UVC devices and have potential applications in creating self-cleaning surfaces [4].

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References

1. N.G. Reed, Public Health Rep. **125** (2010), 15–27.
2. F. Auzel, Chem. Rev. **104** (2004), 139.
3. N. Rebrova; P. Zdeb, K. Lemański, B. Macalik, O. Bezkrovnyi, P.J. Dereń, Inorg. Chem. **63** (2024), 3028–3036.
4. E.L. Cates, M. Cho, J. Kim, Environ. Sci. Technol. **45** (2011), 3680–3686.

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