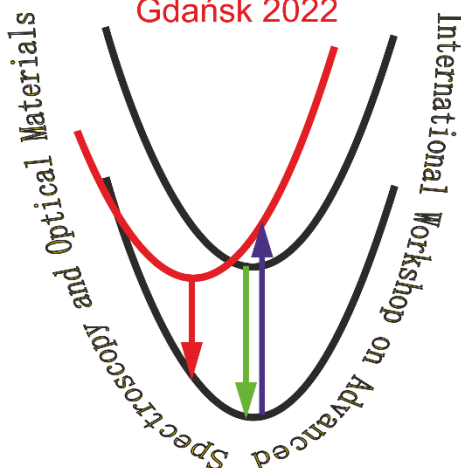


# BOOK OF ABSTRACTS

The Seventh International Workshop  
on Advanced Spectroscopy and Optical Materials  
**10-15 July 2022 Gdańsk, Poland**

## 7th IWASOM

Gdańsk 2022





The Seventh International Workshop  
on Advanced Spectroscopy and Optical Materials  
10-15 July 2022 Gdańsk, Poland

**Organized by:**

Institute of Experimental Physics, University of Gdańsk  
Institute of Physics, Polish Academy of Science, Warsaw  
The Foundation for the Development of the University of Gdańsk

In memory of Professor Marek Grinberg

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## Scientific Program

**Sunday, July 10, 2022**

*Location: Main Hall of the Faculty of Social Sciences, level 200*

*(Faculty of Social Sciences, University of Gdańsk, Jana Bażyńskiego 4, Gdańsk)*

Time	Event
14:00 – 18:00	Registration

**Monday, July 11, 2022**

*Location: Faculty of Social Sciences, University of Gdańsk, level 100,  
Room S204*

Time	Event
08:00 – 09:00	Registration
09:15 – 09:30	Opening ceremony

**Session: Special session in memory of Prof. Marek Grinberg**

Session chair: Marco Bettinelli

Time	Code	Presenting author	Title, authors
09:30 – 10:00	IL1	Andrzej Suchocki	Influence of pressure on Mn <sup>2+</sup> and Fe <sup>3+</sup> ions photoluminescence in solids A. Suchocki
10:00 – 10:30	IL2	Marek Godlewski	Excitons Bound at Rare Earth and Transition Metal Ions. How to see the invisible? M. Godlewski
10:30 – 11:00	IL3	Setsuhisa Tanabe	High pressure spectroscopies on garnet phosphors: what we learned from collaborations with Marek S. Tanabe
11:00 – 11:30		Coffee break	

**Session: Phosphors: recent progress, new materials, and applications I**

Session chair: Marek Godlewski

Time	Code	Presenting author	Title, authors
11:30 – 12:00	IL4	Michele Back	Temperature and pressure sensing in Cr <sup>3+</sup> phosphors M. Back, J. Ueda, S. Tanabe
12:00 – 12:30	IL5	Miroslav Dramićanin	Mn <sup>5+</sup> phosphors revisited – can we use them for luminescence thermometry in the near-infrared? M. D. Dramićanin, Z. Ristić, S. Kuzman
12:30 – 12:45	O1	Quan Vu	Luminescence of Dy <sup>3+</sup> in A <sub>2</sub> MgWO <sub>6</sub> (A = Ca, Sr, Ba) double perovskites T. H. Q. Vu, D. Stefańska, P. J. Dereń
12:45 – 13:00	O2	Yaroslav Zhydachevskyy	Mn <sup>4+</sup> photoluminescence in Ga <sub>2</sub> O <sub>3</sub> - Al <sub>2</sub> O <sub>3</sub> alloys Y. Zhydachevskyy, V. Mykhaylyk, V. Stasiv, V. Hreb, I. Lutsyuk, A. Luchechko, L. Vasylechko, A. Suchocki
13:00 – 14:30		Lunch	

## Session: Phosphors: recent progress, new materials, and applications II

Session chair: Setsuhisa Tanabe

Time	Code	Presenting author	Title, authors
14:30 – 15:00	IL6	Marco Bettinelli	Luminescence Spectroscopy of Eu <sup>3+</sup> in the Rhombohedral Pyrochlore Ca <sub>2</sub> La <sub>3</sub> Sb <sub>3</sub> O <sub>14</sub> A. B. Kulinkin, S. P. Feofilov, F. Piccinelli, A. M. Srivastava, M. Bettinelli
15:00 – 15:30	IL7	Philippe Boutinaud	CuLaO <sub>2</sub> reloaded P. Boutinaud
15:30 – 15:45	O3	Anton Markovskiy	Development of three-layered composite color converters for white LEDs based on the epitaxial structures of YAG:Ce, TbAG:Ce and LuAG:Ce garnets A. Markovskiy, V. Gorbenko, T. Zorenko, O. Sidletskiy, A. Fedorov, M. Pakula, Yu. Zorenko
15:45 – 16:00	O4	Andrea Diego-Rucabado	Tuning optical properties of Y <sub>2</sub> O <sub>3</sub> :Pr <sup>3+</sup> nanocrystals through different synthesis methods A. Diego-Rucabado, M. Candela, F. Aguado, J. González, F. Rodríguez, R. Valiente, R. Martín-Rodríguez, I. Cano
16:00 – 16:30		Coffee break	

## Session: Phosphors: recent progress, new materials, and applications III

Session chair: Philippe Boutinaud

Time	Code	Presenting author	Title, authors
16:30 – 17:00	IL8	Hubert Huppertz	New Developments in the Field of Alkali Lithosilicates H. Huppertz
17:00 – 17:30	L1	Jerzy Sokolnicki	Oxonitridosilicate phosphors for LEDs J. Sokolnicki
17:30 – 17:45	O5	Karol Bartosiewicz	Atom redistribution and defect formation in GAGG:Ce single crystals imposed by Mg <sup>2+</sup> and Li <sup>+</sup> codoping: the impact on the luminescence and scintillation properties K. Bartosiewicz, T. Horiai, D. Szymański, S. Kurosawa, A. Yamaji, A. Yoshikawa, Y. Zorenko
17:45 – 18:00	O6	Winicjusz Drozdowski	Semiconductor Scintillator Development: β-Ga <sub>2</sub> O <sub>3</sub> , MgGa <sub>2</sub> O <sub>4</sub> and ZnGa <sub>2</sub> O <sub>4</sub> W. Drozdowski, A. Bachiri, M. Makowski, M. Witkowski, A. Wojtowicz, Z. Galazka
18:00 – 20:00		Welcome reception	

**Tuesday, July 12, 2022****Session: Radioluminescence, optically and thermally stimulated luminescence in solids I**

Session chair: Agata Kamińska

Time	Code	Presenting author	Title, authors
09:15 – 09:45	IL9	Sergii Ubizskii	The kinetics peculiarities study of the afterglow and OSL in YAP:Mn S. Ubizskii, O. Buryy, V. Degoda, H. Podust
09:45 – 10:15	IL10	Andrzej Wojtowicz	Infra-red stimulated radioluminescence in $\beta$ -Ga <sub>2</sub> O <sub>3</sub> ; a new semiconducting scintillator A. Wojtowicz, M. Witkowski, M. Makowski, W. Drozdowski, K. Irmscher, R. Schewski, Z. Galazka
10:15 – 10:30	O7	Arkadiusz Mandowski	An analysis of radiative recombination and trapping of charge carriers in irradiated feldspar samples A. Mandowski, R. Smyka, E. Mandowska
10:30 – 10:45	O8	Oleg Viahin	Luminescence properties of Lu <sub>2</sub> SiO <sub>5</sub> :Ce,Yb crystals under synchrotron radiation excitation O. Viahin, O. Sidletskiy, Yu. Malyukin, Yu. Zorenko
10:45 – 11:00	O9	Yurii Syrotych	Two and three-layered composite scintillators based on the GAGG and TbAG garnets for simultaneous registration of different types of ionizing radiation Y. Syrotych, V. Gorbenko, R. Kucerkova, J. Mares, M. Nikl, K. Kamada, A. Yoshikawa, Yu. Zorenko
11:00 – 12:00		Coffee break	

**Session: Radioluminescence, optically and thermally stimulated luminescence in solids II**

Session chair: Przemysław Dereń

Time	Code	Presenting author	Title, authors
12:00 – 12:30	IL11	Yuriy Zorenko	Intrinsic and defect-related luminescence of garnet and perovskite compounds Yu. Zorenko, V. Gorbenko, T. Zorenko, K. Bartosiewicz
12:30 – 12:45	O10	Sandra Witkiewicz-Łukaszek	Comparison of X rays beam dose distributions in radiotherapeutic tumor treatment procedure using YAG:Ce and LuAG:Ce crystal detectors S. Witkiewicz-Lukaszek, J. Winięcki, P. Michalska, Yu. Zorenko
12:45 – 13:00	O11	Anastasiia Lysak	Influence of the growth temperature on the optical properties of {ZnO/CdO} <sub>30</sub> superlattices A. Lysak, E. Przeździecka, A. Wierzbicka, A. Adhikari, M. Stachowicz, R. Jakiela, P. Dłużewski, A. Reszka, J. M. Sajkowski, Z. Khosravizadeh, A. Kozanecki
13:00 – 14:30		Lunch	

**Session: Novel fluorophores, optical materials, devices for biosensing, biomedical and environmental applications I**

Session chair: Yuriy Zorenko

Time	Code	Presenting author	Title, authors
14:30 – 15:00	IL13	Przemysław Dereń	Double perovskites - sensors, phosphors P. J. Dereń, T. H. Q. Vu, D. Stefańska, B. Bondzior, N. Miniajluk-Gaweł, K. Lemański
15:00 – 15:15	O12	Agata Kamińska	Luminescent properties of cerium implanted GaInN A. Kaminska, K. Koronski, M. Boćkowski, E. Alves, R. Jakieła, V. Pankratov, V. Pankratova, A. Šarakovskis
15:15 – 15:30	O13	Krzysztof Anders	Low phonon glasses and polymer composites doped with erbium – a comparative study K. Anders, A. Jusza, M. A. Butt, R. Piramidowicz
15:30 – 15:45	O14	Anna Jusza	Dysprosium doped oxide and fluoride glasses for yellow fiber lasers A. Jusza, M. Karczewska, P. Mergo, R. Piramidowicz
15:45 – 16:00		Conference photo	
16:00 – 19:00		Coffee break and poster session	

## Wednesday, July 13, 2022

### Session: Thin films and low-dimensional systems

Session chair: Hubert Huppertz

Time	Code	Presenting author	Title, authors
09:15 – 09:45	IL14	Pablo Molina	Electrostatic doping modulation in monolayer MoS <sub>2</sub> through ferroelectric domain patterns P. Molina, J. Fernandez-Tejedor, D. Gallego-Fuente, P. Ares, J. Gomez-Herrero, L. E. Bausá, M.O. Ramírez
09:45 – 10:15	L2	Shirly Espinoza	Acoustic phonons propagation in thin film and bulk materials explored by pump-probe ellipsometry S. Espinoza, M. Rebarz, M. Zahradník, A. Dubroka, J. Andreasson
10:15 – 10:30	O15	Krzysztof Dorywalski	UV-VUV spectroscopic ellipsometry of PLD-grown PbTiO <sub>3</sub> thin films K. Dorywalski, B. Andriyevskyy, N. Lemée, M. Gharbi, A. Zeinert, M. Piasecki
10:30 – 10:45	O16	Juby Alphonsa Mathew	Luminescence Properties of MBE grown Eu doped ZnMgO thin films on c- and r-oriented Al <sub>2</sub> O <sub>3</sub> substrates J. A. Mathew, V. Tsiumra, A. Wierzbicka, A. Lysak, J. M. Sajkowski, R. Jakiela, Y. Zhydachevskyy, M. Stachowicz, E. Prezdziecka, A. Kozanecki
10:45 – 11:00	O17	Marcin Łapiński	New, hybrid luminescent materials based on thin oxide films doped by rare earth ions and gold plasmonic nanostructures M. Łapiński, R. Koziół, W. Sadowski, B. Kościelska
11:00 – 11:30		Coffee break	

### Session: Hybrid and organic optical materials

Session chair: Pablo Molina

Time	Code	Presenting author	Title, authors
11:30 – 12:00	IL15	Ryszard Piramidowicz	Luminescent polymer composites doped with rare-earth elements R. Piramidowicz, A. Jusza, K. Anders, M. A. Butt, R. Łyszczek, P. Mergo
12:00 – 12:30	L3	Serhii Nedilko	Luminescent oxide fillers in various types of nanocomposites S. G. Nedilko
12:30 – 12:45	O18	Diana Bobrowska	Poly(p-phenylene vinylene)/carbon nanostructures composites: morphology, structure and electrochemical properties D. Bobrowska, K. Gdula, K. Winkler
13:00 –		Lunch and excursion	

## Thursday, July 14, 2022

### Session: Nanoscale optical materials and single nano-objects I

Session chair: Ryszard Pirydzewicz

Time	Code	Presenting author	Title, authors
09:15 – 09:45	IL16	Barbara Kościelska	AuAg nanoalloy plasmonic properties tuned by the assistance of machine learning method B. Kościelska, M. Łapiński, R. Kozioł, P. Syty, J. E. Sienkiewicz, A. Synak, P. Bojarski, W. Sadowski
09:45 – 10:15	IL17	Julien Houel	CdSe/CdZnS quantum dots in adjustable bandgap MAPbX <sub>3</sub> (X = Cl, Br and I) perovskite matrix J. Baronnier, B. Mahler, P. Mai, C. Dujardin, F. Kulzer, J. Houel
10:15 – 10:30	O20	Dawid Piątkowski	Up-conversion luminescence at the nanoscale: benefits and difficulties D. Piątkowski, M. Ćwierzona, K. Wiwatowski, M. Żebrowski, M.A. Antoniuk, K. Sulowska, R. Houssaini, Z. Korczak, M. Szalkowski, A. Bednarkiewicz, M. Nyk, A. Hartschuh, S. Maćkowski
10:30 – 10:45	O21	Maciej Ćwierzona	Up-converting nanocrystals coupled to a single silver nanowire as a source of surface plasmon polaritons for direct measurement of propagation losses M. Ćwierzona, M. Żebrowski, M. A. Antoniuk, K. Sulowska, M. Nyk, S. Maćkowski, D. Piątkowski
10:45 – 11:00	O22	Xavier Guichard	RE <sup>3+</sup> Photoluminescence of Charge Compensated Hafnia Nanoparticle: Solvothermal Synthesis and Colloidal Dispersion X. H. Guichard, A. Lauria
11:00 – 11:30		Coffee break	

### Session: Nanoscale optical materials and single nano-objects II

Session chair: Barbara Kościelska

Time	Code	Presenting author	Title, authors
11:30 – 12:00	IL18	Sebastian Maćkowski	Single up-converting nanocrystals – ideal probes of interactions at the nanoscale S. Maćkowski
12:00 – 12:30	IL19	Marcin Nyk	Advanced colloidal nanomaterials with nonlinear optical and extended functionalities M. Nyk
12:30 – 12:45	O23	Arturas Katelnikovas	Ultrasound-Induced Synthesis of All-Inorganic Lead Perovskite QDs: Fast, Simple, and Highly Reproducible A. Katelnikovas, M. Steponavičiūtė, E. Ežerskytė, V. Klimkevičius
12:45 – 13:00	O24	Dawid Piątkowski	Single up-converting nanocrystals nanothermometry K. Wiwatowski, M. Szalkowski, Z. Korczak, R. Houssaini, A. Hartschuh, A. Bednarkiewicz, S. Maćkowski, D. Piątkowski
13:00 – 14:30		Lunch	

## Session: Theory and modeling

Session chair: Michał Piasecki

Time	Code	Presenting author	Title, authors
14:30 – 15:00	IL20	Jonas Joos	Charge transfers processes in phosphors: emission, quenching and trapping J. J. Joos
15:00 – 15:30	IL21	Anatoli Popov	Thermal annealing of radiation defects in optical and dielectric ceramics for fusion applications A. I. Popov, E. A. Kotomin, V.N. Kuzovkov, A. Lushchik
15:30 – 15:45	O25	Andrii Shyichuk	Electronic trap depths in Pr-doped lutetium oxide doped with Ti, Zr and Hf: ab initio multiconfigurational calculations A. Shyichuk, M. Krośnicki
15:45 – 16:00	O26	Mohamed Taibeche	First-principles calculation of electronic structure of luminescence in Li <sup>+</sup> co-doped Ce <sup>3+</sup> -doped Lu <sub>3</sub> Al <sub>5</sub> O <sub>12</sub> (LuAG) inorganic scintillator M. Taibeche, Z. Akhrib, A.Boukerika, L.Guerbous
16:00 – 16:30		Coffee break	

## Session: Transition metal and rare earth compounds

Session chair: Anatoli Popov

Time	Code	Presenting author	Title, authors
16:30 – 17:00	IL22	Michał Piasecki	Mid-infrared (MIR) fluorescent sources Overview and Structure–Property Relationship M. Piasecki, A. Racu, J. Szczepkowski, A. Wittlin, A. Suchocki, M. Stef, M. Dramicianin, M. G. Brik
17:00 – 17:30	L4	Szymon Chorąży	Multifunctional luminophores constructed from homo- and heteroleptic cyanido metal complexes S. Chorąży, J. J. Zakrzewski, M. Liberka, M. Zychowicz, M. Heczko, J. Rzepiela, J. Wang, K. Kumar, S. Ohkoshi
17:30 – 17:45	O27	Damian Włodarczyk	Spectral and X-ray comparison between novel double perovskites and their derivatives based on tungsten and chosen rare-earths ions. D. Włodarczyk, M. J. Chrunik, M. Amilusik, K. M. Kosyl, M. Strankowski, V. Tsiumra, T. Giela, M. Zając, A. Grochot, K. Jabłońska, A. Reszka, P. Iwanowski, H. Przybylińska, M. Boćkowski, A. Suchocki
17:45 – 18:00	O28	João Marcos Goncavales	Influence of Nd <sup>3+</sup> concentration on laser induced broadband white emission of La <sub>1-x</sub> AlO <sub>3</sub> :xNd <sup>3+</sup> perovskites J. M. Gonçalves, M. Stefanski, R. Tomala, W. Stręk
18:00 – 23:00		Conference Banquet	

**Friday, July 15, 2022**

**Session: Experimental methods for characterizing optical materials**

Session chair: Andrzej Wojtowicz

Time	Code	Presenting author	Title, authors
09:45 – 10:15	IL23	Marcin Szalkowski	Photon avalanching: properties and challenges M. Szalkowski, Z. Korczak, M. Dudek, M. Misiak, K. Prorok, A. Kotulska, A. Bednarkiewicz
10:15 – 10:30	O29	Łukasz Haryński	Experimental Method for the Tauc Exponent and Corresponding Transition Types Determination Ł. Haryński, A. Olejnik, K. Grochowska, K. Siuzdak
10:30 – 10:45	O30	Mateusz Rębarz	Broadband Femtosecond Ellipsometry at ELI Beamlines Facility M. Rebarz
10:45 – 11:00	O31	Jakub Zakrzewski	Dehydration-driven modulation of opto-magnetic properties in $\text{Ln}^{\text{III}}\text{Co}^{\text{III}}$ cyanido-bridged frameworks J. J. Zakrzewski, J. Wang, M. Zychowicz, Y. Xin, K. Nakabayashi, H. Tokoro, B. Sieklucka, S. Ohkoshi, S. Chorazy
11:00 – 11:30		Coffee break	

**Session: Novel fluorophores, optical materials, devices for biosensing, biomedical and environmental applications II**

Session chair: Andrzej Suchocki

Time	Code	Presenting author	Title, authors
11:30 – 12:00	IL24	Dagmara Kulesza	Non-Boltzmann luminescent thermometers D. Kulesza, J. Zeler, P. Bolek, J. Trojan-Piegza, E. Zych
12:00 – 12:30	IL25	Wiesław Stręk	Laser induced white emission phenomena W. Strek, R. Tomala, M. Stefanski, P. Wiewiorski, M. Oleszko, W. Mista
12:30 – 13:00		Closing ceremony	
13:00 – 14:30		Lunch	

## Poster session

CODE	PRESENTING AUTHOR	TITLE, AUTHORS
P01	Abinash Adhikari	Temperature-dependent bandgap study of Eu doped CdO thin film prepared by PA-MBE A. Adhikari, M. Szot, A. Lysak, E. Przeździecka
P02	Jakob Andreasson/ Shirly Esponzoza	Spectroscopic ellipsometry in the vacuum ultraviolet region S. Espinoza, K. Dorywalski, J. Andreasson
P03	Abdellah Bachiri	Gamma Spectroscopy of MgGa <sub>2</sub> O <sub>4</sub> and ZnGa <sub>2</sub> O <sub>4</sub> Semiconductor Scintillators A. Bachiri, M. Makowski, M.E. Witkowski, W. Drozdowski, Z. Galazka
P04	Justyna Barzowska	Improvement of luminescent and mechanoluminescent properties of SrSi <sub>2</sub> N <sub>2</sub> O <sub>2</sub> :Eu J. Barzowska, N. Majewska, M. Kamiński, S. S. Haider, D. Jankowski, M. Grzegorzczak, S. Mahlik, M. Sopicka-Lizer, P. Aleshkevych, Y. Zhydachevskyy, A. Suchocki
P05	Nikola Bednarska	Olivine-type undoped and rare earth doped germanate ceramics for visible and near-infrared luminescence N. Bednarska, M. Kuwik, W. A. Pisarski, J. Pisarska
P06	Paweł Bortnowski	UV and visible emission in thulium-doped ZBLAN glasses P. Bortnowski, A. Jusza, K. Anders, R. Piramidowicz
P07	Viktor Borysiuk	Interaction of cellulose molecules with carbon nanostructures: insights from DFT computational studies V. Borysiuk, T. Isokov, Yu. Hizhnyi, S.G. Nedilko, M. Shegeda, Ya. Zhydachevskyy
P08	Vitalii Chornii/ Serhii Nedilko	Computational studies of atomic and electronic structures of luminescent phosphate glasses and glass-ceramics V. Chornii, V. Boyko, V. Borysyuk, Yu. Hizhnyi, S.G. Nedilko, Ya. Zhydachevskyy
P09	Oksana Chukova/ Serhii Nedilko	Spectroscopy of the lithium-vanadate-borate luminescent glass and glass-ceramics O. Chukova, S.G. Nedilko, V. Scherbatskyi, R. Minikayev, W. Paszkowicz, V. Stasiv, Y. Zhydachevskyy, A. Suchocki
P10	Nikola Cichocka	Optical and structural properties of Eu <sup>3+</sup> /Ce <sup>3+</sup> doped Y-Al-O compounds grown by energy-saving microwave driven hydrothermal technique N. Cichocka, S. Kobayakov, J. Kaszewski, R. Minikayev, A. Reszka, A. Kaminska

P11	Martyna Czarnomska	Revealing trace amounts of xenobiotics in the friction ridge analysis by Raman spectroscopy M. Czarnomska, A. Lewkowicz, P. Bojarski, S. Steinborn, K. Woźniewski
P12	Guna Doke	Optical properties of red-emitting long afterglow phosphor $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x\text{O}_4$ : Mn material G. Doke, G. Krieke, A. Antuzevics, B. Berzina, A. Sarakovskis
P13	Magdalena Dudek	Size-dependent photon avalanching in $\text{Tm}^{3+}$ doped $\text{LiYF}_4$ nano, micro and bulk crystals M. Dudek, M. Szalkowski, M. Misiak, M. Ćwierzona, A. Skripka, Z. Korczak, D. Piątkowski, P. Woźniak, R. Lisiecki, P. Goldner, S. Maćkowski, E. M. Chan, P. J. Schuck, A. Bednarkiewicz
P14	Marek Eggen	The ab-initio study of the Dy(III)-EDTA single ion magnet in various environments: the influence of the structural changes on the spectroscopic and magnetic properties M. Eggen, M. Krośnicki, A. Kędzierski, R. Janicki, M. Korabik
P15	Ernests Einbergs	Mechanoluminescence based approach to mechanical stress visualisation of additively manufactured (3D printed) parts E. Einbergs, A. Zolotarjovs, D. Millers, I. Bite, V. Vītola, A. Spustaka, G. Tunēns, A. Arnautov
P16	Eglė Ežerskytė	Red-Emitting $\text{Ba}_2\text{Y}_5\text{B}_5\text{O}_{17}:\text{Eu}^{3+}$ Phosphors with Efficiencies Close to Unity for Near-UV LEDs E. Ežerskyte, J. Grigorjevaite, A. Katelnikovas
P17	Verena Fritz	Heating the discussion on losses in persistent phosphors: An attempt to quantify non-radiative losses from a set of TL-measurements V. Fritz, D. Van der Heggen, P. F. Smet
P18	Vitaliy Gorbenko	Growth and luminescent properties of undoped and rare-earth doped $\text{MgAl}_2\text{O}_4$ single crystalline films V. Gorbenko, T. Zorenko, S. Witkiewicz, S. Nizankovskiy, Yu. Zorenko
P19	Natalia Górecka	The influence of synthesis conditions on the reduction of $\text{Eu}^{3+}$ incorporated into $\text{CaMgSi}_{2-x}\text{Al}_x\text{O}_6$ matrix N. Górecka, K. Szczodrowski, T. Leśniewski, T. Mykytiuk
P20	Julija Grigorjevaite	Optical properties investigation of upconverting $\text{K}_2\text{Gd}(\text{PO}_4)(\text{WO}_4): 20\%\text{Yb}^{3+}, \text{Ho}^{3+}$ phosphors J. Grigorjevaite, A. Katelnikovas

P21	Yuriy Hizhnyi/ Yaroslav Zhydachevskyy	Electronic structure of Mn-related defects in $\text{YAlO}_3$ crystals Yu. Hizhnyi, Ya. Zhydachevskyy, V. Stasiv, H. Przybylińska, S.G. Nedilko, A. Kamińska, M. Berkowski, A. Suchocki
P22	Estera Hoffman	Photophysical properties and heavy atom effect donor-acceptor structures based on phenazines E. Hoffman, M. Mońka, D. Grzywacz, K. Kozakiewicz, I. Serdiuk, P. Bojarski
P23	Vladyslav Ievtukhov	Investigations of the Donor Effects in Organic Blue Thermally Activated Delayed Fluorescence Emitters V. Ievtukhov, I. Serdiuk, M. Monka, E. Hoffman, P. Bojarski
P24	Dawid Jankowski	Novel handheld system for friction-induced mechanoluminescence measurement D. Jankowski, M. Grzegorzczak, J. Barzowska, S. Mahlik, A. Suchocki
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## **INVITED LECTURES**

## **Influence of pressure on Mn<sup>2+</sup> and Fe<sup>3+</sup> ions photoluminescence in solids**

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

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

Analysis of these effects has to take into account several processes in addition to the crossing between the <sup>4</sup>T<sub>1</sub> and <sup>2</sup>T<sub>2</sub> levels, such as pressure-induced phase transitions of the examined compounds, or pressure induced increase of the electron-phonon coupling. Results of pressure-induced luminescence quenching for different compounds such as NaScSi<sub>2</sub>O<sub>6</sub>:Mn<sup>2+</sup> clinopyroxene [1] and Gd(Zn,Mg)B<sub>5</sub>O<sub>10</sub>:Mn<sup>2+</sup>pentaborate [2], LiGaO<sub>2</sub>:Fe<sup>3+</sup> and others [3] will be presented. Finally, certain consequences for the possibility of observing d<sup>5</sup> ions emission in the infrared region will be shown.

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## **Excitons bound at rare earth and transition metal ions. How to see the invisible?**

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Rare earth (RE) and transition metal (TM) ions can bound excitons. Two possibilities will be discussed resulting in either formation of charge transfer state of TM, RE ions or in exciton binding by these ions. The RE or TM bound excitons (in most of the cases) decay nonradiatively by an energy transfer, which results in intra-shell RE or TM excitation. This is why such excitons are rarely observed and we need indirect methods to confirm their formation.

In the lecture I will discuss mechanisms of exciton binding and why excitons binding may result in efficient RE (TM) emission. Then, I will introduce two experimental methods of Optically Detected Magnetic Resonance (ODMR) and Optically Detected Cyclotron Resonance (ODCR) we applied for investigation of recombination mechanisms in investigated samples. Indirect arguments for exciton binding will be given.

Theoretical model of RE (TM) bound excitons was proposed by late Prof. Marek Grinberg [1]. The model allows to explain why in some cases two excited states of RE or TM can coexist – so-called charge transfer and bound excitonic state.

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## High pressure spectroscopies on garnet phosphors: what we learned from collaborations with Marek

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It is always a pity to lose a friend by unexpected reasons, especially if he is a very charming gentleman and great scientist with whom one enjoyed fruitful collaborations and associations. For me it was probably at the early-stage PRE Workshops in 2005~2010 at Trento/Firenze that I met Marek for the first time. In 2010 European MRS Symposium at Strasbourg, he and I were attending as invited speakers in the luminescent material session. We came to talk about our common interest on electronic structures of phosphor materials. Not only I was invited to Gdansk IWASOM (maybe 4 times), Marek enjoyed to visit me in Kyoto many times. In spring 2012 when I organized the 4th PRE'12 Workshop at Kyoto, he was one of the invited speakers (kindly bringing me a bottle of Żubrówka as a souvenir). He visited Kyoto several times, and we always enjoyed discussion. We started the collaboration on the high-pressure spectroscopies of Ce<sup>3+</sup>-doped YAGG, for which our group have studied/reported temperature dependence of photocurrent excitation spectra, in which clear bands due to the Ce:5d1 and 5d2 are observed [1]. We have reported the bandgap structures, especially the bottom of the conduction band decreases with increasing Ga-content, x in YAG<sub>x</sub>G and YGG (=YA0G5G) was known to show no luminescence at ambient pressure. As a result of the collaboration, we published the first coauthored paper reporting the pressure and temperature dependence of lifetime of Ce<sup>3+</sup> in the garnets and Ce<sup>3+</sup> in YGG showing luminescence at high pressure and lifetime comparable to YAG3G[2]. Dr. T. Lesniewski (then a PhD student of Prof. Grinberg) stayed in our labs of Kyoto in 2016 winter and collaborated on the photoconductivity of Gd<sub>3</sub>Al<sub>5-x</sub>Ga<sub>x</sub>O<sub>12</sub>:Ce<sup>3+</sup> phosphors [3]. Our interest also extended to the persistent phosphor materials we developed, which are codoped with electron trapping elements[4]. Based on the research results, the trap depth should also change with pressure, which would thus be accompanied with the change in the persistence decay behaviors. We knew the Cr<sup>3+</sup> ion as the best trap center in the persistent YAG3G and the Yb<sup>3+</sup> ion as a much deeper trap. The two phosphors codoped with these trap center shows opposite tendency of persistence against pressure, the mechanism of which is very interesting [5]. I will talk onsite about their details and good memories with Marek.

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# Temperature and pressure sensing in Cr<sup>3+</sup> phosphors

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Since the discovery of ruby laser by Maiman in 1960 [1], Cr<sup>3+</sup>-doped phosphors have been attracting a lot of attention and a renewed interest has been recently triggered by their use as near-infrared (NIR) emitting persistent luminescent materials [2], broadband NIR pc-LEDs [3] and temperature sensors [4-8].

The use of Cr<sup>3+</sup> luminescence to probe the temperature has been demonstrated to be particularly promising in terms of sensitivity, reliability, and flexibility [4-8]. The energy gap between the <sup>2</sup>E and <sup>4</sup>T<sub>2</sub> excited states can be controlled by playing on the octahedral site of the host embedding Cr<sup>3+</sup> ions to design a class of thermometers based on the ratio between <sup>4</sup>T<sub>2</sub>→<sup>4</sup>A<sub>2</sub> and <sup>2</sup>E→<sup>4</sup>A<sub>2</sub> transitions working in specific temperature ranges. The different nature of the transitions involved is the key point to understand the promising thermometric performances. Moreover, the shift of the *R*-line of ruby is a common standard to probe the pressure during the pressure dependence experiments performed with the diamond anvil cells, making Cr<sup>3+</sup>-doped phosphors very appealing to combine temperature and pressure sensing. By considering the mullite-type Bi<sub>2</sub>M<sub>4</sub>O<sub>9</sub>:Cr<sup>3+</sup> (*M*=Ga, Al) systems as a case study, advantages and limits of Cr<sup>3+</sup>-based thermometers will be discussed together with their potentials as pressure sensors with respect to the standard ruby [9].

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## Mn<sup>5+</sup> phosphors revisited – can we use them for luminescence thermometry in the near-infrared?

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Temperature measurements using phosphor luminescence have gained significant attention in recent years [1]. This is because the method offers semi-invasive, fast, precise, and reliable two-dimensional thermal imaging of macroscopic and microscopic systems at temperatures ranging from cryogenic to approximately 1700 °C, on moving objects, or within living organisms, within fiber-optic probes, or in harsh environments [2]. When working in the realm of biological and medical application, it is the near-infrared (NIR) wavelength window where light has the greatest tissue penetrating depth; this is the range of wavelengths where both the excitation and detection of luminescent thermometers need to operate. However, the choice of suitable luminescent remote thermal reporters for the NIR is limited compared to one for the visible spectral range.

Herein, we discuss Mn<sup>5+</sup> activated phosphors as excellent luminescence thermometry and bioimaging probes efficiently emitting at wavelengths > 1100 nm in the second biological transparency window. Mn<sup>5+</sup> optical centers have the [Ar]3d<sup>2</sup> electron configuration and always encounter a strong crystal field when tetrahedrally coordinated in crystals. Their lower electronic states have the <sup>3</sup>A<sub>2</sub> < <sup>1</sup>E < <sup>1</sup>A<sub>1</sub> < <sup>3</sup>T<sub>2</sub> < <sup>3</sup>T<sub>1</sub> progression in energy. The ground state (<sup>3</sup>A<sub>2</sub>) is orbitally non-degenerate and the first excited state <sup>1</sup>E has almost no nuclear displacement with respect to the <sup>3</sup>A<sub>2</sub> state and can be split by the low-symmetry ligand field. The main emission comes from the spin-forbidden <sup>1</sup>E → <sup>3</sup>A<sub>2</sub> electronic transition of a genuine electric dipole origin and has a narrow spectral band (FWHM < 10 nm) that can be split into two bands with an energy difference of up to 300 cm<sup>-1</sup>. These emission bands are usually accompanied by vibronic sidebands and have decay times of a few tens to a few hundred microseconds. The thermometry with Mn<sup>5+</sup> phosphors can be realized from temperature-induced changes in <sup>1</sup>E emission spectral position, bandwidth, and decay, as well as from the self-referenced ratiometric intensity measurements between <sup>1</sup>E hot and cold emissions, between integral <sup>1</sup>E and vibronic emissions, and <sup>1</sup>E and <sup>3</sup>T<sub>2</sub> emissions.

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## Luminescence spectroscopy of $\text{Eu}^{3+}$ in the rhombohedral pyrochlore $\text{Ca}_2\text{La}_3\text{Sb}_3\text{O}_{14}$

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In a recent paper Piccinelli et al. [1] have reported on a detailed investigation of the local structure around the cations in the rhombohedral pyrochlores  $\text{M}_2\text{La}_3\text{Sb}_3\text{O}_{14}$  ( $\text{M}=\text{Mg}, \text{Ca}$ ), carried out using X-ray diffraction, room temperature luminescence spectroscopy and decay kinetics of the  $\text{Eu}^{3+}$  dopant ion, and density functional calculations. It was shown that while  $\text{Mg}_2\text{La}_3\text{Sb}_3\text{O}_{14}$  shows an ordered cationic configuration, in  $\text{Ca}_2\text{La}_3\text{Sb}_3\text{O}_{14}$  the  $\text{Ca}^{2+}$  and  $\text{La}^{3+}$  ions are randomly distributed between the cation sites because of their similar ionic radii. In the case of  $\text{Ca}_2\text{La}_3\text{Sb}_3\text{O}_{14}$ , the  $\text{Eu}^{3+}$  ions are expected to occupy centrosymmetric sites, but the presence of disorder in the outer coordination spheres breaks the local inversion symmetry in these sites [2]. This has a strong influence on the  $\text{Eu}^{3+}$  luminescence spectrum and on the radiative decay rate of the  $^5\text{D}_0$  emitting level. In the present work we have extended the previous study by measuring low temperature site selective spectra on  $\text{Ca}_2\text{La}_3\text{Sb}_3\text{O}_{14}$  doped with  $\text{Eu}^{3+}$ . The data clearly show the presence of several different non-centrosymmetric sites for the dopant ion, in general agreement with the structural model proposed in [1].

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## **CuLaO<sub>2</sub> reloaded**

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CuLaO<sub>2</sub> is a green phosphor excitable in the 300 – 450 nm spectral region (Fig. 1). It has first been synthesized in Bordeaux, France, in 1988 [1] and then almost forgotten, despite its attractiveness [2-8]. 34 years later, we re-activate the inspection of its optical properties with the aim to shed light on remaining grey areas.

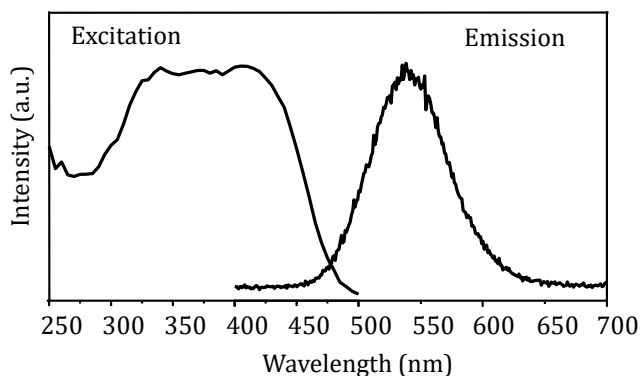


Fig. 1 – Luminescence spectra of CuLaO<sub>2</sub> at room temperature

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## New developments in the field of alkali lithosilicates

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The improvement of LED-based lighting systems has led to a race for new phosphor materials in the past years. In this context, narrow band emitters have become particularly important as they allow to achieve high color purity and maximum accessible color gamut.  $\text{Eu}^{2+}$  has received considerable attraction as an emitter in inorganic phosphors. This is related to its electric dipole-allowed  $4f^7 \leftrightarrow 4f^6 5d^1$  transition located in the visible range that allows an efficient excitation of the  $\text{Eu}^{2+}$  ions without significant droop at high incident flux. Prominent examples for ultra-narrow band emissions can be found in the  $\text{Eu}^{2+}$ -activated nitridolithoaluminate  $\text{Sr}[\text{LiAl}_3\text{N}_4]$  (SLA) at 650 nm close to the edge of the eye sensitivity curve with only 50 nm ( $1180 \text{ cm}^{-1}$ ) FWHM [1] and  $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]$  (SALON) with  $\lambda_{\text{max}} = 614$  nm and a FWHM of 48 nm ( $1286 \text{ cm}^{-1}$ ) [2]. Both compounds have similar structural motifs crystallizing in the so-called  $\text{UCr}_4\text{C}_4$  structure type. Interestingly, alkali lithosilicates have not been in the focus of phosphor research for a long time. A reason why they might have not been initially considered as a host material was presumably the fact that the structure built from monovalent cations was considered unsuitable for doping with strongly absorbing higher valent activator ions. Their structure partially also derives from the previously mentioned  $\text{UCr}_4\text{C}_4$  aristotype. It was not until 2018 that the first publications of  $\text{Eu}^{2+}$ -doped alkali lithosilicates appeared and opened a whole new research field on this substance class. Especially the groups led by Liu, Xia, and Huppertz, established the material class of luminescent alkali lithosilicates by constant extension of new representatives. Fundamental questions about the actual position of the  $\text{Eu}^{2+}$  ions in these hosts have remained speculative. Through a combination of high-resolution photoluminescence spectroscopy at low-temperatures ( $T = 10 \text{ K}$ ), structural refinement based on SCXRD, and ligand-field calculations it was possible to fully elucidate the non-trivial cation distribution in several alkali lithosilicates taking the compound  $\text{K}_{1.6}\text{Na}_{2.1}\text{Li}_{0.3}[\text{Li}_3\text{SiO}_4]_4\cdot\text{Eu}^{2+}$  (0.5 mol%) as an example [3], which is also presented in this overview.

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## **The kinetics peculiarities study of the afterglow and OSL in YAP:Mn**

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The phosphorescence glow decay kinetics in solids was studied in a significant number of materials under the different types of excitation. It gets especial interest in last decades with growing interest to phosphors with so called persistent luminescence (PersL) and their application in many fields. It was found even in the middle of the 19<sup>th</sup> century, that the afterglow decay kinetics of many of irradiated phosphors is well described by the empirical Becquerel decay function  $I(t) = I_0(1 + wt)^{-\alpha}$ , where parameter  $w$  and  $\alpha$  can be found from the approximation of experimental dependence. The integral glow intensity  $\int_0^\infty I(t)dt$  of the afterglow light corresponds to the net amount of stored energy (or dose of irradiation) in storage phosphor. But sometimes the power  $\alpha$  becomes less than one and the Becquerel decay function becomes non-integrable which means formally that the light sum of phosphorescence becomes infinite that, of course, has no physical meaning. It is exactly the case of YAP:Mn crystal being studied as storage phosphor for luminescence dosimetry which demonstrates the kinetics of the Becquerel type in phosphorescence glow and optically stimulated luminescence (OSL) [1]. Similar phosphorescence decay kinetics is observed in some other phosphors studied before [2]. Several approaches are known to explain the hyperbola-like kinetics with  $\alpha < 1$  [2-5], but till now there is no general understanding of this phenomenon. The present work is devoted to analysis of theoretical models of processes occurring during the phosphorescence and to searching of their consistency with observed kinetics described empirically by non-integrable Becquerel function.

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## Infra-red stimulated radioluminescence in $\beta$ -Ga<sub>2</sub>O<sub>3</sub>; a new semiconducting scintillator

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In this report we will present our results on pure, Fe-contaminated, and Mg-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals under the joint project aimed at maximizing scintillation performance of these materials. The  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> technology has been developed, single crystals have been grown and characterized at IKZ-Berlin while scintillation performance of these crystals has been evaluated in Toruń. Basic experiments, such as radio- and thermoluminescence and a new and promising two-beam experiment, in which a sample is excited by an X-ray beam and stimulated by an IR laser diode, have also been performed in Toruń.

Since the UV emission of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> due to recombination of self-trapped holes and free electrons dominate scintillation of this material it is of paramount importance that all the competing recombination paths of electron and hole pairs are reduced or eliminated in order to achieve the highest possible scintillation light yield.

Both Fe and Mg doping compensate n-type conductivity of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. Mg was used as an intentional doping, while Fe is a residual impurity from Ir crucibles used for the growth of bulk crystals by the Czochralski method. Unfortunately two-beam experiments on  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> containing Fe and Mg clearly demonstrate that both of these impurities are likely to introduce competitive processes, such as radiative and nonradiative recombination (via Fe) and/or charge trapping (by Fe and Mg).

Two-beam experiments unequivocally demonstrate that radiative and nonradiative recombination via Fe involving three different charge states of this ion (2+, 3+ and 4+) reduce the UV emission while charge trapping of electrons by Fe and holes by Mg is responsible for both scintillation light loss and reduction of the zero-time amplitude essential for the fast timing scintillation applications.

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## Intrinsic and defect-related luminescence of garnet and perovskite compounds

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The garnets  $A_3B_5O_{12}$  and perovskite  $ABO_3$  compounds are related to the well-known optical materials which are widely used as scintillators, LED convertors, laser media, etc.

From an ordinary point of view, the intrinsic luminescence of hosts and the luminescence of dopants in garnets and perovskites can be investigated, if any of the structural forms of these compounds (crystals, films, ceramics, micro- or nanopowders) are available. But this conclusion is not always correct.

Meanwhile, the substantial differences in the methods and conditions of material preparation from the melt (crystals), melt-solution (films) or solid-state reactions (powders, ceramics) result in the significant differences in their luminescent properties *even for the same oxide compounds*. Such differences are caused by the different types of intrinsic defects, their concentration and distributions over the main volume and surface of a sample as well as by interaction of the defects with impurity centers. For some garnets and perovskites, the contribution of defect centers to the intrinsic luminescence of host or the emission of dopants is so significant, that it can completely mask the native luminescent properties of matrix or impurities. The concentration of intrinsic defects can be strongly reduced in these complex oxides prepared by low-temperature methods using the liquid phase epitaxy growth from the melting fluxes (films) or solid state reactions (powders). At the same time, the oxide films can contain the components of flux which also may influence their optical properties. The luminescent properties of the nano- and micro-powder cores usually differ from the properties of their surface and boundaries of grains with substantially larger content of defects.

Thus, only the detailed comparison of the luminescent properties of complex oxides, prepared in the film, crystal and powder/ceramic forms, gives the possibility to extract the fundamental luminescent properties of the hosts from the background of defect luminescence as well as to detect the “true picture” of the dopant luminescence in these oxides. Using for this purpose the combination of conventional spectral methods and synchrotron radiation (SR) excitation with the energy in the range of fundamental absorption of these compounds opens a unique possibility for correct comparison of the luminescent properties of oxides in the different crystalline forms.

The aim of presentation is to show the characteristic examples of comparison of the structure of intrinsic luminescent centers in crystals and films of undoped  $(Y,Lu)AlO_3$  perovskites and  $(Y,Lu)_3Al_5O_{12}$ ,  $Gd_3(Al,Ga)_5O_{12}$  garnets using the absorption, cathodo-luminescence and time-resolved luminescent spectroscopy under excitation by SR in the exciton range and range of fundamental absorption of these hosts. Main attention is directed on the study of the fundamental optical properties of the mentioned perovskites and garnets such as intrinsic emission of hosts of these oxides caused by the luminescence of various kinds of excitons and the luminescence of the different types of defects (antisite defects (AD), charged oxygen vacancies and their aggregates) in these compounds.

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## Persepective on nanoscintillator

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Scintillators are materials that are able to emit photons when impinged with ionizing radiations. They are currently widely used in many detection systems addressing different fields, such as medical imaging, homeland security, high energy-physics (HEP) calorimetry, industrial control, and oil drilling exploration. Nowadays, the requirements in terms of performance are more and more demanding and scintillating materials developments become very specialized. While material composition impacts light production, the material form plays a key role in light collection. Apart from the performance in terms of stopping power needed in all applications, the light collection aspect plays a major role in imaging and detection systems. The best scintillator becomes useless if appropriate light collection cannot be achieved to reach required performances such as spatial resolution, granularity, or spectral resolution. Reducing materials dimensions down to nano-sizes affect both aspects. On one hand, the nanoparticle shape allows to prepare original geometries offering new oportunies of detection devices. On the other hand, in some cases, when nanoparticles experience quantum confinement, it changes in consequence the light production characteristics under both optical and ionizing radiation excitations. In addition, high energy excitation involves multi-scale along the energy relaxation process, and mean free paths become longer than the particle size rendering the mechanism description rather complex. In this presentation, 3 topics involving nanoscintillators will be developed in order to illustrate the specificity of the scintillating nanoparticles:

- 1- Porous scintillating architectures build up from scintillating nanoparticles assembled as aerogels to detect radioactive gas will be presented.
- 2- Lead Halide nanoperovskite as active centers for liquid scintillation: how to act on the energy transfer from the solvent to the NP
- 3- Nanoparticles of direct bandgap II-VI semiconductors (spherical quantum well and nanoplatelets) as ultra fast emitter for fast timing application. Disussion on the multi-exciton production under X-rays.

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## Double perovskites - sensors, phosphors

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We can say that the 21st century would be the Perovskite era. Such an observation results from the extraordinary plasticity of this structure, easily modifiable by the substitution of various cations, which makes it possible to use perovskites in photovoltaics, as phosphors or pressure or temperature sensors. The structure of perovskite, described by the formula  $ABO_3$ , could be represented as a cube with  $A$  ions at the corners, a much smaller  $B$  cation inside, and oxygen on the walls of the cube. Double perovskites are denoted by the formula  $A_2BB'O_6$ , in the same way as in single perovskites, the  $A$  cations are much larger than  $B$  and  $B'$ , but this time the latter are coordinated by six oxygen atoms, while the  $A$  site has different cation coordination numbers from 8 to 12, depending on the degree of distortion of the crystal structure.

We chose as the object of our research the little-studied double perovskites, where  $A = \text{Ba}$  exchanged against  $\text{Sr}$ ,  $\text{Ca}$  or  $\text{La}$ ,  $B = \text{Mg}$ ,  $\text{Zn}$ , while  $B' = \text{W}$ ,  $\text{Mo}$ ,  $\text{Ti}$  doped with selected  $\text{Ln}^{3+}$  ions ( $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Nd}^{3+}$ ) and transition metal elements such as  $\text{Cr}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{V}^{4+}$  and  $\text{V}^{5+}$ . The samples were prepared by the coprecipitation, mechanochemical and solid state methods.

The spectroscopic properties of these structures were studied in function of the method of synthesis and co-dopants used for the structure modification. According to the temperature (from 80 to 600 K) their utility as phosphors or temperature sensors have been determined.

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## Electrostatic doping modulation in monolayer MoS<sub>2</sub> through ferroelectric domain patterns

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The atomic thickness nature of one layer (1L) transition metal dichalcogenides (TMDs) offers a unique opportunity to modulate the optoelectronic properties of 2D materials by means of the surrounding environment. In this context, ferroelectric crystals acting as substrates for TMDs provide a means for electrostatic doping due to their remnant polarization [1].

In this work, we have studied the photoluminescence (PL) of 1L MoS<sub>2</sub> deposited on the polar surface of an antiparallel ferroelectric domain structure by means of confocal micro-PL. The possibility of lateral modulation of the relative PL intensity generated by excitons and trions recombination is demonstrated. The result is explained by the different electrostatic doping imposed by the alternate polarity of the ferroelectric domains, which modify the Fermi level of the 1L MoS<sub>2</sub>. Accordingly, periodical arrays of lateral p-n homojunctions located on the ferroelectric domain boundaries can be easily obtained. The results open new routes for the design of simple and cost-effective electronic and optoelectronic devices based on 1L MoS<sub>2</sub> a direct bandgap semiconductor.

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## Luminescent polymer composites doped with rare-earth elements

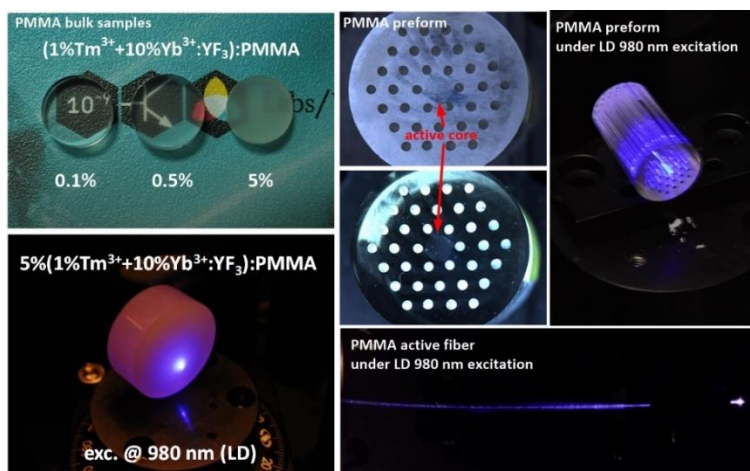
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Since the very beginning of the laser technique, a new active media offering attractive luminescent and laser features have been intensively investigated. As the result, an impressive number of optical materials serving as laser/amplifier hosts, phosphors, etc. have been developed and offered to the market, leaving however plenty of room for the next generations of active media. Polymer composite materials doped with rare-earth elements seem to be among the most interesting, benefiting from the extraordinary mechanical properties of polymer hosts and excellent luminescent features of rare-earth ions.



In this work, the results of our research on polymer composites doped with rare-earths (praseodymium, erbium, dysprosium, and thulium), introduced in a form of active nanocrystals or metal-organic complexes, are presented and discussed in the context of luminescent features, potential applications, and technological

challenges. The specific attention is focused on mastering the methods of manufacturing the composites, preserving the luminescent features of original nanopowders/complexes, and the potential of further processing into the form of optical fibers or waveguides.

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## AuAg nanoalloy plasmonic properties tuned by the assistance of machine learning method

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Nanostructures composed of two or more different metal elements are currently very popular. Their properties are related not only to their size and shape, what is characteristic of nanostructures, but also to their chemical composition. In the case of two-component nan alloys, noble metals, as Au and Ag, play a very important role. Nanoparticles of both of these metals, either separately or in the form of nanoalloys, can form the basis of plasmonic platforms. Their resonance band typically occurs at wavelengths around 420 and 530 nm for Ag and Au, respectively, and depends on the size of nanoparticles [1]. This wavelength range can be controlled not only by selecting the appropriate size and shape of nanostructures, but also, in the case of a bimetallic nanoalloy, by appropriately selected proportions between the components. We would like to present an experimental method of manufacturing of Au / Ag nan alloys, whose plasmon resonance position can be controlled by the machine learning method. Plasmonic platforms built of nan alloys designed in this way can be used to amplify the signal of a specific wavelength.

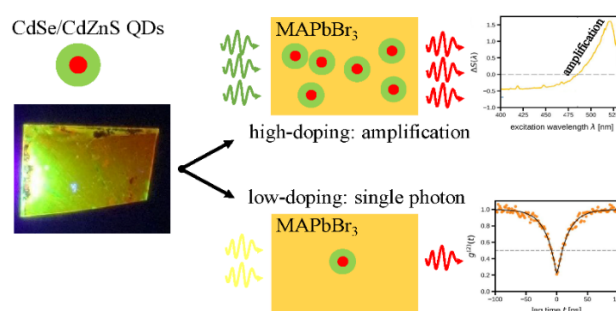
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# CdSe/CdZnS quantum dots in adjustable bandgap MAPbX<sub>3</sub> (X=Cl, Br and I) perovskite matrix

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We present a soft-chemistry method that permits to dope crystalline methylammonium lead chloride/bromide/iodide perovskite thin-films with high fluorescence quantum-yield CdSe/CdZnS core/shell quantum dots (QDs), while retaining their remarkable fluorescence properties [1,2]. The QDs are embedded in the 100-nm thin film after an inorganic ligand-exchange with halide ions, allowing direct contact between the QDs and the perovskite matrix. Ensemble photoluminescence measurements confirm emission of the QDs after incorporation into the MAPbBr<sub>3</sub>.

Photoluminescence excitation characterization of the thin films exhibit different type of wavelength-dependent couplings: from MAPbBr<sub>3</sub> to QDs, and vice-versa. Fluorescence lifetime imaging microscopy experiments on these systems tend to show that QDs act as seeds to increase locally the crystalline quality.

We demonstrate single photon emission from a single QD-in-perovskite hybrid via antibunching measurements and we show that their quantum yield has not been drastically reduced during the doping process.

We have further created bandgap-adjustable QD-in-perovskite hybrid over most of the spectrum covered by the MAPbX<sub>3</sub> compounds. Preliminary results show that QD PL is conserved during the procedure. At high CdSe/CdZnS QD doping level, this work opens the route to hybrid solar concentrator for visible-light harnessing, hybrid-based LEDs and scintillators, while low-doping content would lead to hybrid single-photon sources embedded in field-effect devices for single charge control to serve as an alternative to solid-state quantum dots.

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# Single up-converting nanocrystals – ideal probes of interactions at the nanoscale

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Up-converting nanocrystals, activated by rare-earth ions, turned out to be excellent probed for monitoring interactions at the nanoscale, including plasmonic effects associated with coupling with metallic nanoparticles, and energy transfer in assemblies where they may play a role of either donor or acceptor of energy. Their unprecedented photostability, high intensity of visible light luminescence upon infrared excitation, as well as ability to control the surface have been exploited in various hybrid nanostructures.

The presentation will focus on up to three experiments, where single up-converting nanocrystals are used as probes for quantifying the strength of plasmonic enhancement of luminescence and the efficiency of the energy transfer. In this regard, complex hybrid nanostructures were assembled, where both these effects are present and the interplay between them can be fully investigated on a single emitter level.

Plasmonic interactions are introduced by silver nanowires, elongated plasmonically-active structures, while the energy transfer is induced by incorporating either organic polymers or monolayer graphene. In the case of the first assembly, we observe strong increase of energy transfer efficiency for nanocrystals placed in the vicinity of a silver nanowire and at the same time embedded in a polymer layer. On the other hand, in the case of the structure, where graphene plays a role of the energy acceptor, single nanocrystal microscopy allows for extracting those individuals, where both effects are optimized: the increase of emission intensity due to plasmonic interactions is not diminished by the efficient energy transfer to graphene. Last but not least, the effect of energy dissipation into graphene will be elucidated in the context of surface plasmon polariton propagation along silver nanowires.

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## **Advanced colloidal nanomaterials with nonlinear optical and extended functionalities**

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Nonlinear optical (NLO) response of colloidal inorganic nanomaterials of various sizes, morphology and composition are investigated with the Z-scan and two-photon excited emission techniques using a tunable femtosecond laser system. A great number of studies concerning the nonlinear optical properties measured at a single wavelength were carried out in order to get an insight into features of nanomaterials relevant to their interactions with short pulse lasers. However, it is extremely important to characterize the NLO factors i.e. nonlinear refractive index and as well as nonlinear absorption coefficient in a wide wavelength range which will allow for finding maximal values of the parameters and optimizing them [1]. In this study we provide both: fundamental knowledge about materials engineering of a new class of inorganic nanomaterials i.e. optimization of synthesis and surface modification as well as fundamental knowledge how to correctly characterize those materials using a new approach of femtosecond laser techniques[1,2]. We present a comprehensive study of various group of colloidal nanomaterials i.e. semiconductor QDs [3], plasmonic NPs [4] and lanthanide doped NPs [5]. For example a strong influence of semiconducting QDs composition, size and morphology on their spectrally-resolved nonlinear optical properties was found. Finally, the features of this system can be utilized for multiphoton fluorescence microscopy and other photonic and bio-related applications [3-5].

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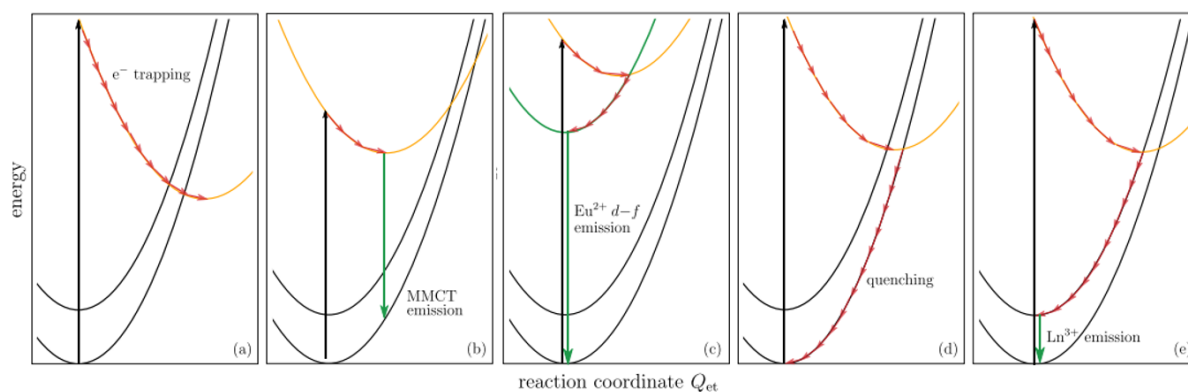
# Charge transfers processes in phosphors: emission, quenching and trapping

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Luminescent materials play a key role in many applications from solid state lighting to emergency signage. While many aspects of the luminescence are already well-understood, the subtle interplay between (co-)dopants sometimes gives rise to phenomena that are not easily explained. Notably electron transfer processes between lanthanide activators can play a crucial role for the functional behavior and performance of luminescent materials.

A multiconfigurational ab initio study revealed how direct metal-to-metal charge transfer (MMCT) between the  $\text{Eu}^{2+}$  luminescence activator and a  $\text{Ln}^{3+}$  co-dopant systematically dictates the luminescence and optical properties of fluoride and sulfide phosphors.[1,2] The luminescence mechanism predicted by the calculations was verified using advanced X-ray absorption and optical spectroscopic techniques thereby illustrating the usefulness of this combined theoretical and experimental approach.



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## **Thermal annealing of radiation defects in optical and dielectric ceramics for fusion applications**

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Radiation-resistant oxide insulators (MgO, BeO, Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub>, etc.) are important materials for use in fusion reactors. It is very important to predict / model not only the kinetics of diffusion-controlled accumulation of defects under neutron irradiation, but also the long-term evolution of the defect structure, including thermal annealing of defects after irradiation.

After introducing some basics on the radiation point defects in halides, binary oxides and oxide perovskites [1] as well as the mechanisms of point defect and metal colloid formation in additive/thermochemically reduced samples or under fast energetic particle irradiation (neutron, ion, proton, electron), *we will review the current understanding of their thermal annealing.*

We will shortly describe recently developed and successfully applied [2-4] theoretical approach based on the formalism of the correlation functions, describing spatial distribution of both similar (F-F centers) and dissimilar defects (Frenkel pair of defects: F center – an interstitial O<sub>i</sub> ion) which allows us to study defect kinetics and aggregation much better than generally accepted rate equations or simple first order kinetics. Thus, the kinetics of the F-type center thermal annealing after electron, heavy ions or neutron irradiation was treated as the bimolecular process with equal concentrations of the complementary F and O<sub>i</sub> defects. It is controlled by the interstitial oxygen ion mobility, which is much higher than that of the F centers. It is demonstrated how the shape of the F-annealing curves is determined by the two control parameters: migration energy E<sub>a</sub> and effective pre-exponential factor, and strongly depends on irradiation fluence and other conditions.

The appropriate migration energies were obtained from available in literature annealing kinetics for electron, neutron and ion irradiated MgO, Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub>, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, BeO, ZnO, YSZ, PLZT etc. The results obtained are used for evaluation of the interstitial oxygen migration parameters and compared with available ab initio calculations. Comparison with another type of experiments, such as F-type center annealing in TCR samples, will be also given for MgO, Al<sub>2</sub>O<sub>3</sub>, ZnO, BeO and YSZ. This allows us to find the activation energies for the F center migration.

Special attention is paid to:

- (1) dose effects on F center annealing in neutron and fast electron irradiated MgO and MgF<sub>2</sub>; (2) a detailed comparison of diffusion-controlled F center thermal annealing in neutron, electron and heavy-ion irradiated MgO, MgF<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub>, BeO, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>.
- (3) thermal transformation and modification of F and F<sub>2</sub> centers during their thermal annealing.

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## Mid-infrared (MIR) fluorescent sources. Overview and structure–property relationship

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The Mid-infrared (MIR) spectral range shown great important for both fundamental and possible applications such as optical communications, pollutants detection, trace chemical analysis as well as the promising imaging devices for remote sensing and medical contrast agents. Most small organic and inorganic molecules have their fundamental absorption features in the wavelength regions from 1.5  $\mu\text{m}$  to 5  $\mu\text{m}$ . Therefore, strong emitting sources in MIR spectral range will be extremely useful in the construction of lidar allowing remote detection of gases (including hazardous gases), which is important for health and environmental protection, chemical rescue, the mining industry or military applications. The wide spectral transparency for chalcogenide or halide crystals [1], glasses [2] or ceramics [3] (from about 300-700 nm to several dozen micrometres) is unique and do not available for oxygen containing materials. In addition, these materials with low energy of the phonon system are predestined at the matrices for embedding active elements (RE or 3d elements) for long-wave luminescence or construction lasers operating in the mid-infrared range. On the other hand, the embedding of rare earth ions in chalcogenide/halide structures is not an easy experimental undertaking. Thereat halide-based matrices [4] can be an alternative to e.g., troublesome and unwieldy in operating (mobile applications) CO<sub>2</sub> lasers operating through non-linear optical effects SHG, THG in MIR range. It is expected that the result of the analysis of the available experimental data give opportunity to establish “structure-property” and “property-property” relations for the system matrices- (luminescence center) and should have great significance for searching new, efficient sources emitting in MIR spectral range.

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## **Photon avalanching : properties and challenges**

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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<sup>3+</sup> doped LaCl<sub>3</sub> [1]. There are several essential requirements necessary to satisfy to observe PA in a given system, such as (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 (2-3 typically) orders of magnitude when exciting with power density slightly exceeding the PA threshold. Until recently, PA was observed mostly in lanthanide doped bulk materials and fibers, often in cryogenic temperatures aiming to get new laser lines or detect medium IR photons. Only recently PA emission was also demonstrated for NaYF<sub>4</sub> nanoparticles doped with Tm<sup>3+</sup> at the room temperature under 1064 and 1450 nm photoexcitation and 800 nm emission [3].

The wide application potential of PA (e.g. super-resolution imaging [3], biosensing [4], nanothermometry [5] etc.) makes it extremely interesting to further study the PA in various lanthanides and various matrices of various sizes. In this lecture, we will summarize the current state-of-the-art on PA emission, we will discuss the PA emission in nano, micro and bulk LiYF<sub>4</sub> crystals and the peculiarities of photon avalanche emission in wider context as the paradigms shift in luminescent materials design.

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## Non-Boltzmann luminescent thermometers

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Pr-activated garnets are specific phosphors in which the  $\text{Pr}^{3+}$  ion can be efficiently excited optically by its  $4f \rightarrow 5d$  allowed absorption transition using UV-C radiation and can produce three types of emissions, afterward. Thus, the  $5d \rightarrow 4f$  broadband luminescence in the UV-blue part of the spectrum as well as narrow lines resulting from the  $^3\text{P}_0 \rightarrow ^3\text{H}_j$  and  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transitions in the bluish-green and red part of the spectrum are generated, respectively. The three emissions have much different properties and, consequently, their temperature dependence is diverse. Therefore we considered the  $\text{Pr}^{3+}$  luminescence very attractive for luminescence thermometry. Since garnets are mostly thermodynamically stable oxides they can withstand drastic changes of temperature from helium to above  $1500^\circ\text{C}$  even. This makes them easy to operate also in quite harsh conditions.

We shall review in detail the possibilities to control complex electronic processes in Pr-activated garnets important for luminescence thermometry. The host lattice-activator interaction will be discussed and conclusions concerning the possibility to design and tune luminescent thermometers for a broad range of temperature sensing will be considered, see Fig. 1. We show that Pr-doped garnets may be attractive luminescence thermometers for measurements at low, intermediate, and high temperatures, which is nowadays a real challenge in this field.

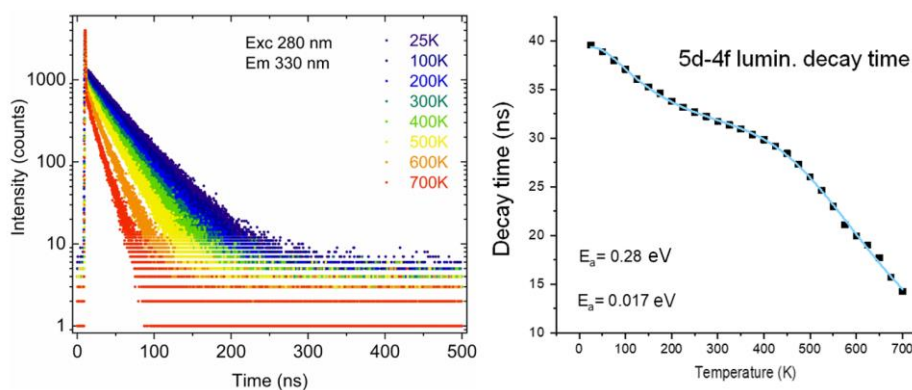


Figure. 1. Temperature dependence of the  $5d \rightarrow 4f$  luminescence of  $\text{Pr}^{3+}$  in  $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Pr}$  and the relative sensitivity derived from the data.

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## **Laser induced white emission phenomena**

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The broadband laser induced white emission (LIWE) is observed upon irradiation of different inorganic materials (nano-and microcrystalline powders, ceramics and crystals) with a focused laser beam. The phenomenon is characterized by the excitation threshold, exponential power dependence. It was found that it is surface related coherent point emission assisted by ejection of hot electrons. The emission process may occur not only in gas atmosphere but also in solvents. The hysteresis of power dependence of emission was observed. The mechanism of LIWE is discussed in terms of multiphoton ionization. A possibilities of application in light emitting sources and photocatalysis are presented.

# **LECTURES**

## 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 in the 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 phosphor 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.

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# Acoustic phonons propagation in thin film and bulk materials explored by pump-probe ellipsometry

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In order to understand the energy transfer processes happening in a material, it is necessary to monitor its optical properties in femtosecond and picosecond time-scale by methods such as pump-probe spectroscopy. Between the many transient effects that follow the photo-excitation, the laser-induced acoustic phonons travel through the material and change the observed optical properties.

Here, we present the application of the femtosecond pump-probe ellipsometry technique [1-6] to follow the propagation of photo-induced acoustic waves in two different systems: bulk Ge [6] and thin films of LaCoO<sub>3</sub> [5].

While working with other ultrafast spectroscopic techniques on LaCoO<sub>3</sub> thin films, it is difficult to differentiate between transient features present on the spectra due to the acoustic phonons and features due to the insulator to metal transition. Additionally pump-probe ellipsometry on metallic La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> thin films of different thickness allow us to discern between these two different phenomena [5].

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## **Luminescent oxide fillers in various types of nanocomposites**

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It is believed that a system is a composite material only if two or more of its different components interact synergistically creating a new material with new properties. Certain intermediate regions (interphase) are formed in the composite between the "pure" initial phases of the components and the composition and structure of those region does not correspond to the composition and structure of the initial phases. The contribution of the interphase to the properties of the material and the interaction between the matrix and the initial phases, may be clarified by the difference in characteristics of simple "filled matrix" and "composite based on that matrix".

The role of interfaces and interphases in determining the macrocharacteristics of hybrid oxide nanocomposite materials is discussed in the contribution. Suitable literature data and the results of our own experimental and computer simulation studies were used for this discussion.

The main direction of interphase behaviour in composite material study is a determination of the relationships between the properties of the material, on the one hand, and the atomic and energy structure, composition of the object, the size of its components - on the other hand. Although the mechanisms of interaction between any possible components of the composite, in principle, are predictable, nevertheless, their role and contribution in the case of a particular type, especially - nanoscale composite material (nanocomposite) containing oxides fillers needs to be clarified.

These issues are discussed here on the base of results obtained for nanocomposites of three types where nanocrystalline dielectric oxides fillers were embedded into: 1) the glass oxide dielectric matrices; 2) the polymer matrices, particularly, microcrystalline cellulose and nanocellulose; 3) carbon nanoforms (nanotubes, graphene and graphene oxide. Optical, electron and atomic force scanning microscopy methods as well as XRD, diffuse optical reflectance and photoluminescence methods were used for study mechanisms of phase interactions and interfaces in noted nanostructured composites and the impact of these mechanisms on optical and luminescent macro-characteristics of materials under study. This work is aimed not only to clarify and explain the role of interphases/interfaces, but also to identify the ways to develop materials with properties that can be used as basic for studied composites practical application.

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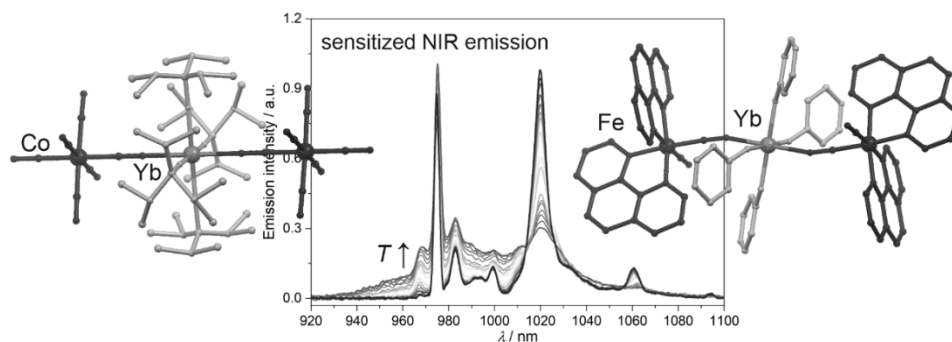
# Multifunctional luminophores constructed from homo- and heteroleptic cyanido metal complexes

Szymon Chorąży, Jakub J. Zakrzewski, Michał Liberka, Mikołaj Zychowicz, Michał Heczko, Jan Rzepiela, Junhao Wang, Kunal Kumar, Shin-Ichi Ohkoshi

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Plenty of important luminescent functionalities, such as strong sensitized photo-luminescence highly sensitive to physical or chemical stimuli for sensing applications or efficient electroluminescence for the construction of LEDs, can be designed and induced using transition and lanthanide metal complexes embedded in coordination polymers or molecules. We have recently shown that diverse luminescent effects can be incorporated in crystalline solids built of cyanido metal complexes of transition metals that are used as metalloligands for emissive lanthanide(3+) ions. This strategy leads to luminophores combining optical properties, such as a luminescent thermometric effect, with other physical functionalities, including molecular magnetism, proton conductivity, porosity, switchable electric properties, and sensitivity to external stimuli. We will show recent examples of such multifunctional luminophores based on homoleptic  $[M^{III}(CN)_6]^{3-}$  ( $M = Co, Rh, Ir$ ) and heteroleptic  $[M^{II}(CN)_2(L_{NN/NC})_x]^{n-}$  ( $M = Fe, Pt$ ) complexes.<sup>[1-6]</sup>



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## **ORAL PRESENTATIONS**

# Luminescence of $\text{Dy}^{3+}$ in $\text{A}_2\text{MgWO}_6$ (A = Ca, Sr, Ba) double perovskites

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The interest in double perovskite materials has significantly increased in recent decades due to their diverse structural and physical properties as well as wide applications because of flexible structural modification [1-2].  $\text{A}_2\text{MgWO}_6$  (where A = Ca, Sr, Ba) double perovskites doped with 2% $\text{Dy}^{3+}$  were synthesized by the co-precipitation method [3]. The crystal structure and luminescent properties of these prepared phosphors were investigated. With an increase of A ionic radius from Ca, Sr to Ba, the crystal structure of  $\text{A}_2\text{MgWO}_6$  changes from monoclinic to tetragonal and then to cubic, respectively (see Fig. 1). Furthermore, the color of the emission excited at 266 nm changes from bright yellow (with the dominance of  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ ) to blue (mainly  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ ) due to the change in site symmetry of  $\text{Dy}^{3+}$  in the structure, from  $C_1$ ,  $C_{4h}$  to  $O_h$ , respectively. The thermal stability of these phosphors was also examined from 80 to 593 K. This study shows how the A cation radius influences the luminescent properties of the studied phosphors.

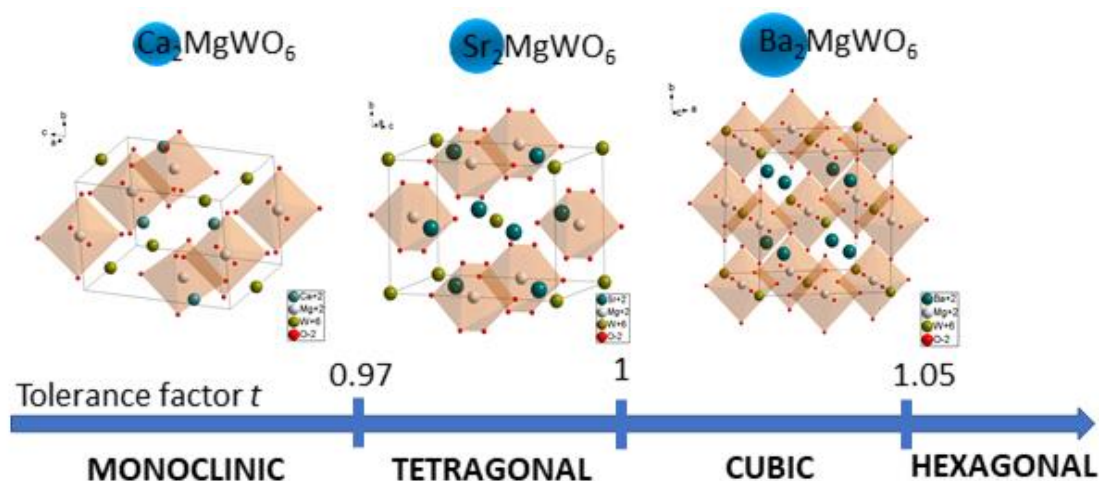


Fig. 1. Crystal structure of  $\text{A}_2\text{MgWO}_6$  (A = Ca, Sr, Ba) double perovskites

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## Mn<sup>4+</sup> photoluminescence in Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> alloys

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Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> alloys (solid solutions) represent interesting host material as their crystal structure and physical properties can be changed by modifying the composition in a wide range. To the best of our knowledge, up to now, there are no reports on Mn<sup>4+</sup> emission in any of the Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> compounds except pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. So, it is unknown how the emission of Mn<sup>4+</sup> will behave when the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystal lattice will be modified by the addition of Ga. Here one can expect the influence of at least three factors. First is the weakening of the crystal field strength experienced by Mn<sup>4+</sup> ions in the Ga-modified corundum structure. The second is decreasing a band gap of the host lattice with increasing Ga content. Finally, the corundum structure of the host will switch to the monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-type structure at about 15% of Ga. To get insight into these issues, photoluminescence properties of Mn<sup>4+</sup> ions in the Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> solid solutions have been studied in the temperature range from 4 to 500 K. For this purpose, a series of samples with nominal composition (Al<sub>1-x</sub>Ga<sub>x</sub>)<sub>2</sub>O<sub>3</sub>: Mn(0.05at.%), Mg(0.05at.%) with  $x = 0; 0.05; 0.10; 0.15; 0.2; 0.25; 0.5; 0.75$  and  $1.0$ , were obtained by the sol-gel citrate method and afterward calcined at temperatures up to 1500°C. The phase composition and crystal structure of the studied materials and their evolution with calcination temperature from 900 to 1500°C have been analyzed in detail using corresponding powder XRD data.

Three different types of Mn<sup>4+</sup> centers have been revealed in the studied compounds calcined at 1500°C depending on their chemical composition. The first one, Mn( $\alpha$ ), ( $\lambda_{\text{ZPL}}=676.2$  nm), coinciding with the known Mn<sup>4+</sup> emission in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, is observed in the corundum phase hosts ( $x = 0...0.15$ ). Another one, marked by us as Mn<sub>I</sub>( $\beta$ ), ( $\lambda_{\text{ZPL}}=652.1...659.9$  nm) is observed in the monoclinic-type hosts with  $x = 0.2...0.75$ , while the third one, Mn<sub>II</sub>( $\beta$ ), ( $\lambda_{\text{ZPL}} = 709.7$  nm) was revealed only in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> ( $x = 1.0$ ) of the same type of the monoclinic structure. The temperature behavior of the Mn<sup>4+</sup> emission and their evolution with the Al/Ga ratio has been studied systematically for each of the types of Mn centers. Obtained results confirm wide opportunities for the chemical tuning of Mn<sup>4+</sup> emission in Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> alloys, and indicate the prospects for use of the studied phosphors for low-temperature luminescence thermometry.

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# Development of three-layered composite color converters for white LEDs based on the epitaxial structures of YAG:Ce, TbAG:Ce and LuAG:Ce garnets

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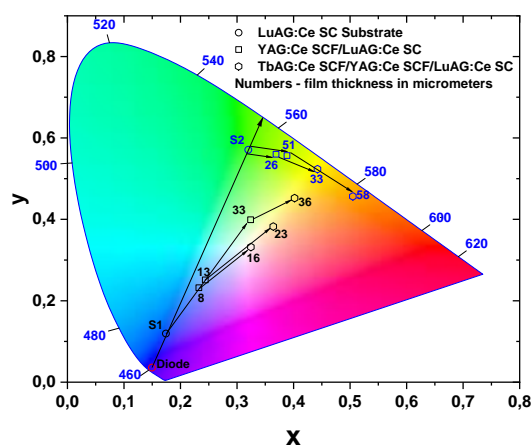
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Development of the Planar-Chip-Level Conversion (PCLC) approach for WLEDs, where the phosphor is free-standing and separated from the LED chip, [1] requires the investigation of novel durable phosphors which can be excited with high power blue/UV LEDs or lasers. For this purpose, it is urgently needed to design and investigate the new high structural quality and high-temperature stable converters in form of single crystals (SCs) and single crystalline films (SCFs) [2].  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  (LuAG:Ce) garnet is considered as an excellent temperature stable phosphor for greenish-white lighting emission diodes. Furthermore, the quenching temperature for  $\text{Ce}^{3+}$  emission in the LuAG host is the highest for all Al-based garnets with the onset of the quenching above 700 K [3].

This work is dedicated to the development of novel types of composite phosphor converter (CCC) based on the LPE grown epitaxial structures containing  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  (YAG:Ce) and  $\text{Tb}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  (TbAG:Ce) SCFs, steeply grown using liquid phase epitaxy (LPE) method onto LuAG:Ce SC substrate. The influence of  $\text{Ce}^{3+}$  concentration in LuAG:Ce substrate as well as the thickness of subsequent YAG:Ce and TbAG:Ce films on the luminescence and photoconversion properties of three-layered CCCs were investigated. The CCCs exhibit the broader emission due to the compensation of cyan-green dip by the additional LuAG:Ce substrate emission along with yellow-orange emission from YAG:Ce and TbAG:Ce SCFs allowing to obtain a wide spectrum of WLEDs. In turn, the variation in the thickness of activator concentration in each element of the composite converter allows obtaining almost any shade from green to orange emission on the chromaticity diagram.



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## Tuning optical properties of $\text{Y}_2\text{O}_3:\text{Pr}^{3+}$ nanocrystals through different synthesis methods

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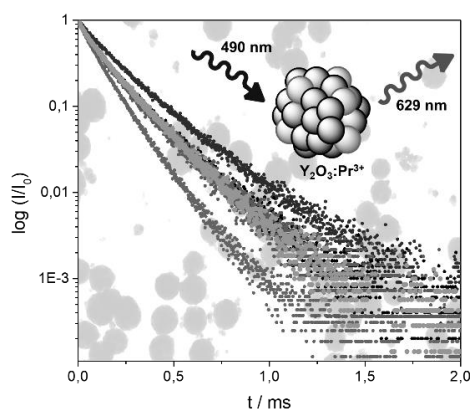
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Here we present an in-depth comparative study of optically active nanocrystals (NCs) based on  $\text{Pr}^{3+}$ -doped  $\text{Y}_2\text{O}_3$ . These NCs are promising materials in the field of photonics as an alternative to current lasers since this approach provides simpler and cheaper routes for the fabrication of fibre lasers by mixing luminescent NCs and glass nanoparticles. Specifically,  $\text{Pr}^{3+}$  exhibits long emission decay rates and efficient luminescence in the second biological window and it can also be used as an amplifier in the second telecom window due to its  $1.3\ \mu\text{m}$  emission. In addition, yttrium oxide ( $\text{Y}_2\text{O}_3$ ) has proven to be a very suitable host matrix due to its high thermal and chemical stability as well as appropriate optical and mechanical properties.

In this work, several synthesis methods have been tested and compared to study their influence on the physical and optical properties of the NCs. Our study highlights that size, dispersion and morphology are critically affected by the preparation method and the modification of the involved parameters. Besides, emission intensities and decay rates are also highly dependent on the synthesis procedure and conditions. Among all the tested procedures, solvothermal and homogeneous precipitation proved to be the most suitable ones in terms of structural and optical characteristics, since they produce NCs with adequate sizes to survive to certain thermal treatments and to avoid light scattering processes, and the most intense luminescence together with the longest emission lifetimes.



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# Atom redistribution and defect formation in GAGG:Ce single crystals imposed by Mg<sup>2+</sup> and Li<sup>+</sup> codoping: the impact on the luminescence and scintillation properties

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Intensive research on single crystal Gd<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>:Ce (GAGG:Ce) started in 2011 after its successful growth using the micro-pulling down method [1]. One year later, the bulk GAGG:Ce single crystal was successfully grown by the Czochralski technique [2]. Later optimization of the crystal growth process significantly improved the scintillation parameters. Recently, the GAGG:Ce crystal shows an extremely high light yield of 56,000 ph/MeV with a scintillation decay time of around 90–120 ns [3], which is approximately 2 times longer than Ce<sup>3+</sup> in simple garnets [1]. Therefore, further optimization of the scintillation response is in high demand. Aliovalent codoping, for example, Mg<sup>2+</sup> and Li<sup>+</sup>, significantly accelerated the scintillation decay time and reduced the afterglow, however, at the same time reduced the light yield [4]. Aliovalent codoping, due to charge compensation, imposes formation of stable Ce<sup>4+</sup> ions. The Ce<sup>4+</sup> as efficient electron trap competes with particular defects for capturing electrons from the conduction band and thus improving scintillation parameters. Additionally, the charge compensation mechanism is responsible for the formation of particular types of defects and clusters of defects which deteriorate the efficiency. This research deals with the melt growth of GAGG:Ce crystals codoped with Mg<sup>2+</sup> and Li<sup>+</sup> ions. The target garnet phase was checked by powder X-ray powder diffraction. The effect of Mg<sup>2+</sup> and Li<sup>+</sup> codoping on atom redistribution and defects formation was studied using SEM-EDS, thermoluminescence, and synchrotron radiation methods at 10 and 300 K. The optical, photoluminescence, and scintillation properties were compared.

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## Semiconductor scintillator development: $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, MgGa<sub>2</sub>O<sub>4</sub> and ZnGa<sub>2</sub>O<sub>4</sub>

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Although less extensively investigated and appreciated in the scintillator market compared to dominant inorganic insulators, semiconductor scintillators seem to arouse an increasing interest due to various potential applications unattainable for insulators. Recently, a lot of attention has been focused on  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals [1], indicating the factors that determine their scintillation performance and leading to a better understanding of its scintillation mechanism. In particular, the room temperature scintillation light yield of about 9000 ph/MeV has been observed for lightly semiconducting samples of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. In contrast, highly semiconducting samples of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>:Si have shown 2-3 times lower yields, but much faster scintillation decays (mean decay times below 100 ns) [1].

In this Communication we show our latest results achieved for Czochralski-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals. Moreover, we extend our research area onto two Ga-based spinels, i.e. ZnGa<sub>2</sub>O<sub>4</sub> and MgGa<sub>2</sub>O<sub>4</sub> grown at Leibniz-Institut für Kristallzüchtung by the Vertical Gradient Freeze and Czochralski method, respectively [2-4], reporting for the first time their basic scintillation properties, including light yields close to 3000 ph/MeV. For all three materials, we discuss the key factors for their scintillation performance and weigh up the perspectives for further improvement.

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## **An analysis of radiative recombination and trapping of charge carriers in irradiated feldspar samples**

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Most of the Earth's crust is made of feldspar minerals. These natural crystals exhibit good luminescent properties after exposure to ionizing radiation. The emission is usually observed in thermoluminescence (TL) and optically stimulated luminescence (OSL) phenomena. Surprisingly, the infrared stimulated luminescence (IRSL) is very effective. Both TL and IRSL are used for dating samples in geology.

It is well known that feldspars are very complex materials containing many different defects that may be irregularly distributed in the bulk. This picture is well confirmed by recent spectrally resolved thermoluminescence (SR-TL) measurements. Therefore, this is a challenge for mathematical models describing TL glow curves and OSL/IRSL decay. Indeed, the IRSL decay curves have an unusually long initial rise time followed by a non-exponential decay.

Experimental data were analyzed in terms of discrete as well as continuous distribution energy models. It seems, that additional features related to non-homogeneous spatial distribution of traps and recombination centers have to be included in the model, as they are necessary to understand the character of long-lived luminescence in the studied feldspars.

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# Luminescence properties of $\text{Lu}_2\text{SiO}_5\text{:Ce,Yb}$ crystals under synchrotron radiation excitation

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$\text{Lu}_2\text{SiO}_5$  (LSO) crystals doped with cerium (LSO:Ce) were developed as scintillators for application in PET scanners [1]. In addition to a number of positive properties, such as a large atomic number and a high light yield (LY) these crystals (without  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  co-doping) also have such an undesirable property as significant level of afterglow associated with large concentration of traps in the crystal lattice caused by the oxygen vacancies [2].

One of the ways to reduce the afterglow in scintillators is the method of co-activation of  $\text{Ce}^{3+}$  with other codopant ions. Our earlier studies have shown that codoping of LSO:Ce crystals with Yb ions can significantly reduce the level of afterglow [3]. However, along with a decrease in the afterglow, co-activation with Yb leads to quenching of the  $\text{Ce}^{3+}$  luminescence resulting in a decrease in the light yield (LY) of LSO:Ce,Yb crystals.

To investigate the possible causes of such quenching, the time-resolved luminescence measurements were performed on LSO:Ce,Yb crystals with different  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  contents at Superlumi station (DESY, Germany) under excitation by pulsed synchrotron radiation in the 3.7-25 eV energy range. It is shown that the  $\text{Ce}^{3+}$  related bands are present in the excitation spectrum of  $\text{Yb}^{3+}$  luminescence (Fig.1). In addition, the decay time of  $\text{Ce}^{3+}$  emission strongly decreases with increasing Yb content. These facts indicate an energy transfer between the  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  ions. Other mechanism of LY decreasing in LSO:Ce,Yb crystals is connected with  $\text{Ce}^{4+}\text{-Yb}^{2+}$  pair center. The possible dominant mechanisms of the energy transfer and  $\text{Ce}^{3+}$  luminescence quenching in LSO:Ce,Yb crystals were discussed.

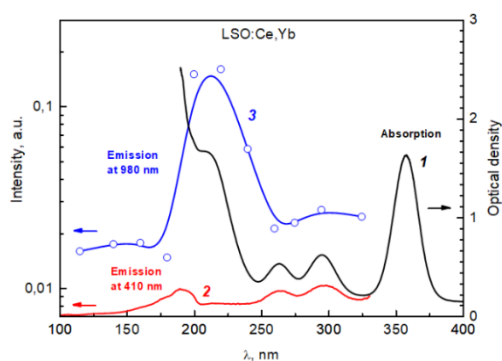


Fig. 1. Absorption spectrum (1), excitation spectrum of  $\text{Ce}^{3+}$  luminescence (2), excitation spectrum of  $\text{Yb}^{3+}$  luminescence (3) of LSO:Ce,Yb crystals.

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# Two and three-layered composite scintillators based on the GAGG and TbAG garnets for simultaneous registration of different types of ionizing radiation

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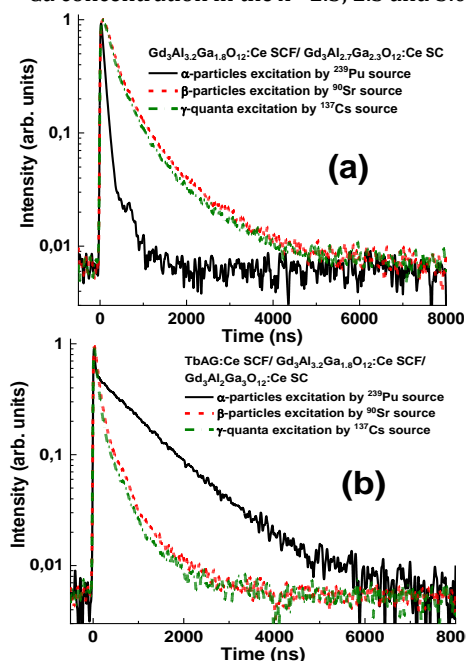
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The liquid phase epitaxy growth method enables development of luminescent materials in the single crystalline film (SCF) forms based on the different oxide compounds [1]. Nowadays, the LPE technology is also used for creation of the advanced composite luminescent materials based on the SCFs and single crystal (SC) substrates with the same (homoepitaxy) or close crystalline structure (quasi-homoepitaxy) [2, 3].

This work presents our last results in the development of composite scintillators based on the SCFs and SC of garnet compounds for radiation monitoring of different components of mixed ionization fluxes. Such composite scintillators presents the two and three layered epitaxial structures consisting two SCFs of Ce<sup>3+</sup> doped garnets, namely Gd<sub>3</sub>Al<sub>5-x</sub>Ga<sub>x</sub>O<sub>12</sub>:Ce (GAGG:Ce) garnet with Ga content x=0.18–2.25 as first film layer and Tb<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce (TbAG:Ce) garnet as second film layer. As a substrates, the Gd<sub>3</sub>Al<sub>5-x</sub>Ga<sub>x</sub>O<sub>12</sub>:Ce (GAGG:Ce) single crystals with variable Ga concentration in the x= 2.3, 2.5 and 3.0 range were used.



The samples of GAGG:Ce SCF/GAGG:Ce SC and TbAG:Ce SCF/GAGG:Ce SCF/GAGG:Ce SC composite scintillators with different GAGG:Ce SCF and TbAG:Ce SCF thickness in the ranges 15–29 μm and 15–108 μm, respectively, and GAGG:Ce SC substrates with Ga content of 2.3, 2.5 and 3.0 and thickness of 1 mm were crystalized by the LPE method using PbO-B<sub>2</sub>O<sub>3</sub> flux. The combinations of mentioned garnet compounds for SCF and SC scintillators were chosen in order to provide better separation of the scintillation decay curves under registration of different components of the mixed ionization fluxes, including particles and quanta. Namely, the scintillation properties of the respective epitaxial structures (pulse height spectra, light yield and scintillation decay kinetics) were investigated under excitation by α- (<sup>239</sup>Pu) and β- (<sup>90</sup>Sr+<sup>90</sup>Y) particles and γ-quanta (<sup>137</sup>Cs). The main results of this study are presented in Fig.1. The best results are achieved for Gd<sub>3</sub>Al<sub>3.2</sub>Ga<sub>1.8</sub>O<sub>12</sub>:Ce SCF/Gd<sub>3</sub>Al<sub>2.7</sub>Ga<sub>2.3</sub>O<sub>12</sub>:Ce SC and TbAG:Ce SCF/Gd<sub>3</sub>Al<sub>3.2</sub>Ga<sub>1.8</sub>O<sub>12</sub>:Ce SCF/Gd<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>:Ce SC compositions (Fig.1).

The work was supported by Polish NCN 2018/31/B/ST8/03390 and Czech project and the Czech MEYS SOLID21 CZ.02.1.01/0.0/0.0/16\_019/0000760 project.

Fig.1. Scintillation decay of proposed GAGG:Ce SCF/GAGG:Ce SC (a) and TbAG:Ce SCF/GAGG:Ce SCF/GAGG:Ce SC (b) epitaxial structures under excitation

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## **Comparison of X rays beam dose distributions in radiotherapeutic tumor treatment procedure using YAG:Ce and LuAG:Ce crystal detectors**

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Radiation dosimetry plays a crucial role in the Quality Assurance (QA) in radiotherapy [1]. The primary goal of therapy is this optimizing the treatment procedure so that a sufficiently large dose of radiation is delivered to tumor at minimizing the irradiation of healthy tissues.

Thermoluminescence (TL) dosimetry is a versatile tool for the assessment of ionizing radiation dose. Recently for control of photon beam dose distributions of clinical radio-therapeutic equipment we discussed the possibility application of the non-conventional TL detectors based on the crystals of Ce<sup>3+</sup> doped Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce garnet (YAG:Ce) with a density  $\rho=4.5$  g/cm<sup>3</sup> and effective atomic number  $Z_{\text{eff}}=35$ . The previous results shows that this garnet is suitable TL material for application in radiotherapy with 6MV photon beams due to its excellent radiation stability, high intensity TL response at typical therapeutic dose of 2 Gy and good position of main TSL peak around 280 K [2]. Meanwhile the intensity of the TL glow curves is strongly influenced not only by the dose but also by the energy of X ray radiation in the 6-15 MeV range. For this reason, the radiation effect has a very strong dependence on the density and effective atomic number of the absorbed TL materials especially at the registration of the high energy (above 6 MeV) parts of X rays.

Based on the previous data obtaining with YAG:Ce TL detectors, the next step of our research is connected with the investigation the TL detectors with higher density and effective atomic number. We investigated in this work the sets of TL detectors based on the crystals of Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce garnet (LuAG:Ce) with  $\rho=6.7$  g/cm<sup>3</sup> and  $Z_{\text{eff}}=61$ . The two sets of LuAG:Ce TL detectors with 10\*10\*0.5 mm dimension were prepared from two different Czochralski grown crystals. Samples of LuAG:Ce crystals were irradiated with 6MV and 15MV X Rays using linear accelerator Clinac 2300 C/D from Varian Medical Systems located in Oncology Center in Bydgoszcz. The contained results were analyzed in comparison with YAG:Ce TL detectors. Based on the data obtaining with YAG:Ce and LuAG:Ce TL detectors, the creation of composite TL detectors based on the YAG:Ce single crystalline film/LuAG:Ce crystal detectors were considered using LPE growth method [3].

This work was performed in the frame of Polish NCN 2018/31/B/ST8/03390 project.

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## Influence of the growth temperature on the optical properties of {ZnO/CdO}<sub>30</sub> superlattices

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One of the promising ternary alloys is ZnCdO, which reduces the band gap of a pure ZnO as well as expands the radiation range from UV to the visible range, and as a result, significantly expands the functionality of devices and elements made on ZnO-basis[1,2].

In this work we present the results of investigation of {ZnO/CdO} superlattices (SLs) deposited on *m* - plane Al<sub>2</sub>O<sub>3</sub> substrates at different growth temperature (360 – 550 °C) by PA-MBE. The obtaining SLs were post growth annealed at different temperatures in an O<sub>2</sub> atmosphere for 5 min. The formation of SLs quasi ternary alloys were confirmed by TEM and SIMS measurements. The presence of satellite peaks on the 2 $\theta$ - $\omega$  XRD scans confirmed both good periodicity and smoothness of the interfaces. To study the optical properties of as grown and annealed SLs, temperature dependent photoluminescence (PL) and transmittance were carried out. Both growth temperature and annealing parameters influences on the optical properties of the samples. In particular, growth temperature applied strongly influences the defect luminescence observed in all annealed samples. Especially, the samples grown at different temperatures and annealed in one process have significantly different luminescence(Fig 1).

Growth temperature influences on the growth rate of CdO and ZnO as well as the number of defects. During annealing, defects contribute to Cd diffusion. Finally, by the growth temperature it is possible to influence the optical properties ZnCdO ternary alloy through annealing.

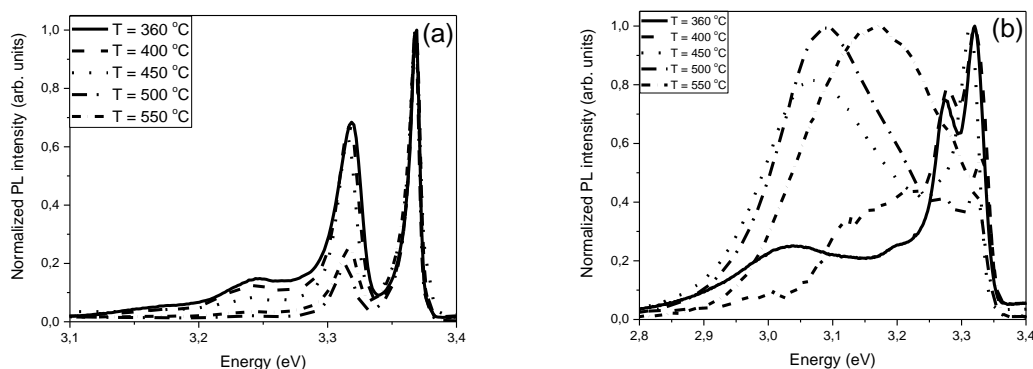


Fig. 1. Normalized PL spectra at LT of (a) as grown {ZnO/CdO}<sub>30</sub> SLs (b) annealed SLs.

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## Luminescent properties of cerium implanted GaInN

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Rare earth (RE) ions doped semiconductors are the subject of research due to the unique combination of their optical and electrical properties providing the high potential of these materials in new optoelectronic devices [1]. Wide bandgap semiconductors, like gallium nitride, doped with RE are especially interesting because of the weak temperature quenching of the RE luminescence. Among the RE ions family,  $\text{Ce}^{3+}$  has the simplest  $4f^n$  configuration ( $n = 1$ ). Upon excitation, electrons of cerium ions are promoted from the  $4f$  to the  $5d$  state, and then strong broadband emission occurs, originating from parity allowed inter-configurational  $4f^05d^1 \rightarrow 4f^15d^0$  transition. The outer-shell  $5d$  electrons are weakly shielded from the lattice, so the observed transition energies are significantly affected by the crystal field strength, and in various host crystals cerium ions show emission from the near UV up to red spectral range [2].

In this work, we studied the possibility of controlling the luminescent properties of  $\text{Ce}^{3+}$  ions implanted into  $\text{Ga}_{1-x}\text{In}_x\text{N}$  matrices ( $x = 0, 0.04, 0.08$ ) by the changes of host energy gap and crystal field strength induced by replacing some amount of  $\text{Ga}^{3+}$  cations by  $\text{In}^{3+}$  cations with larger ionic radius. The samples revealed bright and thermally stable broadband photoluminescence (PL) with the PL peak wavelengths decreasing from 680 nm in  $\text{GaN:Ce}$  to 570 nm in  $\text{Ga}_{0.92}\text{In}_{0.08}\text{N:Ce}$ . The room-temperature decay kinetics consisted of two main components: short-time component in nanosecond time scale, compatible with  $4f^05d^1 \rightarrow 4f^15d^0$  transition, and long-time component with the decay times decreasing from 34  $\mu\text{s}$  for  $\text{GaN:Ce}$  to 23  $\mu\text{s}$  for  $\text{In}_{0.08}\text{Ga}_{0.92}\text{N:Ce}$ . The possible causes of the observed effects will be discussed.

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## **Low phonon glasses and polymer composites doped with erbium – a comparative study**

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The previous two decades were a time of intensive development of highly-efficient, compact light sources operating in the visible spectral range. The demand for this type of light sources results from several application areas like information recording and processing techniques, sensing, medical diagnostic, imaging techniques, lighting, and optical telecommunication (specifically Li-Fi) as well. Although the main research effort has been focused on the development of the technology of wide bandgap semiconductors, there is still a lot of room for compact diode-pumped solid-state lasers (DPSSL), which are indispensable in these application fields, which require high quality of the laser beam.

In this work, we present the results of research on luminescent properties of erbium-doped materials – low phonon glasses and polymer composites doped with active nanocrystals, operating in the visible spectral range. In particular, the luminescent properties of Er:YF<sub>3</sub> nanopowders and polymer composites doped with them were carefully studied and compared with the features offered by erbium-doped low phonon oxide and fluoride glasses. Specific attention was given to the analysis of the up-conversion phenomena and the influence of hosts' type on the optical properties of erbium ions.

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# Dysprosium doped oxide and fluoride glasses for yellow fiber lasers

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Although several rare-earth ions may be used as active dopants for visible light emitters, the dysprosium seems to be particularly interesting because of its unique luminescent features. In particular, it offers the possibility of obtaining emission and lasing in yellow spectral range, hardly available to other laser types, including laser diodes. Additionally, the favorable energy scheme of this ion (see Fig. 1) allows using wide-bandgap InGaN/GaN semiconductor diodes as pumping sources (the presently available wavelength range is shown in Fig. 1 against energy levels' distribution). Visible emission in dysprosium doped materials results from 4f intraconfigurational radiative transitions originating from metastable  $^4F_{9/2}$  level with energy gap to next lower energy level around  $7800\text{ cm}^{-1}$ , which results in the only slight contribution of multiphonon relaxation processes in the depopulation of excited energy level. This, in turn, should potentially allow obtaining laser action in matrices with higher phonon energies, than fluoride glasses. A long fluorescence lifetime of  $^4F_{9/2}$  level observed in glassy materials (above 1 ms) and a four-level yellow lasing system should facilitate obtaining the population inversion in this kind of active media.

In this work, we present the latest results of our studies on the visible luminescence (with particular emphasis on the yellow spectral range) of a set of oxide and fluoride glasses doped with dysprosium ions. The fluorescence dynamics profiles, recorded for different concentrations, together with emission and excitation spectra enabled discussion of mechanisms responsible for populating  $^4F_{9/2}$  level and potential lasing properties of investigated materials.

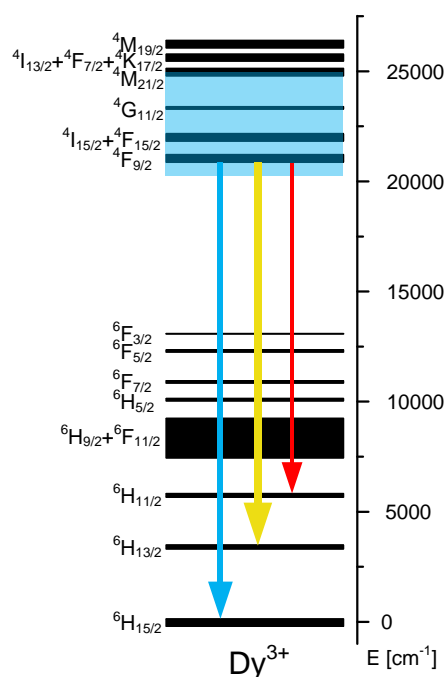


Fig. 1. Energy levels scheme of  $\text{Dy}^{3+}$  ions together with visible emission transitions (the blue area is the available wavelength range of InGaN/GaN LDs: 400-488 nm).

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## UV–VUV spectroscopic ellipsometry of PLD-grown PbTiO<sub>3</sub> thin films

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Lead titanate PbTiO<sub>3</sub> thin films with the nominal thickness of 150 and 290 nm were grown on the single crystalline (001) SrTiO<sub>3</sub> substrates by the pulsed laser deposition using KrF excimer laser ( $\lambda = 248$  nm). The ellipsometric spectra  $\Psi(E)$ ,  $\Delta(E)$  were measured in the photon energy range  $E$  of 2–10 eV using standard instrument and unique synchrotron-based VUV setup. The spectra are analysed with the help of a layered optical model and the real and imaginary parts of the dielectric function are derived together with the critical points energies. Differences in the optical function behaviour for various film thicknesses are attributed to the appearance of strain effects in the interface region, caused by lattice constants mismatch between film and substrate, which is confirmed by the results of the performed *ab-initio* calculations.

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## **Luminescence properties of MBE grown Eu doped ZnMgO thin films on c- and r- oriented Al<sub>2</sub>O<sub>3</sub> substrates**

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Eu doped ZnMgO thin films were grown on c- and r- oriented sapphire substrates by Plasma assisted Molecular Beam Epitaxy, under the same ambient experimental conditions. Dopant concentration analysis was done by secondary Ion Mass Spectrometry technique. We investigated the photoluminescence (PL) and structural properties of as grown films. It is found that the substrate orientations has an influence on the luminescence properties of Eu doped ZnMgO films. HR-XRD studies confirmed hexagonal wurtzite crystal structure for Eu doped ZnMgO films. Lattice parameters were determined accurately. Sample grown on c-Sapphire was preferentially oriented in 0002 direction. Eu: ZnMgO/C-Sapphire was found to have dominating Eu luminescence in comparison to Eu: ZnMgO/r- sapphire which was oriented along 11-20 direction. PL excitation measurements indicated energy transfer from host ZnMgO lattice to the dopant Europium centers.

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## **New, hybrid luminescent materials based on thin oxide films doped by rare earth ions and gold plasmonic nanostructures**

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Integration of the luminescence materials with plasmonic nanostructures may open new applications possibilities. Especially when it leads to enhance its luminescent intensity. Such a hybrid structure can be formed by thin oxide layers doped with rare earth ions, deposited on metal nanostructures. The oxide material, used as a matrix, can here be, for example,  $\text{TiO}_2$  or  $\text{TeO}_2$ . Titanium dioxide seems to be one of the most popular oxide material, as a matrix for rare-earth ions. On the other hand, tellurium dioxide can be also considered as excellent in hosting rare-earth ions because of its low phonon energy (ca.  $700\text{--}800\text{ cm}^{-1}$ ), what allows to minimize the non-radiative losses. Among all rare earth ions, europium (Eu) has been intensely studied for a few decades, due to its high intensity red luminescence. Whereas Eu usually assumes trivalent oxidation state ( $\text{Eu}^{3+}$ ), divalent one is also stable ( $\text{Eu}^{2+}$ ), but characterized by different luminescent properties. As a red light emitter,  $\text{Eu}^{3+}$  may be employed in various optical devices. In turn, a very special metal, among various plasmonic materials, is gold. This is due to two properties of Au: plasmon resonance in the visible range of electromagnetic radiation and high chemical stability. Moreover, research shows that Au nanoparticles can positively influence the intensity of rare earth ion luminescence emission.

Here the study of the optical properties of europium doped titanium dioxide and tellurium dioxide thin films ( $\text{TiO}_2\text{:Eu}$  and  $\text{TeO}_2\text{:Eu}$ ) enhanced by gold plasmonic nanostructures is presented. Plasmonic platforms were manufactured by thermal annealing of gold thin film, deposited on a Corning glass substrate. As a result of thermal treatment, gold hemispherical nanostructures with average dimensions of 50 nm were obtained. Luminescent  $\text{TiO}_2\text{:Eu}$  or  $\text{TeO}_2\text{:Eu}$  films were deposited by RF magnetron sputtering from mosaic targets. Morphology of gold nanostructures were investigated by SEM and TEM microscopes, while composition of oxides films were analyzed by XPS methods. Luminescence properties were studied on the basis of excitation and emission spectra. Experiments have shown that such structures exhibit interesting luminescent properties and could be potential candidates for optoelectronics.

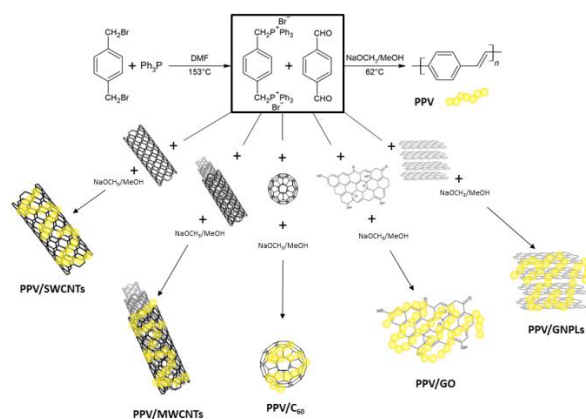
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## Poly(*p*-phenylene vinylene)/carbon nanostructures composites: morphology, structure and electrochemical properties

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Composites of poly(*p*-phenylene vinylene) (PPV) and different carbon nanostructures, such as fullerene C<sub>60</sub>, multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs), graphene oxide (GO), and graphene nanoplatelets (GNPLs), were produced by Wittig's soluble precursor procedure. During the synthesis, carbon material nanoparticles were coated with the polymeric phase.



**Scheme 1.** Syntheses of the composites containing PPV and carbon nanomaterials.

These composites were investigated using infrared and Raman spectroscopy, scanning electron microscopy, adsorption/desorption of N<sub>2</sub> measurement, and electrochemistry. The morphology of the obtained composites was strongly dependent on the shape, size and dimensions of the carbon nanostructures. Carbon nanostructural components significantly enhance the electrochemical performance of polymeric materials in composites. This leads to a significant reduction in the gap energy in the polymer incorporated in the composite compared to unmodified PPV. Such behavior is particularly advantageous for the application of composites in solar energy conversion and optoelectronic devices.

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## **Recording microstructures utilizing up-conversion luminescence in system of $\text{Tm}^{3+}$ and $\text{Yb}^{3+}$ doped $\text{NaYF}_4$ nanoparticles mixed with SU8 photoresist with/without organic compounds**

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This work demonstrates a method essential for building up an experimental setup for the up-conversion (UC) luminescence photolithography system. In a common photolithography method exposure is performed through the sample (photoresist + additional compounds) surface, but there is a drawback - in thick samples, UV radiation is mostly absorbed in the upper layers of the sample, as the results deeper layers are unexposed. Such a problem can be solved when light emitting sources are placed into a photoresist – like nanoparticles emitting UC luminescence (UCNP's). UC is a process in materials, where absorbed light with low photon energy (IR), emits luminescence with higher photon energy (blue light or UV) [1].

UCNP's were synthesized by a thermolysis method in two-day long process. UC luminescence was excited by 976 nm laser diode. Intensive UV and blue up-conversion luminescence can be observed from synthesized nanoparticles with a hexagonal core ( $\text{NaYF}_4\text{:Tm}^{3+}$ ,  $\text{Yb}^{3+}$ )-shell ( $\text{NaYF}_4$ ) structure (nanoparticle size ~35 nm) under IR excitation. The same laser diode as well as other lasers were used for a photolithography to record structures in a system of UCNPs with SU8 photoresist with/without organic compounds.

Several aspects have been considered to successfully develop and improve a photolithography experimental setup to record structures in system of UCNPs mixed with SU8 photoresist with/without organic compounds. The developed method is an alternative of a traditional i-line lithography. It is an innovative approach for recording of high-resolved three-dimensional structures.

This research is funded by the Latvian Council of Science, project “Up-conversion luminescence photolithography in organic compounds using nanoparticles/photoresist composition”, project No. lzp-2019/1-0422. Institute of Solid State Physics, University of Latvia as the Center of Excellence has received funding from the European Union's Horizon 2020 Framework Programme H2020-WIDESPREAD-01- 2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART<sup>2</sup>.

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## Up-conversion luminescence at the nanoscale: benefits and difficulties

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Up-conversion nanocrystals activated by rare-earth ions opened a new chapter in the field of anti-Stokes luminescence processes. Due to their nanoscopic dimensions, comparable with the range of electrostatic interactions, they can easily couple to the surroundings forming more complex systems. Such multi-component nanostructures usually offer new functionality but also show additional, desired or unwanted physical effects. In this talk, we will present our newest results, illustrating the benefits and fundamental problems of applying up-conversion materials at the nanoscale.

In the last years, much attention has been paid to developing hybrid nanostructures comprising nanocrystals and various metallic nanoparticles. Interaction between such objects often modifies the up-conversion processes. We will show that gold nanospheres, for instance, due to their relatively narrow resonance, may act very selectively, e.g., enhancing the red emission of  $\text{Er}^{3+}$  and, at the same time, quenching the green one. On the other hand, elongated metallic nanoparticles like silver nanowires, featuring spectrally broad plasmonic resonance, can enhance all  $\text{Er}^{3+}$  emission lines and significantly improve the absorption. Moreover, silver nanowires can support surface plasmon polaritons, transporting the energy along the nanowire. Our recent results show that energy transfer up-conversion ( $\text{Er}^{3+}/\text{Yb}^{3+}$ ) and photon avalanche up-conversion ( $\text{Tm}^{3+}$ ) processes can be activated exclusively by plasmons without the participation of photons.

We also noticed some problems and complications associated with implementing the up-conversion materials at the nanoscale. We will demonstrate that even a little uncontrolled interaction with surfactants can disturb the up-conversion mechanisms and reduce efficiency. Moreover, local temperature fluctuations (e.g., operating laser) can intensify nonradiative relaxation channels. We will show how the latter affects the single nanocrystal's up-conversion thermometry. We will demonstrate the temperature readout from a single nanocrystal monitoring a warm single nanowire and point out parasitic processes disrupting such a measurement.

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## Up-converting nanocrystals coupled to a single silver nanowire as a source of surface plasmon polaritons for direct measurement of propagation losses

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In this work, we discuss a prototype hybrid nanostructure consisting of Er<sup>3+</sup>/Yb<sup>3+</sup>-doped up-conversion nanocrystals (NCs) and a single silver nanowire (NW). In this case, nanocrystals serve as a very efficient, multi-band source of surface plasmon polaritons (SPPs) propagating along the nanowire. Based on efficient infrared excitation, large anti-Stokes shift, and optical cutting technique, we developed a new experimental approach for direct measurements of SPPs propagation losses.

Examined nanostructure consists of silver nanowires dispersed on the surface of the microscope coverslip. One good quality nanowire, about 15 µm long, was chosen for the experiment. Next, a few-femtoliter droplet of nanocrystals was deposited on one end of the nanowire, forming NCs-NW coupled system. It has been reported that emission activated at one NW end can be transported to the opposite end by SPPs [1].

The experiment was realized using a scanning confocal microscope optimized for the anti-Stokes emission and equipped with two (top and bottom) coaxial objectives. An infrared laser operating at 980 nm was focused by the top objective directly on the NCs droplet. Usually, excited nanocrystals emit to free space, but some can launch SPPs propagating toward to opposite nanowire end. The intensities of the up-converted emission collected from the free end of the nanowire by the bottom objective, measured for different nanowire lengths, give information about SPPs propagation losses. Importantly, the length of the NW was gradually reduced using a precise laser cutting technique. Also dimensions of the NW were controlled optically by analyzing the complex character of the interaction between the NW and modes of tightly focused Gaussian beam. The presented approach shows great potential for advanced and cheap examination of metallic nanostructures for nanophotonic applications.

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## **RE<sup>3+</sup> photoluminescence of charge compensated hafnia nanoparticle: solvothermal synthesis and colloidal dispersion**

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Luminescent materials activated by rare earths are employed in a wide range of applications, from lighting and display technologies to scintillators for high-energy radiation detection. New syntheses allowing colloidal stability of materials without major agglomeration induced by heat treatment are of main interest to develop new deposition and processing methods and enabling their potential use in bio imaging/therapy. Additionally the incorporation of the dopant is extremely important to tailor the photo-physics of the doped nanoparticles.

In the case of HfO<sub>2</sub>, rare earth doping, from 3 at.% on, is well known to induce the room temperature stabilization of higher symmetry crystal phases. [1] Several reports suggest therefore that the charge compensation by pentavalent ions such as Nb<sup>5+</sup> or Ta<sup>5+</sup> allows to suppress this structural effect and to be beneficial to the photoluminescence. [2] However, the synthesis of charge compensated materials often needs high temperatures to achieve good incorporation of all dopants and to observe phase pure monoclinic HfO<sub>2</sub>, strongly limiting its dispersibility.

HfO<sub>2</sub> nanocrystals co-doped with Nb<sup>5+</sup>/Eu<sup>3+</sup> or Ta<sup>5+</sup>/Eu<sup>3+</sup> were synthesized through a solvothermal route, providing colloiddally stable dispersions of phase pure monoclinic HfO<sub>2</sub> up to 6 at.% of Eu<sup>3+</sup>. [3] The photoluminescence measurements on dispersions enabled to linearly correlate the intensity of the Eu<sup>3+</sup> emission to the doping and particle loading. We also highlighted the role of Nb<sup>5+</sup> in improving the luminescence at higher excitation wavelengths suggesting its essential role in increasing the cross-section of the doped particle system to UV excitation.

In this talk the control over the structure/function relationship in such HfO<sub>2</sub> doped nanoparticle dispersion systems and their implications towards advanced bio-imaging and functional inks for innovative deposition/assembly of nanoparticle-based optical materials will be discussed.

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# Ultrasound-induced synthesis of all-inorganic lead perovskite QDs: fast, simple, and highly reproducible

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All-inorganic perovskite quantum dots (QDs), due to their outstanding power conversion efficiency, narrow and tunable emission band, and strong absorption, have already found applications in LEDs, solar cells, photodetectors, etc. Thus, simple, easy, and highly reproducible lead perovskite QDs synthesis routes are very desirable. This study presents a novel approach to obtain perovskite QDs. The crucial synthesis parameters, such as temperature, isolation conditions, or optical density on the changes in optical properties, were taken into account. The detailed verification of different parameters showed that the proposed ultrasound-induced synthesis method (see Figure 1) is superior to the conventional hot-injection method since it offers not only the higher reproducibility but also a significantly shorter synthesis time, i.e., from several hours via the traditional hot-injection method to merely 20-30 minutes by our proposed method.

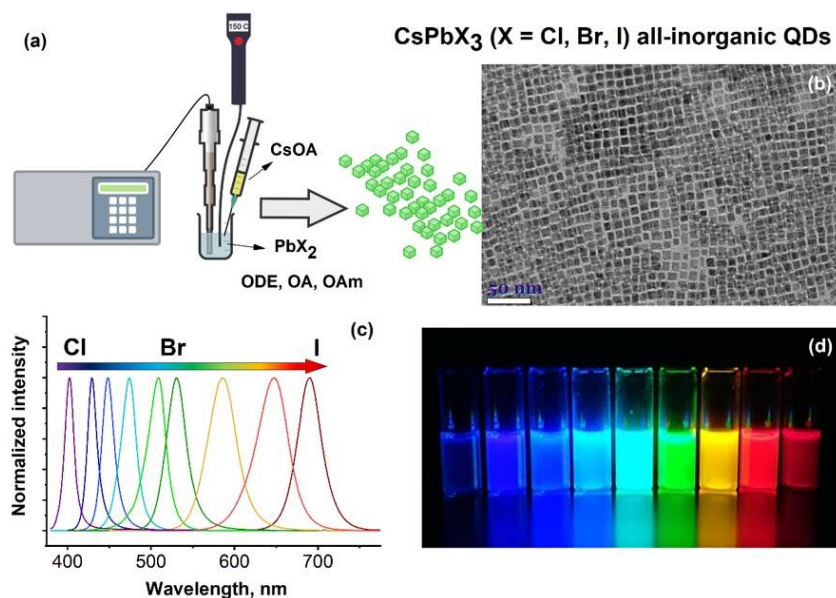


Figure 1. Graphical illustration of the ultrasound-induced synthesis of all-inorganic lead perovskite QDs (a); TEM image of the obtained CsPbBr<sub>3</sub> QDs (b); PL emission spectra (c) and emission color gamut of CsPbX<sub>3</sub> QDs with various compositions ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) (d).

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## Single up-converting nanocrystals nanothermometry

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Temperature measurement at the nanoscale is a great challenge today. It requires a non-invasive approach, where temperature can be monitored using individual nanoprobes [1]. Among a variety of temperature indicators, one can distinguish fluoride up-converting nanocrystals doped with rare-earth ions. Due to their high optical stability, the temperature readout can be based on luminescence spectra analysis, which does not disturb the investigated system thermally [2]. Of course, detailed exploration of the temperature nanoprobes requires a reference heat source of the same scale. Therefore, very promising heaters are metallic nanostructures, e.g., silver nanowires, where heat generation can be controlled electrically in the Joule process [3].

In this work, we demonstrate a high-resolution technique for temperature monitoring using  $\text{Er}^{3+}/\text{Yb}^{3+}$ -activated single up-converting nanocrystals. A low concentration of nanocrystals solution was dispersed around a single silver nanowire, the temperature of which was controlled by an external  $\mu\text{A}$  power supply due to ohmic heating. The temperature readout is performed using means of ratiometric thermometry, where the intensity ratio of  ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$  and  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  emission peaks changes with temperature according to Boltzmann distribution [4]. Our results show that single nanocrystals can precisely monitor the temperature of an individual nanowire and its surroundings. Namely, due to the anti-Stokes nature of up-converting nanocrystals luminescence, the signal-to-noise ratio was high enough to detect temperature gradient in the vicinity of the nanoheater. These results break the barrier of using truly single nanoprobes for the luminescence thermometry at the nanoscale.

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# Electronic trap depths in Pr-doped lutetium oxide doped with Ti, Zr and Hf: *ab initio* multiconfigurational calculations

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Long-term energy storage and thermoluminescence in phosphors based on cubic  $\text{Lu}_2\text{O}_3\text{:Pr}$  are achievable via introduction of d metal co-dopants. It was assumed from the vast experimental data that by photoionization of  $\text{Pr}^{3+}$  to  $\text{Pr}^{4+}$  occurs, and that d orbitals of the co-dopants contain (trap) the electrons formed upon excitation.

In this research, we have used RASSCF / CASPT2 / RASSI-SO ( $\text{PrO}_6^{9-}$  cluster,  $\text{Pr}^{3+}$ ;  $\text{PrO}_6^{8-}$  cluster,  $\text{Pr}^{4+}$ ;  $\text{MO}_6^{9-}$  clusters,  $\text{M}^{3+}$ ,  $\text{M}=\text{Ti, Zr, Hf}$ ) and CCSD ( $\text{MO}_6^{8-}$  clusters,  $\text{M}^{4+}$ ) in order to obtain the total energies of the mentioned clusters of metal cations and their surrounding oxygens. The clusters were embedded in an Ab Initio Model Potential (AIMP) and point charges embedding representing the c- $\text{Lu}_2\text{O}_3$  lattice. The two-cluster total energy as a function of the two configurational coordinates forms a potential energy surface. The surfaces of the two states ( $\text{Pr}^{4+}$ ,  $\text{M}^{3+}$  and  $\text{Pr}^{3+}$ ,  $\text{M}^{4+}$ ) intersect at a line which has a minimum. The energy difference between the minimum of  $\text{Pr}^{4+}$ ,  $\text{M}^{3+}$  system and the minimum of the intersection is taken as the trap depth in the adiabatic approximation. Other energetic properties were analyzed as well. Trap population and depopulation/quenching mechanisms were analyzed – all of them based on metal-to-metal charge transfer not involving conduction band.

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## First-principles calculation of electronic structure of luminescence in $\text{Li}^+$ co-doped $\text{Ce}^{3+}$ -doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG) inorganic scintillator

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The scintillator materials continue attract much more interests for their distinct uses in the radiation detection applications. The interaction between the rare earth ions and electronic states of the host material has an effect the optical properties and performance of  $\text{RE}^{3+}$  activated materials, and consequently, it is important to improve the understanding of this interaction [1]. We are interested in this work to the theoretical study, using ab-initio methods, the structural and electronic properties of garnet type nanoscintillator  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  co-doped  $\text{Li}^+$  and  $\text{Ce}^{3+}$  (LuAG:  $\text{Ce}^{3+}$ ,  $\text{Li}^+$ ). The ab-initio method based on Density Functional Theory (DFT) used in this study to calculate the ground state energy of garnet dope ( $\text{Li}^+$ ,  $\text{Ce}^{3+}$ ), as well as the structural and electronic properties using VASP code (Vienna Ab-initio Simulation Packages) [2]. In fact, LuAG:  $\text{Ce}^{3+}$  garnet material is very known experimentally to be a good single crystal scintillator. Also, it was reported that cooping by  $\text{Li}^+$  ions can improve the structural and optical properties of some inorganic materials [3, 4]. In this study, we have undertaken the calculation on LuAG:  $\text{Ce}^{3+}$  system and studying the effect of co-doping with  $\text{Li}^+$  ion on these properties. In this calculation, we have used DFT+U approach to predict the 4f orbital position relative to maximum of the valence band and hybrid DFT (HSE) calculation to determinate the band gap.

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## Spectral and X-ray comparison between novel double perovskites and their derivatives based on tungsten and chosen rare-earths ions

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Double perovskites are rock-salt type minerals named after the resemblance to regular  $ABX_3$  perovskite structures having one simple exception in mind – they share corner arrangement of both, unique  $BX_6$  and  $B'X_6$  clusters within one, double-sized unit cell having general  $A_2BB'X_6$  formula. A-site cations are most commonly considered to be divalent, alkaline metals (Ca, Sr, Ba). B or B' have different yet suitable combinations of rare-earth ions (i.e. Ce, Pr) and d-block metals (like W). X-sites can vary depending on chemical flexibility – these atoms could be related to halides, nitrides, and even sulfides. In this particular case, they would be  $O^{2-}$  anions. Since those compounds were constantly investigated since early 1950's, they have found their way into many applications such as optoelectronics, superconductors, catalysts, dielectrics, piezoelectrics, various temperature sensors, electrodes, and components used to form well-developed fuel or solar cells. Broad literature review [1] alongside with own experimental studies, regarding popular  $BaWO_4:Ce$  scintillator [2], inspired researchers to figure out an original, non-trivial approach in order to form a new group of compounds amongst such broad family of materials. Thus, investigation was later recognized and founded by Preludium grant 2019/33/N/ST5/02317 to find whether or not there is a possibility to apply such compounds in any aforementioned field of scientific interest.

Personally, these novel materials were created using solid-state reaction in an inert atmosphere and high pressure, in hopes of finding a new, efficient NUV-NIR downconverter or at least a photobleacher - NUV sensor. However, part of them turned out to be so called ilmenites [3] or quaternary perovskites [4] which are considered to be weak phosphors.

(High and low) Temperature and pressure stability were checked in terms of possible phase transitions (polymorphism) or eventual decomposition of those newly created materials. Techniques like powder XRD, XPS, XAS, EPR, Raman, and FTIR spectroscopies or even DSC with TG were involved to thoroughly describe any behavioral changes in yet undoped materials. This presentation will briefly show few of these results in order to show whether or not these materials are worth further energy-transfer research and could be successfully implemented into tasks related to future industrial energy conversion.

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## **Influence of Nd<sup>3+</sup> concentration on laser induced broadband white emission of La<sub>1-x</sub>AlO<sub>3</sub>:xNd<sup>3+</sup> perovskites**

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Perovskite materials have been extensively explored over the years for their ferromagnetic, magnetoresistance, ferroelectric, superconducting, piezoelectric, and catalytic properties [1]. They possess a general formula ABX<sub>3</sub> and present flexibility to the introduction of dopants to the matrix, which can improve or modify their properties. When doped with lanthanide ions their optical properties may be altered and render them new applications. Herein, we present the laser induced broadband white emission on La<sub>1-x</sub>AlO<sub>3</sub>:Nd<sup>3+</sup> (x = 0.01; 0.05; 0.20; 0.40; 0.60, 0.75 and 1) perovskites and the influence of Nd<sup>3+</sup> concentration on this optical phenomenon. The materials were obtained using Pechini method and, according to XRD, presented the cubic perovskite phase (Pm-3m space group), with lack of impurities or secondary phases. The broad band white light was generated when the perovskites were excited by a focused continuous wave laser diode (λ = 808 nm) which, unlike other materials that exhibit this type of emission [2], present a few well-defined bands which may be due to reabsorption of the Nd<sup>3+</sup> ions. This emission of white light exhibited a threshold behavior, and when the excitation power exceeded this threshold value, the intensity showed a non-linear increase according to power law I ∝ P<sup>N</sup>, typical of multiphoton absorption. In addition, they showed a strong non-linear pressure dependence according to the expression I = I<sub>0</sub> exp(-p/p<sub>0</sub>), with the highest intensity observed in low pressure and a sharp decrease in higher values of pressure. Both the N parameter in the power dependency and p<sub>0</sub> in the pressure dependency exhibited an exponential variation with Nd<sup>3+</sup> concentration. The kinetics of the emission were also studied, showing a rise time in the order of a few seconds. This observation, coupled with the threshold behaviors might indicate a photon avalanche process.

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# Experimental Method for the Tauc Exponent and Corresponding Transition Types Determination

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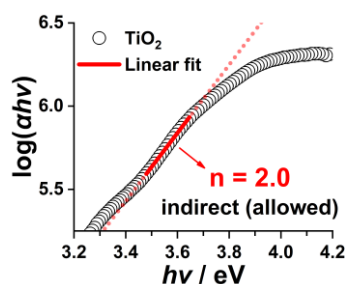
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Ultraviolet-visible spectroscopy is a widely used technique to investigate optical properties of the materials. The registered data can be further used to estimate optical band gap *via* fitting it to the Tauc equation. However, to do so, an information regarding the transition type is required, and studying the literature, one can find that in most cases the authors select  $n$  value based on other references without any justification.

In this work, a facile method allowing for determination of the Tauc exponent directly from the measured UV-vis spectroscopy data is demonstrated. It is based on the Taylor expansion of the logarithmic version of the Tauc equation. Compared to other methods reported in the literature (e.g. [1]), no information regarding the investigated material such as band gap width is required. Therefore, the method particularly applies for materials with unknown transition type (including nanosized or composite materials).

As an exemplar materials, nanocomposites based on the TiO<sub>2</sub> nanotubes[2] decorated with thin films of transition metal oxides from 13<sup>th</sup> group were chosen. For the bare TiO<sub>2</sub> nanotubes the estimated Tauc exponent is equal to 2.0 which directly corresponds to the well-estimated indirect (allowed) transition of TiO<sub>2</sub>. In the case of TiO<sub>2</sub> nanotubes decorated with Cr oxides an additional direct (allowed) transition was found, whereas molybdenum and tungsten oxides exhibit direct (forbidden) transitions. From quantum mechanics it is known that direct transitions are more probable comparing to indirect whereas forbidden are unlikely to occur. Interestingly, photoresponse measurements revealed that TiO<sub>2</sub> nanotubes with Cr oxides exhibit superior photoresponse comparing to bare TiO<sub>2</sub> nanotubes whereas TiO<sub>2</sub> nanotubes with Mo and W oxides deteriorated. Therefore, it is anticipated that the information regarding the estimated transition is essential and contributes to the better understanding of the optical properties of semiconductors.

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## Broadband femtosecond ellipsometry at ELI beamlines facility

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The optical constants of metals, semiconductors and insulators can change rapidly upon external electromagnetic excitation affecting operational parameters of many electronic and optoelectronic devices. A deep understanding of such changes requires monitoring of ultrafast temporal evolution of the complex dielectric function of the applied materials. Employment of ultrashort laser pulses in time-resolved spectroscopic techniques allows such changes to be followed with femtosecond precision. In particular time-resolved ellipsometry seems to be an excellent tool for this purpose because it outclasses transient reflectance and transmittance experiments giving unambiguous distinction between the real (refraction) and imaginary (absorption) part of the dielectric function. However, propagation of ultrashort and ultrabroadband pulses through polarizing optics requires special care due to dispersive and chromatic effects. In consequence, obtaining high quality ellipsometric data with fs resolution is challenging and many technical as well as methodological issues have to be addressed.

Here, we present a versatile experimental platform, located in ELI Beamlines facility in Czech Republic, dedicated to ultrafast pump-probe ellipsometry with time resolution about 100 fs [1]. The whole system is based on 1 kHz Ti:Saph laser which produces fundamental ultrashort (20-35 fs) NIR (800 nm) pulses subsequently transformed into desired pump and probe beams. The setup is devoted to UV-VIS-NIR spectral range and the broadband probe pulses obtained by supercontinuum generation cover 350-1300 nm region. The narrowband pump pulses are produced by optical parametric amplification and can be tuned from 190 nm to 20  $\mu$ m. The current capabilities and experimental details of this cutting edge ellipsometric platform will be presented with the example results obtained on the excited semiconductors [2].

ELI is thought as a user facility open to all scientists. Details of how to submit a proposal to carry on experiments using ELI Beamlines capabilities will be also provided.

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## Dehydration-driven modulation of opto-magnetic properties in $\text{Ln}^{\text{III}}\text{Co}^{\text{III}}$ cyanido-bridged frameworks

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Among modern magnetic materials, single-ion magnets (SIMs) gather enormous scientific interest due to the perspective applications in high-density data storage and molecular spintronics.<sup>1</sup> The last several years of research in this field indicated that achieving the best performance SIMs is ensured by the exploration of lanthanide(3+) ions. At the same time, 4f metal complexes were highly recognized for their emissive features utilized for chemical sensors or light-emitting devices.<sup>2</sup> Moreover, lanthanide luminescence can be efficiently exploited for the construction of optical thermometers whose emission signal serves for contactless temperature sensing.<sup>3</sup> Finally, lanthanide-based molecular materials combining magnetic and photoluminescent features were also reported, enabling correlations between single-ion magnetism and the electronic structure illustrated by high-resolution low-temperature emission spectra.<sup>4</sup> Lately, the idea of building optical thermometers using SIMs emerged due to their prospective application for the construction of opto-magnetic devices with the self-monitored temperature. Here, we present the impact of post-synthetic dehydration upon magnetic properties, as well as luminescent features of lanthanide(III)-hexacyanidocobaltate(III) frameworks.<sup>5,6</sup> Our results indicate that such treatment may result not only in the proper enhancement of magnetic anisotropy but also in the strong modification of  $\text{Dy}^{\text{III}}$  emission color towards white-light emission<sup>5</sup> and sensing parameters of  $\text{Tb}^{\text{III}}$ -based single-band and  $\text{Tb}^{\text{III}}\text{Co}^{\text{III}}$ -oriented double-band optical thermometry.<sup>6</sup>

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## POSTER PRESENTATIONS

# Temperature-dependent bandgap study of Eu doped CdO thin film prepared by PA-MBE

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CdO is one of the oldest known semiconductor oxides that have been studied widely because of its high transparency, high electron mobility, low resistivity, high electron concentration, and high exciton binding energy. In this work, thin layers of CdO and Eu doped CdO were grown on quartz substrate using plasma-assisted molecular beam epitaxy (PA-MBE) technique. The temperature-dependent fundamental bandgap of CdO, and CdO:Eu was performed from 10 to 290 K using absorption spectroscopy. It is observed that, Eu doping with CdO causes a decrease in fundamental bandgap energy (as shown in Fig.1) and it strongly depends upon the doping level in CdO thin film. In order to gain a better understanding of bandgap behavior with temperature, the obtained results were fitted using Varshni's model [1] and Bose-Einstein model [2]. From fitting the parameters, Debye temperature ( $\beta$ ) and average phonon temperature ( $\theta$ ) were estimated. Temperature coefficient of bandgap narrowing was determined to be 0.5 meV/K. This study will be useful in developing optoelectronic devices such as solar cells which are affected by daily temperature variation.

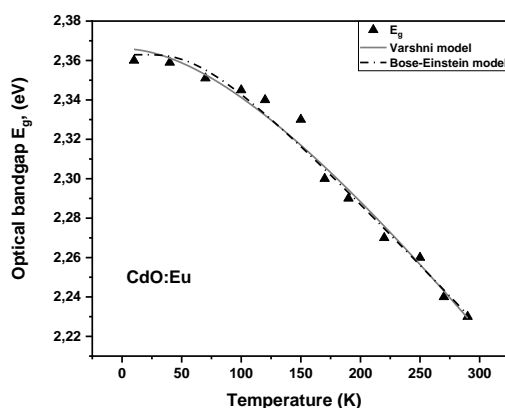


Fig.1. Variation of optical bandgap with temperature for Eu doped CdO film

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# Spectroscopic ellipsometry in the vacuum ultraviolet region

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Spectroscopic ellipsometry is a well-established tool to measure film thickness and optical properties of a material. Commercial ellipsometers are built for the infrared, visible, and ultraviolet region reaching up to the photon energy  $E$  of around 8.5 eV (145 nm). By using a beam of shorter wavelength, the penetration depth of the light in a given material is smaller and, then, a better sensitive towards surface characterization is obtained. With this shorter wavelength, it is possible to study the optical properties of wide band gap semiconductors films, which critical points are at high photon energies. For  $E > 10$  eV, there is a unique user-oriented ellipsometer at the Metrology Light Source of the Physikalisch-Technische Bundesanstalt (PTB) in Berlin which uses synchrotron light and can measure up to 40 eV [1].

At the ELI Beamlines facility, another vacuum ultraviolet (VUV) ellipsometer is being built as an user oriented end-station [2-3]. It uses a VUV beam generated by an HHG source which energies reach up to 120 eV. We present the results of current studies where VUV ellipometry has been used, and we also present the state of the implementation of the new VUV ellipsometer.

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## Gamma spectroscopy of $\text{MgGa}_2\text{O}_4$ and $\text{ZnGa}_2\text{O}_4$ semiconductor scintillators

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Semiconductor scintillators are gaining appeal in the existing scintillator market, which is still dominated by inorganic insulators. Recently, Ga-based oxides have defined a new and interesting class of materials by incorporating the possibility of novel operability. With respect to scintillation characteristics, Czochralski-grown  $\beta\text{-Ga}_2\text{O}_3$  crystals with moderate free electron concentration have been found to yield about 9000 photons per each 1 MeV of absorbed energy of incident gamma radiation, while those with much higher free electron concentration offer significantly faster scintillation decays, but with lower light outputs [1].

In this Communication, as a sequel of our research on Ga-based oxides, we present for the first time the basic scintillation properties of  $\text{ZnGa}_2\text{O}_4$  and  $\text{MgGa}_2\text{O}_4$  crystals grown at Leibniz-Institut für Kristallzüchtung by the Vertical Gradient Freeze and Czochralski method, respectively [2-4]. We prove that these two Ga-based spinels do scintillate under gamma irradiation, currently displaying scintillation yields up to about 3000 ph/MeV, which could possibly be further improved. We also compare the scintillation properties of  $\text{ZnGa}_2\text{O}_4$  and  $\text{MgGa}_2\text{O}_4$  with those of  $\beta\text{-Ga}_2\text{O}_3$ , and show a correlation between the three quantities: scintillation yield, mean scintillation decay time, and free electron concentration.

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## Improvement of luminescent and mechanoluminescent properties of $\text{SrSi}_2\text{N}_2\text{O}_2\text{:Eu}$

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$\text{SrSi}_2\text{N}_2\text{O}_2\text{:Eu}$  is a well-known phosphor, used mainly for white LEDs fabrication. It had been shown that  $\text{SrSi}_2\text{N}_2\text{O}_2\text{:Eu}^{2+}$  luminescence can be improved by co-doping [1], inter alia it was reported that co-doping with Mn ions enhances luminescence [1, 2, 3]. This phenomenon was explained up to now in two contradictory ways: as the result of energy transfer from Mn to Eu ions [3] or as energy transfer from Eu to Mn ions [2].

We studied a series of  $\text{SrSi}_2\text{N}_2\text{O}_2\text{:Eu}$  samples synthesized in solid state reaction method with the addition of several Mn compounds. Our results confirmed reported by others fact that the addition of Mn compounds during the solid-state synthesis of  $\text{SrSi}_2\text{N}_2\text{O}_2\text{:Eu}^{2+}$  significantly increases the quantum yield of this phosphor, but surprisingly we found that Mn ions are not incorporated into the crystal lattice, which excludes both previously proposed mechanisms of luminescence quantum yield increase. Using electron paramagnetic resonance and optical techniques, we showed that Mn is not incorporated into the  $\text{SrSi}_2\text{N}_2\text{O}_2$  host. We propose another mechanism of the studied effect. Namely, we show that the attempts to introduce Mn ions into  $\text{SrSi}_2\text{N}_2\text{O}_2\text{:Eu}$  result in the increased number of defects that enhance the energy storage capacity of this material, resulting in increased luminescence, thermoluminescence, and persistent luminescence. We also verified that it improves the mechanoluminescence properties of this phosphor, which extends potential applications of  $\text{SrSi}_2\text{N}_2\text{O}_2\text{:Eu}$  into other areas than white LEDs.

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## Olivine-type undoped and rare earth doped germanate ceramics for visible and near-infrared luminescence

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Olivine-type germanate ceramics with general formula  $\text{Li}_2\text{AGeO}_4$  (where  $\text{A} = \text{Zn}, \text{Mg}$ ) are promising inorganic compounds due to their excellent low-permittivity microwave dielectric properties [1]. They crystallized into an orthorhombic or monoclinic phase and monoclinic (low-temperature)  $\leftrightarrow$  orthorhombic (high-temperature) reversible phase transformation can occur. Further investigations indicate that ceramics  $\text{Li}_2\text{MgGeO}_4$  doped with transition metals are also interesting from the optical point of view.  $\text{Li}_2\text{MgGeO}_4:\text{Mn}^{2+}$  is known as a green long persistent phosphor [2]. However, germanate ceramics doped with rare earth ions ( $\text{RE}^{3+}$ ) have not been often examined and their spectroscopic and luminescence properties are less documented in the literature.

Here, we present preliminary results for undoped and  $\text{RE}^{3+}$  doped germanate ceramics  $\text{Li}_2\text{MgGeO}_4$ . Rare earths ( $\text{RE}^{3+}$ ) are limited to  $\text{Er}^{3+}$  and  $\text{Ho}^{3+}$ . Similar to  $\text{Li}_2\text{SrGeO}_4:\text{RE}^{3+}$  [3], trivalent  $\text{RE}^{3+}$  preferentially occupy divalent  $\text{Mg}^{2+}$  site in the crystal structure. Thermal and structural aspects for germanate ceramics are examined using different experimental techniques. Luminescence properties of  $\text{Li}_2\text{MgGeO}_4$  and  $\text{Li}_2\text{MgGeO}_4:\text{RE}^{3+}$  ( $\text{RE} = \text{Er}$  and  $\text{Ho}$ ) in the visible and near-infrared spectral ranges are presented and discussed in details.

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## **UV and visible emission in thulium-doped ZBLAN glasses**

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Compact, low-cost, coherent, short-wavelength light sources have been under high development in recent years. The reason for this is the wide range of applications of these devices, in fields like photolithography, medicine, mass spectroscopy, fiber Bragg gratings writing, and 3D printing. Currently, the market is dominated by wide bandgap semiconductors with some share of diode-pumped solid-state lasers with frequency multiplication. Although compact and cost-efficient, short-wavelength laser diodes typically suffer from relatively low beam quality and limited output powers available. It should be noted here, that short-wavelength fiber lasers might potentially provide relatively high output powers and efficiency combined with the single transverse mode operation, extremely attractive for many applications.

In this work, we focus on the luminescent properties in the short-wavelength part of the spectrum of thulium-doped and thulium and ytterbium doubly-doped ZBLAN glasses. These will be presented and discussed in the context of obtaining the UV emission and lasing in such a system. It should be noted here, that up to now there is only one report on successful UV lasing at 287 nm in thulium-doped ZBLAN glass [1], which was achieved using an extremely inefficient pumping scheme consisting of three up-conversion and two energy transfer processes. As we have the ambition to propose a more efficient pumping scheme, we have investigated the luminescent features of thulium-doped ZBLAN glasses of different activator concentrations and analyzed the up-conversion mechanisms, discussing both singly-doped (Tm:ZBLAN) and doubly-doped (Tm+Yb:ZBLAN) systems. As conclusion, the new excitation schemes were proposed and discussed.

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## **Interaction of cellulose molecules with carbon nanostructures: insights from DFT computational studies**

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Chemical functionalization of carbon nanostructures, particularly carbon nanotubes (CNTs), modifies their physical and chemical properties and improves their performance for specific applications. Theoretical modeling of such molecular adsorption on the CNTs surfaces is a powerful tool that allows predicting some important properties of materials perspective for mentioned use. Nanocomposite materials based on cellulose and carbon nanostructures are actively studied at present as perspective multi-functional, particularly, optical materials [1]. Despite intensive studies, several key problems regarding the peculiarities of the interaction of the components of nanocomposites "cellulose-CNTs" still remain unsolved. This work aims to clarify such questions using computational research methods.

This work presents computational studies of interaction of cellulose molecular clusters with carbon nanostructured materials - carbon nanotubes and graphene. The studies are carried out in form of calculations of the electronic structure performed by the quantum chemical method in the DFT approximation [2]. The calculations revealed the mechanisms of adsorption of molecular cellulose on the surface of carbon nanotubes CNT(5,5) and single-layered graphene sheets, both bare and doped with boron or nitrogen. Binding energies and inter-nuclear distances between adsorption components were calculated and analyzed

Calculations showed no covalent interatomic bonds between cellulose molecules and the surface of undoped CNTs. Interaction of cellulose molecules with graphene surface should be more pronounced if compared to the case of nanotube surface because the obtained interatomic distances between cellulose and graphene atoms are significantly shorter. These data were analyzed in comparison with experimental data obtained from diffuse reflection and photoluminescence measurements performed under "nanocellulose"-graphene" nanocomposites

Calculation results were discussed in view of the possible influence of doping and surface functionalization of carbon nanostructures on cellulose optical (light absorption) characteristics.

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## Computational studies of atomic and electronic structures of luminescent phosphate glasses and glass-ceramics

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The computational materials design has been regarded as powerful tool for developing of new materials, in particular composite ones [1]. Interphases regions in glass-ceramic composites are formed by mutual interaction between crystalline and amorphous phases due to diffusion processes. Such regions can reveal unique physical properties those hard to predict. Currently molecular dynamics (MD) methods allow obtaining of atomic structure of the composite. This atomic structure can be used as input for ab-initio calculation methods for obtaining the mechanical, electrical and optical properties of composite materials.

Computational studies of the atomic and electronic structures of glasses and crystal-glass interfaces were carried out using computational programs of Materials Studio 2019 software package [2]. Two types of phosphate glasses of  $K_2O-P_2O_5-MoO_3-Bi_2O_3$  and  $K_2O-P_2O_5-WO_3-VO_3$  compositions were studied. The  $KBi(MoO_4)_2$  and  $K_2Eu(PO_4)(WO_4)$  polycrystals were used as crystalline components for glass-ceramics simulations in molybdenum and tungsten-containing vitreous systems, respectively. The atomic structures of glasses and interfaces were calculated by MD methods implemented in Amorphous Cell and Forcite programs. The electronic structure calculations were performed in the DFT approximation using the band-periodic plane wave pseudopotential method CASTEP, for which the cells of smaller sizes were used. The partial densities of states, spatial distributions of electron densities were calculated with use of GGA-PBE exchange-correlation functional. Calculations of the excited electronic states energies and optical absorption spectra of particular oxyanionic molecular groups of interface regions were performed by the TD-DFT method with use of Gaussian program.

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## Spectroscopy of the lithium-vanadate-borate luminescent glass and glass-ceramics

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Oxide-based glass-ceramics (GCs) are promising class of solid state materials since they consist of thermally stable and chemically inert oxide glass matrix which can be filled with oxide micro or nanosized crystalline particles. One of the oxide starting components of the developed glass matrix should be boron oxide,  $B_2O_3$ , because it is one of the best well known glass-forming oxides. Addition of some network modifiers to boron oxide, usually alkali oxides, improves mechanical properties of the glass. In our work we use lithium oxide as the second glass-forming component. An advantage of some recently developed glass-ceramic materials is, as well, be an ability of glass matrix to emit own luminescence radiation. Some of the borate glass are able to emit intensive own luminescence. The lithium-vanadate-borate glasses are among them. Understanding of processes responsible for luminescence excitation and emission in such glass is very important to study of glass-ceramics amorphous and crystal phases interaction as such type materials can be used for creation of luminescent covers for WLEDs elaboration.

A series of lithium-vanadate-borate glass samples of  $xLi_2O-yV_2O_5-(100-x-y)B_2O_3$  composition was synthesized using the melt quenching procedure. Phase compositions of the synthesized samples were studied using a Philips X'Pert Pro Alpha1 diffractometer. Absorption spectra were measured using a Varian Cary-5000 spectrometer. Luminescence properties were studied using a Horiba Fluorolog-3 spectrofluorometer. The XRD analysis has confirmed that obtained samples are amorphous as it is indicated by a broad XRD bump located around  $2\theta = 21-23^\circ$  and a less intense broad bump around  $2\theta = 45^\circ$ . Absorption spectra of the glass matrix consist of the main wide band with maxima positions located near 3.9 eV for the sample with the lowest  $Li_2O$  concentration and shifting to 4.1 eV for the sample with the highest  $Li_2O$  concentration. The spectra showed also long wavelength shoulder near 3.5 eV and less intensive band at 2.65 eV, the intensity of these bands is found to decrease with increase of  $Li_2O$  content. The UV excited glasses of low  $Li_2O$  content showed luminescence in the wide 1.6 – 3.1 eV spectral range with the main maximum located near 2.4 eV and two weakly resolved long-wavelength bands. Adding of the  $LaVO_4:RE$  ( $RE = Eu, Sm$ ) nanoparticles to the glass compositions led to glass-ceramics formation which manifest linear emission spectra caused by  $f-f$  transitions in  $Eu^{3+}$  or  $Sm^{3+}$  ions. It was supposed that wideband glass emission is associated with the radiation transitions in the vanadate groups and recombination of self-localized holes on bridge oxygen between the  $(BO_4)^4-$  and  $(BO_3)^{3-}$  groups.

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## Optical and structural properties of $\text{Eu}^{3+}/\text{Ce}^{3+}$ doped Y-Al-O compounds grown by energy-saving microwave driven hydrothermal technique

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Rare-earth (RE) doped Y-Al-O compounds have been drawing large attention due to their optical and photovoltaic properties. Recently it has been shown that RE doped ceramic nanopowder can be very efficient at absorbing light and enable the construction of smaller and cheaper devices to capture the same amount of solar energy compared to conventional absorbers [1].

At present, many methods of obtaining nanomaterials require high vacuum, very high temperature and high purity of reagents to ensure crystals of sufficiently good quality [2]. Considering the growing use of nanomaterials, more research on quick, cheap and simple methods of their production is being conducted. Among the fast and relatively cheap growth techniques, the microwave driven hydrothermal method is a very promising way to yttrium aluminum oxide nanopowders production.

The work presents the study of structural and optical properties of Y-Al-O compounds doped with europium or cerium, synthesized as nanopowders using microwave driven hydrothermal technique. It is shown that the selection of appropriate growth parameters allows to control of the content of pure phases of yttrium aluminum garnet, yttrium aluminum perovskite or yttrium aluminum monoclinic in the obtained nanopowders and to minimize the presence of other parasitic phases.

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## Revealing trace amounts of xenobiotics in the friction ridge analysis by Raman spectroscopy

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Fingerprints from a crime scene are often a key piece of evidence for us and a source of much information. They allow us to identify the person to whom they belong, mainly through minutiae analysis. However, these traces provide us with much more information than our identity. The result of the research clearly shows that, if the right parameters are chosen, it is possible to identify the substance with which the person leaving the traces came into contact.

The widespread and easy availability of over-the-counter xenobiotics results in the uncontrolled use of many drugs with serious health complications. Paracetamol, as one such substance, is an example of both conscious and unconscious overdose, but also of serious liver damage associated with unconscious consumption in wrong doses, which ultimately can also lead to failure and death [1,2].

This work presents a preliminary study on the analysis of low concentrations of paracetamol from various producers in the fingerprint traces using Raman spectroscopy.

This research was supported by the grant: 2021/41/B/HS5/03250 (K.W., A.L., M.Cz.) financed by National Science Centre.

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## Optical properties of red-emitting long afterglow phosphor $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x\text{O}_4$ : Mn material

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The persistent luminescence, sometimes called afterglow luminescence and long-lasting phosphorescence, is a process characterized by emission of light for a long period of time, usually tens of minutes or more after the removal of the excitation source, that has aroused widespread interest among scientists and industry for the past two decades. Currently in the literature it is possible to find several hundred combinations of materials and activators that exhibit persistent luminescence, however vast majority of studies are devoted to persistent luminescence processes in materials with emission in the blue and green spectral range, while the number of publications on the afterglow in the red and near-infrared spectral range is considerably lower.

In the course of this work  $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x\text{O}_4$  ( $x = 0.0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0$ ) materials doped with 0.1 mol% Mn were produced using solid state reaction synthesis in ambient atmosphere.

Photoluminescence and subsequent persistent luminescence of manganese ions in the red spectral region have been observed for over 16 h in the case of the best persistent phosphor -  $\text{Mg}_2\text{Si}_{0.1}\text{Ge}_{0.9}\text{O}_4$ : Mn. It was concluded that although both  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  are present in samples, persistent luminescence originates from  $\text{Mn}^{2+}$ , thus broad band emission between 600 – 800 nm with maximum around 650 nm. In-depth analysis of thermally stimulated luminescence measurements showed that there are three distinct trap centres with trap depth values  $E1 = 0.87$  eV,  $E2 = 0.99$  eV and  $E4 = 1.84$  eV. Between  $E2$  and  $E4$  a quasi-continuous distribution of closely overlapping trap levels appear.

Summarizing the results, conclusions were drawn about the processes of long persistent luminescence of  $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x\text{O}_4$  ( $x = 0.0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0$ ) materials doped with 0.1 mol% Mn.

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## Size-dependent photon avalanching in Tm<sup>3+</sup> doped LiYF<sub>4</sub> nano, micro and bulk crystals

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Among different upconversion processes, the Photon Avalanche (PA) is exceptional, due to very non-linear increase of luminescence intensity during minute rise of pump power density. Initially PA emission was reported in lanthanide (e.g. Pr<sup>3+</sup>, Ho<sup>3+</sup>, Tm<sup>3+</sup>, Er<sup>3+</sup>) doped bulk materials and fibers [1]. Only recently the PA was observed in nanocrystals NaYF<sub>4</sub> doped with Tm<sup>3+</sup> ions [2] as well as in NaYF<sub>4</sub> nanoparticles co-doped with Yb<sup>3+</sup> and Pr<sup>3+</sup>, Tm<sup>3+</sup> or Ho<sup>3+</sup> ions [3]. Due to wide application potential of PA, it is very interesting to study and understand the role of size and surface of crystals impact on the PA features. Therefore, in this work we investigated materials of the same composition in different sizes. Namely, we compared LiYF<sub>4</sub> bulk single crystal doped with 3% of Tm<sup>3+</sup> [4], with corresponding microcrystals and two types of nanocrystals – i.e. core and core-passive shell, having the same composition. Additionally, we prepared LiYF<sub>4</sub> microcrystals, core nanocrystals and core-passive shell nanocrystals doped with 8% of Tm<sup>3+</sup> ions, because this amount of doping was previously reported as an optimal for PA occurrence [2]. In all samples, PA emission at 475 and 800 nm was observed and PA threshold was decreasing with increase of crystal size. Theoretical simulations performed, provided an understanding of the physical processes that affect PA performance. In addition, the novelty of the work is photon avalanche single beam super-resolution imaging (PASI), which was realized in LiYF<sub>4</sub> core-shell nanoparticles doped with 3% of Tm<sup>3+</sup> ions. The presented results provide a solid foundation for further development and applications of new optimized PA materials.

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## The ab-initio study of the Dy(III)-EDTA single ion magnet in various environments: the influence of the structural changes on the spectroscopic and magnetic properties

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The rise of the interest in the Lanthanide--based SMMs (Single Molecule Magnets) and SIMs (Single Ion Magnets) can be associated with the fact that these materials show a premise of many possible applications, namely: in quantum information processing; as MRI contrast agents; as molecular spintronic and high density data storage devices. The main challenge in this field is to design a SIM material in a way that will improve its magnetic performance and help keep its magnetization in higher temperatures.

The structure surrounding the Lanthanide ion influences its magnetic anisotropy and when the anisotropy changes then the magnetic properties also change. We have explored several structure models based on Dy(III)-EDTA SIM in order to investigate how the spectroscopic and magnetic properties of a cluster can be affected by the molecules of a certain solvent in the second coordination sphere and by the neighbor clusters that surround the molecule under study.

We compare the theoretical calculations based on the ab-initio methods with the experimental data. The experiments and theoretical calculations for all the structure models have been performed at many different ranges of temperatures and for diverse magnetic fields to better understand the magnetic behavior of the studied materials in various environments. We discuss the crucial role of choosing an adequate solvent in designing molecular magnets and how the solvent influences the effective energy barrier for the magnetization reversal and most of all - how the right solvent can enhance the performance of a given molecular magnet. We also explore how high pressure affects the magnetic performance of the Dy(III)-EDTA complex.

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## **Mechanoluminescence based approach to mechanical stress visualisation of additively manufactured (3D printed) parts**

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Mechanical parts are manufactured using 3D printing. Parts intended for difficult applications must go through one of the most critical processes in complicated part design: stress-strain analysis, which is time-consuming and requires a lot of knowledge. We investigated a new method for spatial stress analysis of printed mechanical parts in this study. A 3D printed photopolymer sample containing SrAl<sub>2</sub>O<sub>4</sub>:Eu, Dy particles is evaluated, and a data processing approach for spatial stress mapping is proposed. The empirical stress distribution maps have been shown to match the computed stress distribution and can thus be improved further for technological applications, providing a useful supplement to computational stress-strain analysis. It enables the evaluation of complex unequal forces on complex parts in real-time.

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## Red-emitting $\text{Ba}_2\text{Y}_5\text{B}_5\text{O}_{17}:\text{Eu}^{3+}$ phosphors with efficiencies close to unity for Near-UV LEDs

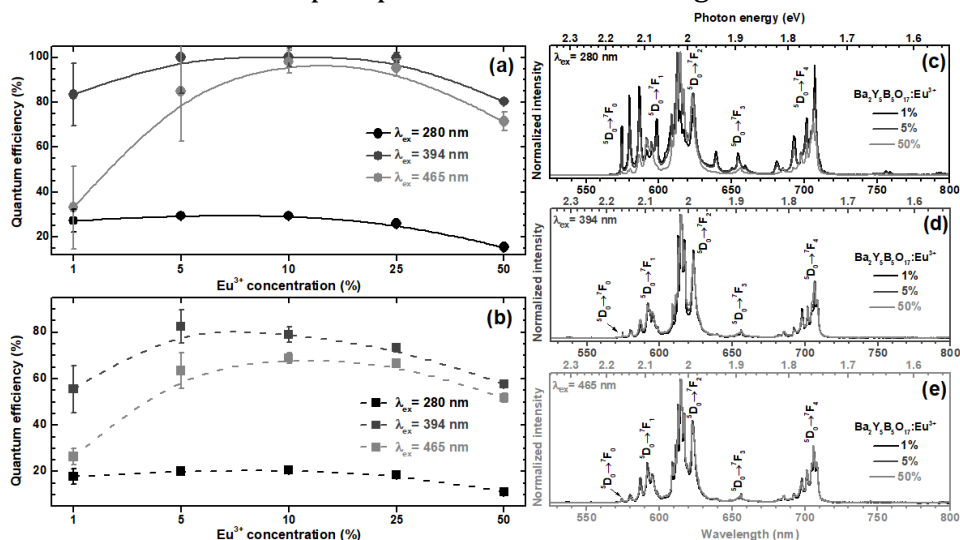
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To improve the luminous efficacy of near-UV LEDs, different red line emitting  $\text{Eu}^{3+}$ -doped phosphors are being investigated as they distinguish themselves as the best compromise between luminous efficacy and colour rendering [1].

Phase pure  $\text{Ba}_2\text{Y}_5\text{B}_5\text{O}_{17}:\text{Eu}^{3+}$  phosphors emitting in the red spectral area (Fig. 1. (c-e)) were synthesized via high-temperature solid-state reaction [2]. Fig. 1. (a, b) reveals that several samples in the synthesized series demonstrate quantum efficiency (QE) close to 100% (the “effective” QE values were as high as 80% (emission range 500-650 nm)).

X-ray diffraction patterns, reflection, excitation, temperature-dependent emission spectra, photoluminescence (PL) decay curves, PL lifetime values, CIE 1931 colour space coordinates of  $\text{Ba}_2\text{Y}_5\text{B}_5\text{O}_{17}:\text{Eu}^{3+}$  phosphors were also investigated and will be discussed.



**Fig. 1.** Quantum efficiencies of  $\text{Ba}_2\text{Y}_5\text{B}_5\text{O}_{17}:\text{Eu}^{3+}$  samples as a function of  $\text{Eu}^{3+}$  concentration and excitation wavelength for 500–800 nm range (a) and 500–650 nm range (b). Emission spectra of 1%, 5% and 50%  $\text{Eu}^{3+}$ -doped specimens under 280 nm (c), 394 nm (d), and 465 nm (e) excitation.

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## **Heating the discussion on losses in persistent phosphors: An attempt to quantify non-radiative losses from a set of TL-measurements**

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Persistent phosphors are special types of luminescent materials that have the distinctive ability to continue emitting light long after excitation has ceased. Beyond their current applications as safety signage and glow-in-the-dark toys, their potential use as glowing road marks [1], and in areas of dosimetry [2] and in-vivo imaging are also being investigated. In order for the material to act as such an optical battery, it must have special defects, so-called traps, where the energy can be stored for a certain amount of time. However, a large amount of these trapped charges never result in the emission of a photon, hinting at losses in the material that are not well understood. For the most part, the evaluation of persistent phosphors focuses on the emission spectrum, the afterglow decay curve, and the total duration of persistent luminescence. These measurements, however, do not allow insight into these losses, let alone explain them. To gain a more detailed understanding of the losses we propose to use a well-chosen, standardized set of thermoluminescence measurements that can be compared to a simple model, to give insight in the underlying mechanisms. This way it becomes possible to start unravelling the nature of the losses and we can attempt to decouple them into losses of trapped charges and losses at the activator ion.

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## Growth and luminescent properties of undoped and rare-earth doped $\text{MgAl}_2\text{O}_4$ single crystalline films

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This work is devoted to the search for new luminescent materials that can be obtained in the single crystalline film (SCF) form using Liquid Phase Epitaxy (LPE) growth method. Magnesium aluminate spinel  $\text{MgAl}_2\text{O}_4$  is a synthetic material with cubic crystal structure and excellent chemical, thermal, dielectric, mechanical and optical properties. The possibility of growing high-quality  $\text{MgAl}_2\text{O}_4$  single crystals (SCs) and SCF films has triggered a great interest on this material, as a very promising candidate for applications in deferent areas such as materials for optically transparent windows, domes and armors, and for certain refractory applications [1].

The first results on growth of the undoped and rare earth ( $\text{RE} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Eu}^{3+}$ ) doped  $\text{MgAl}_2\text{O}_4$  SCFs by the LPE method onto  $\text{MgAl}_2\text{O}_4$  substrates from  $\text{PbO-B}_2\text{O}_3$  flux are reported in this work. Substrates were obtained from undoped  $\text{MgAl}_2\text{O}_4$  crystals grown by the Horizontally Directed Crystallization method. Typically SCFs of oxide compounds, grown from  $\text{PbO}$  based flux, contain  $\text{Pb}^{2+}$  ions, which act as the luminescent and trapping centers in these materials [2]. Therefore, significant influence of these flux-related ions on optical properties in the undoped and RE doped  $\text{MgAl}_2\text{O}_4$  SCFs is expected as well.

The optical properties of undoped and RE doped  $\text{MgAl}_2\text{O}_4$  SCFs were studied using conventional spectral technique such as the absorption, cathodoluminescence and photoluminescence spectra in comparison with the properties of reference  $\text{MgAl}_2\text{O}_4$  substrates. The luminescent properties of nominally undoped  $\text{MgAl}_2\text{O}_4$  crystals and SCFs at 10 K were also compared using synchrotron radiation excitation with energy in the 3.6-25 eV range. The results were discussed in the frame of influence of RE ions and lead ions on the intrinsic luminescence centers of  $\text{MgAl}_2\text{O}_4$  host.

This work was performed in the frame of Polish NCN 2018/31/B/ST8/03390 projects.

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## The influence of synthesis conditions on the reduction of $\text{Eu}^{3+}$ incorporated into $\text{CaMgSi}_{2-x}\text{Al}_x\text{O}_6$ matrix

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The purpose of the research is to explain the influence of the diffusion process of the chemical species in a solid state on the reduction process of the  $\text{Eu}^{3+}$  ions in  $\text{CaMgSi}_2\text{O}_6$  matrix codoped with  $\text{Al}^{3+}$ . When a calcium ions ( $\text{Ca}^{2+}$ ) are replaced by  $\text{Eu}^{3+}$  ions, a positively charged defect related to the  $\text{Eu}_{\text{Ca}}^{\bullet}$  is formed. Due to the principle of electroneutrality, such a substitution demands that a compensating defect is created to counterbalance the excess positive charge. One of the naturally occurring compensating defects is a negatively charged metal vacancy, e.g.  $V_{\text{Ca}}''$  due to the low formation energy. Besides the naturally occurring compensators, it is also possible to modify the matrix in order to induce the creation of the so-called chemically induced compensating defect (in this case:  $\text{Al}_{\text{Si}}'$ ).

The reduction process is generally connected with an electron uptake by a given chemical species ( $\text{Eu}^{3+}$  in this case). However, some results suggest that the presence of additional electrons is a necessary but insufficient condition for the reduction process to take place in solid state. Another condition is connected with eliminating a formerly created compensator of  $\text{Ln}_{\text{Me}}^{\bullet}$  defect from the immediate surroundings of the reduced lanthanide ion [4, 5]. The given compensator can be eliminated either by creating another defect in the vicinity of the original compensator (a secondary compensator) or by physically removing the former compensator via its migration in the crystal lattice from the reduced lanthanide ion to the crystal surface. In order to describe both options it is necessary to consider the effect a diffusion process during the reduction of a lanthanide (the rate of defects migration depends on the type of compensator and is the greatest for  $V_{\text{Ca}}''$  defect, which can move freely to the surface of the matrix, compared with  $\text{Al}_{\text{Si}}'$  defects).

In this contribution the influence of different concentration of flux, such as  $\text{H}_3\text{BO}_3$ , different methods and conditions of  $\text{CaMgSi}_2\text{O}_6$  synthesis on the reduction as well as sites occupancy of  $\text{Eu}^{3+}$  will be shown.

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# Optical properties investigation of upconverting $\text{K}_2\text{Gd}(\text{PO}_4)(\text{WO}_4):20\%\text{Yb}^{3+},\text{Ho}^{3+}$ phosphors

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The up-conversion (UC) is a process when materials are excited with two or more low-energy photons, usually from laser excitation, and emit higher energy photons. This research represents a new inorganic  $\text{K}_2\text{Gd}(\text{PO}_4)(\text{WO}_4):20\%\text{Yb}^{3+}$  matrix doped with  $\text{Ho}^{3+}$ . These materials show typical  $\text{Ho}^{3+}$  emission spectra when excited with 980 nm (laser) radiation. The most intense emission line was observed in the red spectral region and attributed to the  $^5\text{F}_5 \rightarrow ^5\text{I}_8$  transition (see Fig. 1). The 0.5%  $\text{Ho}^{3+}$  doped sample showed the highest emission intensity. The overall emission intensity gradually decreases with increasing  $\text{Ho}^{3+}$  concentration (see inset of Fig. 1).

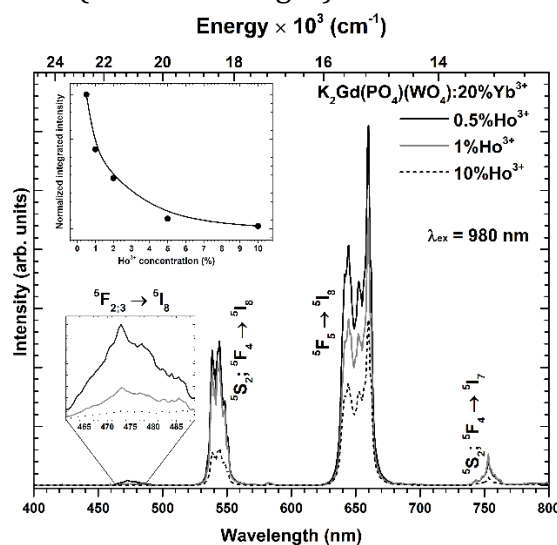


Fig. 1 Upconversion emission spectra of  $\text{K}_2\text{Gd}(\text{PO}_4)(\text{WO}_4):20\%\text{Yb}^{3+}$  as a function of  $\text{Ho}^{3+}$  concentration under 980 nm excitation. The inset shows normalized integrated upconversion emission intensity.

The obtained phosphors' optical properties (room temperature excitation, emission, and reflection spectra; temperature-dependent emission spectra and, PL decay curves) will be discussed during the presentation.

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## Electronic structure of Mn-related defects in $\text{YAlO}_3$ crystals

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The yttrium aluminium perovskite  $\text{YAlO}_3$  is a well-known host for luminescent ions. Such crystals are intensively studied at present as optical materials for laser and scintillation techniques [1]. The Mn-doped  $\text{YAlO}_3$  crystals attract particular research interest due to their potential application in holographic recording and optical data storage, as well as in dosimetry of ionizing radiation with the use of thermally (TSL) or optically stimulated (OSL) luminescence [2]. Manganese ions in  $\text{YAlO}_3\text{:Mn}$  crystals can be present in the form of  $\text{Mn}^{4+}$  ions in octahedral coordination ( $\text{Al}^{3+}$  sites) as well as  $\text{Mn}^{2+}$  ions are in strongly distorted dodecahedral coordination ( $\text{Y}^{3+}$  sites). Despite a large volume of accumulated experimental data on optical and TSL properties of  $\text{YAlO}_3\text{:Mn}$ ,  $\text{YAlO}_3\text{:Mn,Si}$  and  $\text{YAlO}_3\text{:Mn,Hf}$  crystals the mechanisms of charge transfer processes in Mn-doped  $\text{YAlO}_3$  require deeper understanding.

In this work, the results of computational studies of the electronic structure of a wide set of point defects related to Mn substitutions in  $\text{YAlO}_3$  perovskite crystal are presented. The calculations are carried out by the band-periodic DFT-based Plane-Wave Pseudopotential method. Geometry-optimized spin-polarized calculations with various exchange-correlation functionals were applied to  $(2 \times 2 \times 2)$  super-cells of  $\text{YAlO}_3$ . Several single- and multi-node point defects like  $\text{Mn}_{\text{Al}}$ ,  $\text{Mn}_{\text{Y}}$ ,  $\text{Mn}_{\text{Al}} + \text{Mn}_{\text{Y}}$ ,  $\text{Mn}_{\text{Al}} + \text{Hf}_{\text{Y}}$ ,  $\text{Mn}_{\text{Y}} + \text{Si}_{\text{Al}}$ ,  $\text{Mn}_{\text{Y}} + \text{V}_{\text{O}}$  and  $\text{Mn}_{\text{Y}} + \text{V}_{\text{O}} + \text{V}_{\text{Al}}$  were modelled in the super-cells. The partial densities of states, spatial distributions of the electronic charges, and energy depths of the defect levels with respect to the band edges are calculated. Results of the calculations are analysed against existing experimental data on ESR, TSL, optical absorption, and photoluminescence of Mn-doped  $\text{YAlO}_3$  crystals.

The results of the calculations are analyzed in the context of a possible role of Mn ions in charge trapping processes in the  $\text{YAlO}_3$  perovskite crystal. The discussion is related to, in particular, the nature of charge carrier traps which determine the TSL glow curves of  $\text{YAlO}_3\text{:Mn}$  crystals, the possible charge states of Mn dopants in  $\text{YAlO}_3$  host, and the main peculiarities of trapping and recombination processes in  $\text{YAlO}_3\text{:Mn}^{2+}$  crystals.

The work was supported by the Polish National Science Centre (project no. 2018/31/B/ST8/00774).

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## Photophysical properties and heavy atom effect donor-acceptor structures based on phenazines

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Thermally activated delayed fluorescence is based on a spin-flip from excited triplet to singlet state followed by light emission. There are few features of TADF which make this phenomenon of high applicative potential in various fields. Apart from the widely explored possibility of efficient harvesting of triplet excitons generated under electric excitation for application in organic light emitting diodes (OLEDs), TADF emitters offer very long lifetimes of emission reaching milliseconds and seconds. This is particularly useful for time-gated fluorescence imaging (TGFI), a rapidly evolving, technically simple, and relatively cheap imaging technique for highly sensitive biological and biochemical analyses [1].

Dyes suitable for TGFI should fulfill the following requirements: long lifetime of emission, high photoluminescence quantum yield, photostability and water solubility. Most of TADF emitters follow the above mentioned requirements, but are completely insoluble and non-emissive in water. To face this problem, we investigated red phenazine-based TADF emitters in water micelles. To further elongate the emissive heavy atom effect was applied via chemical modification of the emitter.

To compare external and internal heavy-atom effect, different types of hosts were used to separate dye-molecules embedded in micelles. The main task was to optimize parameters of each component, namely select an appropriate host and surfactant, regarding the best emission efficiency and/or the heavy atom effect.

To describe steady-state properties the absorption and emission spectra were measured. The obtained water solutions show strong UV and visible absorption, and red TADF. Basic photophysical parameters were also investigated using time-resolved measurements. Our results indicate high potential of the investigated emitters for TGFI.

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## Investigations of the donor effects in organic blue thermally activated delayed fluorescence emitters

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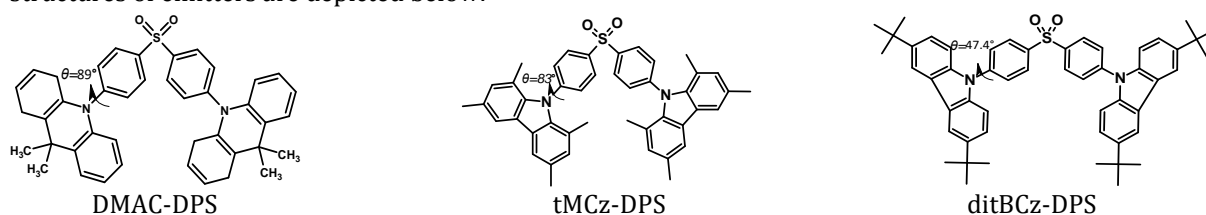
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Thermally Activated Delayed Fluorescence (TADF) emitters, is a relatively new class of OLED materials that promise efficient and long-lifetime performance without any heavy metals. The TADF emitters' research started in 2012, and their first commercial status appeared in 2019.

In our work, we focused on the study of the most demanded blue TADF emitters. Finding efficient and long-lasting blue emitter will allow to solve the main problem of OLED technology. The most efficient TADF emitters have donor-acceptor structure and are based on charge transfer (CT) effect from the lowest excited singlet <sup>1</sup>CT and triplet <sup>3</sup>CT to unexcited state S<sub>0</sub>. Strong CT character of electronic transitions enables efficient conversion of "dark" triplet excitons to emissive singlet excitons in OLEDs[1]. The ideal TADF emitter thus should make such a conversion fast and maintain high fluorescence quantum yield. For this, two main parameters should be reached: (i) high value of reverse intersystem crossing rate constant ( $k_{\text{rISC}}$ ) and (ii) high radiative rate constant ( $k_{\text{r}}$ ). High value of  $k_{\text{rISC}}$  enables conversion of <sup>3</sup>CT state to <sup>1</sup>CT. On the other hand, high value of  $k_{\text{r}}$  will allow to increase fluorescent quantum yield on the way of radiative deactivation.

The main dilemma of TADF molecular design is that the increase of one of the latter parameters causes the decrease of another one. It was found that the dihedral angle ( $\theta$ ) between the donor and acceptor is the main structural parameter which defines  $k_{\text{rISC}}$  and  $k_{\text{r}}$ . In the search of the "golden mean" of satisfactory  $k_{\text{rISC}}$  and  $k_{\text{r}}$ , we designed diphenylsulphone (DPS) emitters with donors of different sizes and thus different value of  $\theta$  angle. Various carbazole (Cz) and 9,10-dihydroacridine (DMAC) donors were investigated. The structures of emitters are depicted below:



Absorption, steady state and time-resolved fluorescence measurements supported by quantum-chemical calculations enabled complete photophysical characterization of emitters. The conducted research affords a compromise between  $k_{\text{rISC}}$  and  $k_{\text{r}}$  basing of the optimal donor-acceptor structure.

Research financed by the National Science Center under the SONATA 16 project, contract number UMO-2020/39/D/ST5/03094. Quantum-chemical calculations were carried out with the use of computers of the Wrocław Center for Networking and Supercomputing (WCSS).

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## Novel handheld system for friction-induced mechanoluminescence measurement

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We present the purpose-built, novel, simple, and effective measuring apparatus for friction-induced mechanoluminescence. Before the ML experiment sample is irradiated with a chosen wavelength and for a given time and a mechanically induced emission signal is realized by dragging a rod across the sample layer. The irradiation time, the force with which the rod is pressed to the sample, and the parameters of the rod movement (such as the range of motion, speed, repetition frequency) are controlled and recorded using the dedicated custom-made software. The mechanoluminescence signal is acquired in the whole luminescence spectral range using Schamrock 500 spectrometer with TEC camera iDus420 (Andor Technology). Repeatability of exposure time, waiting time after irradiation, mechanoluminescence generation, and camera synchronization with a sample plate and a rod movement is provided by a hand-made mechanical system controlled by a computer with the LabView environment. The capabilities and limitations of the setup were tested using the commercial ML powders, namely  $\text{SrAl}_2\text{O}_4\text{:Eu}$ , Dy and  $\text{Sr}_{0.95}\text{Ca}_{0.05}(\text{SO}_4)\text{:Mn}$ .

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## Unexpected behavior of $\text{Eu}^{2+}$ and $\text{Ce}^{3+}$ in AlN under high pressure

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With the growing need of finding a way to produce an energetically efficient light source that is a white light emitting diode (WLED), nitride phosphors have again taken on significance. Among them, AlN with its wide band gap, high thermal conductivity, and high stability, when doped with lanthanide ions is a suitable candidate.<sup>1,2</sup> Appropriate spectroscopy measurements had been performed.

High-pressure spectroscopy measurements show an unusual difference in results between AlN: $\text{Ce}^{3+}$  and AlN: $\text{Eu}^{2+}$ . Both ions exhibit emission caused by d-f transitions ( $5d^1 \rightarrow 4f^7$  for AlN: $\text{Eu}^{2+}$  and  $5d^1 \rightarrow {}^2F_{5/2}$  for AlN: $\text{Ce}^{3+}$ ). The emission and excitation spectra measurements under pressure allowed for a calculation of the pressure induced shift rate:  $dS\hbar\omega/dP$  is  $1.36 \text{ cm}^{-1}/\text{kbar}$  for AlN: $\text{Eu}^{2+}$  and  $-5.49 \text{ cm}^{-1}/\text{kbar}$  for AlN: $\text{Ce}^{3+}$ . This allowed for a calculation of the  $K_Q$  parameter.<sup>3</sup> Additionally, temperature dependent emission spectra were measured. It showed familiar PL intensity and FWHM trends for AlN: $\text{Eu}^{2+}$ , when the ones for AlN: $\text{Ce}^{3+}$  were rather unusual. Finally, kinetic luminescence measurements were performed where AlN: $\text{Eu}^{2+}$  decay times behaved differently than AlN: $\text{Ce}^{3+}$ .

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## Microwave hydrothermal synthesis of ZnO:Eu, Mg nanoparticles for supplementation of magnesium

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Microwave hydrothermal synthesis of nanoparticles allow to obtain crystals with narrow distribution of sizes. It opens the opportunity to employ it in supplementation of magnesium. Our former attempts of elements supplementation in animals were successful in the case of iron [1, 2]. Zinc oxide nanoparticles were found to be absorbed in the living organism with oral administration. Also it was found to cross the barriers in animals [3].

In present work we show the route of nanoparticulate ZnO:Mg synthesis. Additional samples were prepared where ZnO:Mg nanoparticles were codoped with Eu<sup>3+</sup> ions performing as indicator of local structure in material. Samples were prepared using zinc chloride, zinc acetate, zinc nitrate(V) dihydrate and zinc nitrate(V) anhydrous as zinc sources. As magnesium sources magnesium chloride hexahydrate and magnesium nitrate(V) hexahydrate were used. Various combinations of substrates were used to obtain the highest remaining magnesium concentration in the final material. Samples containing 1, 5, 10 and 20 molar % of magnesium were prepared. Structural properties of resulting nanomaterials were measured using XRD, SEM and EDX methods. Luminescence properties of ZnO nanoparticles were determined using ultraviolet and electron beam excitation to find defect properties of the nanocrystals.

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## All-inorganic lead perovskites: single synthesis – multicolor emission

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Recently, halide perovskites have become one of the most promising solar cell materials due to their outstanding photoelectric performance. Among them, all-inorganic metal halide perovskites ( $\text{CsPbX}_3$ ; where X denotes a halogen) show superior thermal and photo stability [1]. Numerous publications related to all-inorganic perovskite synthesis and application show the importance of such unique materials in applied sciences [2]. Thus the development of new synthetic approaches to obtain such particles and/or improve their optical properties is essential.

In this study, we present the ability to generate multicolor emission via post-synthesis surface modification of perovskite QDs obtained from a single synthesis. The obtained results are summarized in Figure 1.

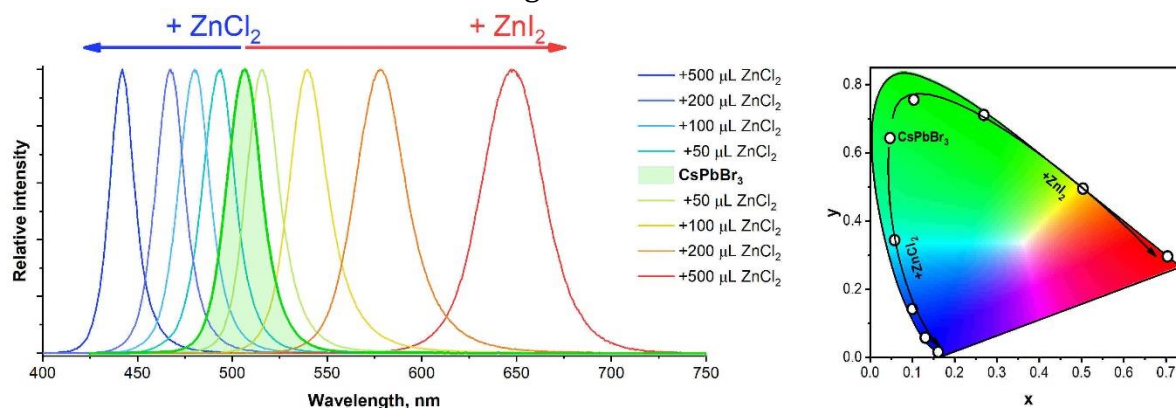


Figure 1. Emission spectra (a) and change of color coordinates, presented in CIE 1931 color space diagram (b) of  $\text{CsPbBr}_3$  QDs before and after treatment using zinc halogenides.

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## Yb<sup>3+</sup> doped titanate-germanate glasses for near-IR luminescence applications

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Ytterbium-doped inorganic glasses, due to optical properties have attracted a great interest for their suitability for laser and optical amplifier applications [1]. Spectroscopic changes of near-IR emission band corresponding to  $^2F_{5/2} \rightarrow ^2F_{7/2}$  transition of Yb<sup>3+</sup> ions will be dependent on glass-host matrices containing various network-formers and network-modifiers [2]. As experimentally verified, TiO<sub>2</sub> depending on its concentration has the positive effect on luminescence properties of rare-earth ions [3]. It paves the way to fabricate and study the spectroscopic properties of Yb<sup>3+</sup> doped barium gallo-germanate glasses modified by TiO<sub>2</sub>.

Here, we demonstrate that the spectral linewidths for near-infrared luminescence band at 1030 nm associated with the  $^2F_{5/2} \rightarrow ^2F_{7/2}$  transition of Yb<sup>3+</sup> are influenced by quantitative relationship between GeO<sub>2</sub> and TiO<sub>2</sub>. Furthermore, the main luminescence band is enhanced significantly in the presence of TiO<sub>2</sub>. The presented research may be important in terms of potential luminescence applications in the near-infrared range. Hence, our preliminary spectroscopic results concerning on near-infrared luminescence properties of titanate-germanate glasses doped with Yb<sup>3+</sup> ions will be continued and discussed in details.

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## **Tailoring of the optical properties in the Cu-based plasmonic platforms**

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Throughout the last several years, metallic nanostructures have gained the attention of many researchers due to the localized surface plasmon resonance that induces their exceptional optical properties and opens up a wide range of applications in many fields, e.g. photovoltaics, detection, information technology, photocatalysis, and spectroscopy techniques. Due to its unreactive nature, and hence the easiest fabrication process, most of the previously conducted studies focused on Au. However, increasing interest in tuning optical properties led to different metals examination and different synthesis methods incorporation. For instance, recently, bimetallic nanostructures become increasingly intriguing thanks to their unique properties shaped by synergistic effects. Since the Cu interconnect has replaced Al technology in high-performance Si microelectronic devices, it became quite straightforward to anticipate their dominance until some new paradigm is developed [1]. On the other hand, one of the well-established methods for plasmonic platform creation is solid-state dewetting, a process through which thin metallic film agglomerates in the form of isolated islands, decreasing the surface to volume ratio, and hence minimalizing the free energy of the system. Generally, dewetting progresses through hole formation followed by their growth until the whole film translates into islands [2]. Only a few studies on the dewetting of thin metallic films have paid attention to Cu, and hence fundamental information about the dewetting of Cu films is yet not fully understood.

In the present work, monometallic Cu, and bimetallic AuCu/AgCu plasmonic platforms have been successfully obtained through the dewetting process of nanometer-thin layers. As prepared films were annealed in temperatures well below the melting temperatures of used metals. The surface morphology of prepared plasmonic platforms was investigated by means of SEM, while its plasmonic quality was reflected in the UV-vis absorption spectra.

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## Electronic structure calculations of $\text{CaF}_2\text{:Th}$

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The radioisotope  $^{229}\text{Th}$  has low-energy isomeric state with a transition energy of 8.3 eV (which corresponds to transition in vacuum UV) and an expected lifetime of 5 h [1]. That means there is a possibility that nuclear levels will couple to electronic ones. If the electronic transitions are allowed one can manipulate nuclear levels via “electron bridge”. Therefore knowledge of the electronic structure of a thorium activated material is of great importance for applications in nuclear clocks. Here we will discuss preliminary results of ab-initio calculations of the electronic structure of  $\text{CaF}_2\text{:Th}$ . We use AIMP embedding potentials to model thorium ion in a  $\text{CaF}_2$  lattice. The electronics calculations are carried out using RASSCF/RASPT2/RASSI sequence of methods.

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## **Wavelength and temperature dependent trap filling in sintered $\text{Lu}_2\text{O}_3\text{:Tb,M}$ (M= Ti, Hf) ceramics**

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Energy storage ability in sintered  $\text{Lu}_2\text{O}_3\text{:Tb}$  ceramics co-doped with Ti, Nb and Hf have been investigated in the past [1]. Especially the Hf or Ti co-dopants greatly enhanced the materials energy storage capacity in comparison to their singly doped  $\text{Lu}_2\text{O}_3\text{:Tb}$  counterpart. In result their TL glow curve are composed of a well-separated single TL peak at  $\sim 230^\circ\text{C}$  (Tb, Hf), or  $\sim 355^\circ\text{C}$  (Tb, Ti). The relatively deep traps giving rise to the TL of these materials combined with linear dose-response dependence over a very broad range, reaching seven-orders of magnitude make them important and interesting storage phosphors deserving still deeper understanding of their properties [2].

The new, advanced experiments based on thermoluminescence excitation spectra (TLES) and charging of the materials with different UV wavelengths at wide range of temperatures shed new light on energy storage mechanism. By selection of a specific wavelength (360 nm) we can selectively populate a specific trapping centre. The trapping centre corresponds with a low temperature glow peak around  $80^\circ\text{C}$ . Consequently for that wavelength the phosphor shows not reported till now Persistent Luminescence (PL) while for other wavelengths there is no or very little PL [3].

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## Dual role of oxygen-related defects in luminescence kinetics of AlN:Mn<sup>2+</sup>

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This study presents the impact of temperature and pressure on AlN:Mn<sup>2+</sup> luminescence kinetics. Unusual behaviour of Mn<sup>2+</sup> optical properties during UV excitation is observed, where a strong afterglow luminescence of Mn<sup>2+</sup> occurs even at low temperatures. When the temperature increases, the contribution of afterglow luminescence is further enhanced, causing a significant increase in the luminescence intensity. The observed phenomena may be explained by an energy diagram in which O<sub>N</sub>-V<sub>Al</sub> complex in AlN:Mn<sup>2+</sup> plays a key role. Hence the O<sub>N</sub>-V<sub>Al</sub> complex defect in AlN:Mn<sup>2+</sup> plays a double function. When the O<sub>N</sub>-V<sub>Al</sub> defect is located close to Mn<sup>2+</sup> ion, it is responsible for transferring excitation energy directly to Mn<sup>2+</sup> ions. However, when the O<sub>N</sub>-V<sub>Al</sub> defect complex is located far from Mn<sup>2+</sup> ions, its excited state level acts as an electron trap responsible for afterglow luminescence. Additionally, three models have been tested to explain the structure of the emission spectrum and the strong asymmetry between excitation and emission spectra. From the most straightforward configuration coordinate diagram through the configuration coordinate diagram model assuming different elastic constants in the excited and ground-state ending by a model based on Jahn–Teller effect. We proved that only the Jahn–Teller effect in the excited <sup>4</sup>T<sub>1</sub> electronic state with spin-orbit coupling could fully explain the observed phenomena. Finally, high-pressure spectroscopic results complemented by the calculation of Racah parameters and the Tanabe-Sugano diagram are presented.

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## Luminescence and electron paramagnetic resonance of carbon-doped sol-gel silica glass

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High purity synthetic silicon dioxide ( $\text{SiO}_2$ ) glass is widely used in deep ultraviolet (UV) optics, optical fibers, high-power laser optics due to its high optical transmittance, radiation toughness, and large bandgap [1]. Due to the detrimental effects of chlorine on environment and on optical properties of  $\text{SiO}_2$  glass [2], its synthesis increasingly shifts from using  $\text{SiCl}_4$  precursor to silicon-organic precursors, for example, tetraethyl orthosilicate (TEOS). However, this may introduce C impurities. There is ample information on effects of high concentrations of carbon in  $\text{SiO}_2$  (Si oxycarbide glasses, see e.g., review [3]), however, very few data are available on the effects of low concentrations of carbon (C) impurities. The aim of the present work is to obtain the photoluminescence (PL) and electron paramagnetic resonance (EPR) properties of C impurities in silica.

In this work, carbon was introduced in silica samples as a by-product of glass sol-gel synthesis from TEOS silicon-organic precursor. Its presence could be confirmed by the characteristic PL spectra of polycyclic aromatic hydrocarbons [4]. Alternatively, carbon was introduced by sintering  $\text{SiO}_2$  nanoparticles using hot vacuum pressing (HVP) with graphite press-form. The optical absorption (OA), Raman scattering, PL and electron paramagnetic resonance spectra were measured.

Green PL band emerged in sol-gel glass after annealing at  $1200^\circ\text{C}$ . EPR spectra of all samples showed signals at  $g=2.0006$  due to Si E'-centers. Sintering of  $\text{SiO}_2$  nanoparticles by HVP method at  $1200^\circ\text{C}$  gives rise to a PL band with a maximum in NIR region at 795 nm. Raman spectra showed signals at  $1349\text{ cm}^{-1}$  and  $1613\text{ cm}^{-1}$  that corresponds to C in  $\text{SiO}_2$ .

The support from Latvian Science Council project lzp-2021/1-0215 and from the EU Horizon 2020 Framework Program H2020-WIDE- SPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART<sup>2</sup> is acknowledged.

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## Thermal sensitive paints based on the $\text{LaVO}_4\text{:Dy,Ca}$ for high temperature identification

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Phosphor thermometry is a promising non-destructive temperature identification technique including harsh environment conditions and in the presence of reactive flow and radiative heat exchange [1]. The need of health monitoring of components i.e. turbine vanes and the transition ducts of the combustion chambers after being exposed to extreme conditions as well as temperature measurements in the areas with difficult access are becoming increasingly important [2], [3].

In this work, we present thermal history paints composed of temperature sensitive nanocrystalline powder of lanthanum orthovanadate ( $\text{LaVO}_4$ ) co-doped with  $\text{Dy}^{3+}$  and  $\text{Ca}^{2+}$  ions and commercial ceramic binders as a base.

The  $\text{LaVO}_4\text{:Dy}^{3+},\text{Ca}^{2+}$  was synthesized by solid state method. The first calcination was carried out in  $600^\circ\text{C}$  and second were in  $700^\circ\text{C}$ - $1200^\circ\text{C}$  [4]. The powder in amorphous phase (after first calcination) is ready to be combined to binders. A gravity spray method was used for applying the thermal paint on the  $\text{Al}_2\text{O}_3$  substrates. After air drying, samples were heat-treated in a furnace in temperatures  $800^\circ\text{C}$ - $1200^\circ\text{C}$ . All samples, pure powders and paints, were characterized using PL spectra, XRD and SEM analysis. The calibration curves of  $\text{LaVO}_4\text{:Dy}^{3+},\text{Ca}^{2+}$  powder and thermal history paints with  $\text{LaVO}_4\text{:Dy}^{3+},\text{Ca}^{2+}$  show the temperature dependence of ratios of the integrated areas of blue and yellow group of emission peaks after laser excitation at 325 nm.

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## **Excitonic emission of Cs<sub>2</sub>AgInCl<sub>6</sub> double perovskite phosphor**

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Perovskite materials have gained a lot of attention in several branches of material science due to their simple yet modifiable crystal structure, vast array of chemical compositions etc. In recent years, a derivative group of perovskites, called double perovskites was extensively researched for application in solar cells, etc. Curiously, several of these compounds can exhibit broadband, visible luminescence, which is understood to be excitonic in nature. While interesting from a scientific point of view, the excitonic emission has a low threshold for thermal quenching of luminescence, which prevents this group of material from practical use.

Here we present results of an investigation of optical properties Cs<sub>2</sub>AgInCl<sub>6</sub>, which exhibits extremely broad emission band (~200 nm FWHM), The phosphor was modified by codoping with various ions (Bi<sup>3+</sup>, Er<sup>3+</sup>, Na<sup>+</sup>) in order to increase the thermal stability of luminescence. A number of experimental techniques, such as high pressure spectroscopy, photocurrent excitation spectroscopy. The comparison of photoluminescence excitation, photocurrent excitation and diffuse reflectance spectra helped to identify the features in PLE spectrum of the compounds – band to band transitions, excitons, impurity stated.. High pressure spectroscopy have been used to explain the nature of the Cs<sub>2</sub>AgInCl<sub>6</sub> peculiar emission, and identify different excitonic states of the compound, namely the self-trapped exciton (emitting state) and higher lying free exciton state. A crossover of the free exciton and the self trapped exciton has been achieved at elevated pressures, which leads to changes in the character of luminescence. Finally, a energy diagram of the system has been constructed based on the experimental data, which explains the observed optical spectra and kinetic processes.

We believe that comprehensive investigations of the properties of excitonic emission in perovskites is of great value in finding ways to tune the characteristics of double perovskite energy structure, and thus obtain even better performing perovskite phosphors in the future.

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## Spectroscopic properties of 1,8-diazafluoren-9-one in rigid media as visualization agent for Friction Ridge Analysis

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Fingerprints are unique, unchangeable, and irremovable. This information has become the basis for the widespread use of latent prints for personal identification. Particularly problematic substrates for securing dactyloscopy traces are porous substrates characterized by a porous structure, into which components of the sweat and fatty substances are absorbed. Currently, some of the methods used to visualize dactyloscopy traces on absorbent substrates are based on the creation of toxic solutions containing the molecule DFO (1,8-diazafluoren-9-one), which combines with  $\alpha$ -amino acids from the sweat-fat substance to produce a colored reaction product [1, 2].

An attempt to modify the procedures and a preliminary analysis of the spectroscopic properties of DFO in rigid media was proposed. The initial analysis of the spectroscopic properties of DFO in rigid systems predicts a later application for friction ridge analysis [3,4].

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## **The NIR emission from Cr<sup>3+</sup> ions in modified Ga<sub>2</sub>O<sub>3</sub> matrix**

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Due to potential biological applications, the Cr<sup>3+</sup>-activated luminescent materials have recently become a research hotspot worldwide.[1, 2] Recently, Cr<sup>3+</sup>-activated luminescent materials that can produce either sharp-line or broadband spectra have become a promising candidate in phosphor-converted IR light-emitting diodes (pc-IR LEDs). It found application in the food's freshness, quality, and composition analysis.[3] One of the main goals is to find the material with efficient broadband NIR luminescence. One of the promising materials for NIR sources is Ga<sub>2</sub>O<sub>3</sub> activated by Cr<sup>3+</sup> ions. These materials are characterized by efficient NIR luminescence in 650–900 nm range, with the maximum at 740 nm. Here the luminescence studies, time resolve studies, and high-pressure spectroscopy are shown for Cr<sup>3+</sup> activated Ga<sub>2</sub>O<sub>3</sub> doped with Sc, and Al.

Co-doping the Ga<sub>2</sub>O<sub>3</sub> matrix with the ion with a bigger ion radius like scandium allowed us to shift the maximum emission to 850 nm with a high efficiency >90%. Ga<sub>1.594</sub>Sc<sub>0.4</sub>O<sub>3</sub>:0.006Cr<sup>3+</sup> exhibits high internal quantum efficiency (99%). Time-resolved spectra are utilized to further examine the subtle change in the microstructures of Cr<sup>3+</sup>. For the undoped sample, only one luminescence center is observed. By contrast, for the Sc doped samples, the two emission spectra taken in different time interval are considerably different, which suggest that the distribution of crystal field strength spans over the crossing point of the <sup>2</sup>E and <sup>4</sup>T<sub>2</sub> states, and the Cr<sup>3+</sup> luminescence centers are located in strong and weak crystal fields. Accordingly, we can simultaneously observe broadband and line emissions even at low temperatures. For a series of Ga<sub>1.98-x</sub>Al<sub>x</sub>O<sub>3</sub>:0.02Cr<sup>3+</sup> phosphors, structural evolution reveals a crystal phase change with the incorporation of Al ions. The phase transition is also observed by high-pressure studies. Between 120-140 kbar, the luminescence spectra and the decay times change, which suggests the phase transition from β-Ga<sub>2</sub>O<sub>3</sub> (monoclinic) to α-Ga<sub>2</sub>O<sub>3</sub> (trigonal). The high-pressure study reveals the emission from the exchange-coupled Cr<sup>3+</sup> pairs and the phase transition under high pressure.

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## Luminescent and scintillation properties of $(\text{Gd}_{1-x-y}\text{Lu}_x\text{Y}_y)_3\text{Al}_5\text{O}_{12}:\text{Ce}$ ( $x=0,2$ ; $y=0,001$ ) single crystals grown by micro pulling down technique

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The thermodynamically stable LnAG garnets only exists for the  $\text{Ln}^{3+}$  cations smaller than  $\text{Gd}^{3+}$ . For this reason the stoichiometric  $\text{Gd}_3\text{Al}_5\text{O}_{12}$  (GdAG) garnet starts to decompose at  $\sim 1300^\circ\text{C}$  and can be crystalized only via low temperature synthesis. Due to its structural metastability, the properties GdAG crystals has been much less studied than YAG and LuAG. However, compared with YAG and LuAG, GdAG hold some of merits for optical applications: (1) the intrinsic  $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$  transition of  $\text{Gd}^{3+}$  (at 275 and 317 nm) can be used as efficient excitation source for some types of rare-earth ions, and enhanced luminescence of these dopants may be obtained via an efficient energy transfer from  $\text{Gd}^{3+}$  cations; (2) the GdAG host is more covalent than YAG and LuAG due to the lower electronegativity of  $\text{Gd}^{3+}$  ( $\chi=1.2$ ) than  $\text{Y}^{3+}$  (1.22) and  $\text{Lu}^{3+}$  (1.27), which may result in improved emission intensity; (3) GdAG with significantly higher density ( $5.97 \text{ g/cm}^3$ ) and effective atomic number  $Z_{\text{eff}}=60$  than YAG ( $\rho=4.55 \text{ g/cm}^3$ ,  $Z_{\text{eff}}=34.5$ ) is much more desirable for scintillation applications.

One possible ways to stabilize the garnet lattice of GAG is partially replacing  $\text{Gd}^{3+}$  with a smaller  $\text{Ln}^{3+}$  to form  $(\text{Gd}_{1-x}\text{Ln}_x)_3\text{Al}_5\text{O}_{12}$  solid solution. Lu and Y ions are the main choice in this case due to stable crystallization of LuAG and YAG garnets for different applications.

In this work, the luminescent and scintillators properties of the single crystal of  $\text{Ce}^{3+}$  doped  $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}:\text{Ce}$  and  $(\text{Gd}_{1-x-y}\text{Lu}_x\text{Y}_y)_3\text{Al}_5\text{O}_{12}:\text{Ce}$  ( $x=0,2$ ;  $y=0,01$ ) garnets (GLAG:Ce and GLYAG:Ce) were investigated. GLAG:Ce and GLYAG:Ce crystals were grown by micro-pulling down ( $\mu\text{PD}$ ) method. Obtained crystals were compared with well-known scintillation crystals of  $\text{Gd}_{3-x}\text{Ga}_x\text{Al}_5\text{O}_{12}:\text{Ce}$  ( $x=3,2,5$ ) (GAGG:Ce) and of  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  (YAG:Ce) garnets. In order to characterize properties of crystals under study, the measurements of their absorption, cathodoluminescence (CL), thermoluminescence (TL) glow curves, photoluminescence (PL) emission and excitation spectra as well as PL decay kinetics were performed. The scintillation properties of crystals (light yield (LY) and decay kinetics) were measured under excitation by  $\alpha$ -particles of  $^{239}\text{Pu}$  (5.15 MeV) source.

Comparison of the absorption and luminescent properties of mentioned crystals was performed depending on the garnet content. The maximum peak positions of  $\text{Ce}^{3+}$   $E_1$  and  $E_2$  of 4f-5d bands [2, 3] were examined using both the absorption and PL excitation spectra. Changing the ion radius from 1.053 for  $\text{Gd}^{3+}$  to 1.019 Å for  $\text{Y}^{3+}$  and for  $\text{Lu}^{3+}$  [4] in the dodecahedral position of garnet host leads to increase of the crystal field strength and causes a red shift of the CL and PL spectra. Occurrence of defects in crystal structure of GLAG:Ce and GLYAG:Ce crystal as emission and trapping centers were examined using CL spectra, TSL glow curves and scintillation properties.

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## **Thermoluminescence emission spectra of irradiated feldspar samples**

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Feldspars are common minerals constituting more than 50% of the earth's crust components. They have aroused the interest of geologists due to their ability to collect information about the absorbed dose of ionizing radiation over a long period of time. Feldspars have the potential to date various geological processes over thousands of years. However, these materials have a very complex structure. They contain many localized energy levels of varying depth and spatial arrangement. Therefore, obtaining the desired dosimetric information is a very difficult task. The energy levels have continuous distribution resulting in broad thermoluminescence (TL) peaks and long optically stimulated luminescence (OSL) decay tails. Microcline crystals from the Strzegom Massif were used in this research. The samples were irradiated with a  $^{90}\text{Sr}/^{90}\text{Y}$  source of beta radiation with doses up to kGy. Spectrally resolved thermoluminescence (SR-TL) measurements were performed to show the emission properties of the potassium feldspars. The data were analyzed using advanced theoretical models taking into account continuous distribution of energy levels.

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## Preparation of polycrystalline $\text{CaSiO}_3\text{:Eu}$ thin films - preliminary studies

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Luminescent thin films have been known for a long time and have found numerous practical applications such as fluorescent lamps and cathode-ray tubes so far [1]. There are many methods for the deposition of luminescent films, including pulsed laser deposition, sputtering, liquid phase epitaxy and the sol-gel process. The advantages of the last method are availability, manufacturability, in most cases the method ensures uniformity. This method besides the amorphous materials, allows also to prepare polycrystalline compounds in the form of powder, monolith [2] and thin films [3], while the thickness of the films can be adjusted both by the density of the original sol and by the number of applied layers.

The main goal of this work is the synthesis of  $\text{CaSiO}_3$  material, doped with Eu, using the sol-gel method in the form of thin films. The thin films were obtained by spin-coating technique. For this, the obtained sol was applied on the prepared substrate and distributed at high speed of spinning. If necessary, the procedure was repeated. This allows to control the thickness of the obtained films.

As part of the work, the thin films of the  $\text{CaSiO}_3$  material, doped with Eu were synthesized *via* the sol-gel method. XRD measurements and analysis were performed. The optimum synthesis temperature, which is necessary to obtain defined phase composition, has been investigated. Spectroscopic measurements (emission and excitation spectra) were carried out using standard optical layout to study of the influence of the thin film thickness on the luminescence of the investigated materials.

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## Electrical properties of Mxene/PAANa thin films

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Mxene ( $\text{Ti}_3\text{C}_2$ ) as a promising material is used for various applications such as energy storage, materials for protection against electromagnetic noises, reinforced composites, gas- and biosensors, lubricants, photo-, electro- and chemical catalysts [1]. The sodium salt of polyacrylic acid (PAANa) additive promotes wetting of substrate surface, thus allowing the formation of a uniform conductive Mxene/PAANa films, and isolates of Mxene nanosheets from the surrounding environment. The aim of this study are as follows to prepare thin Mxene/PAANa films and study their electrical properties. The Mxene colloidal solution (5 g/l) was mixed with PAANa at different ratios and applied to a glass substrate ( $S = 1.4 \text{ cm}^2$ ) by spraying. The amount of deposited material was controlled by changing the weight of the substrate. The electrical resistance of the samples was measured using a multimeter APPA 505 True RMS by two-point method. The approximate thickness of the Mxene/PAANa films was about 500 nm. The dependence of the resistance on the content of Mxene is shown in Figure. The Mxene (90 %)/PAANa film is characterized by a close resistance value to a pure Mxene film of about  $2,4 \times 10^{-6} \text{ Ohm} \times \text{m}$ . A decrease in the content of Mxene down to 58 % led to an increase in the resistance of the composite by 3.6 times. A sharper increase in the electrical resistance of the composite was observed with a further decrease in the Mxene content. For a PAANa/Mxene sample containing 8 % of Mxene, the resistance was about  $2,315 \times 10^{-3} \text{ Ohm} \times \text{m}$ . Pure Mxene film was characterized by a layered structure. Individual 2D particles were stacked on top of each other. This ensured good contact between the individual Mxene particles, that led to the low resistance of pure Mxene films. The Mxene/PAANa films were also characterized by a layered structure. The thickness of the layers in the composite structure increased with an increase in the amount of the polyelectrolyte additive (PAANa). The PAANa polyelectrolyte was sorbed on the surface of Mxene particles, worsening the contact between individual 2D particles and increasing the resistance of the Mxene/PAANa film. However, it should be noted that the preservation of the layered structure in the Mxene/PAANa films caused a rather high conductivity of them.

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## Temperature reading from $\text{Dy}^{3+}$ , $\text{Cr}^{3+}$ double activated YAG

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$\text{Dy}^{3+}$ ,  $\text{Cr}^{3+}$  double activated yttrium aluminum garnet – YAG phosphors were synthesized via the Pechini method. The structure was confirmed by X-ray diffraction analysis and morphology was investigated using scanning electron microscopy. Photoluminescence emission spectra of the  $\text{Dy}^{3+}$ ,  $\text{Cr}^{3+}$  double activated YAG consist of both blue and yellow  $\text{Dy}^{3+}$  emissions as well as broad, red  $\text{Cr}^{3+}$  emissions. A decrease of the  $\text{Dy}^{3+}$  emission with the  $\text{Cr}^{3+}$  increase indicates efficient energy transfer from  $\text{Dy}^{3+}$  to  $\text{Cr}^{3+}$  calculated to be  $\sim 90\%$ .

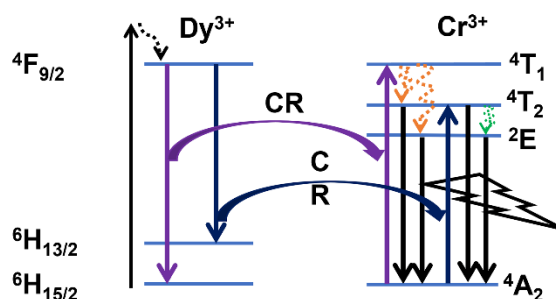


Figure 1. Representation of the energy transfer from  $\text{Dy}^{3+}$  to  $\text{Cr}^{3+}$  ions

Temperature-dependant photoluminescent emission measurements are performed and the noted alterations of luminescence with temperature present an excellent base for studying the multiparametric temperature readouts. The luminescence intensity ratio, the most frequently exploited luminescent thermometry temperature readout method, was tested using: i) the combination of  $\text{Dy}^{3+}$  and  $\text{Cr}^{3+}$  emissions, ii) using the double excitation approach, and iii) using  $\text{Cr}^{3+}$  emission only, with relative sensitivities of  $0.64\% \text{K}^{-1}$  at 175 K,  $0.96\% \text{K}^{-1}$  at 200 K and  $2.2\% \text{K}^{-1}$  at 200 K, respectively.

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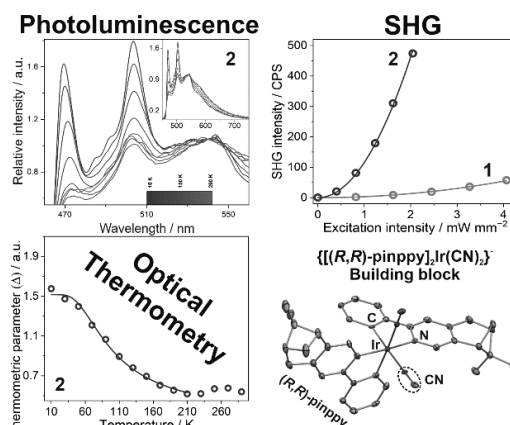
# Optical thermometry and non-linear optical property of dicyanidoiridates(III) based molecular materials

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Cyclometalated iridium(III) complexes are effective molecular building blocks for the construction of novel optical materials due to their strong and tunable emission ranging from visible to NIR regions.<sup>[1]</sup> They were also explored for advanced photonic application as a chiral luminophores exhibiting circularly polarized luminescence (CPL).<sup>[2]</sup> On the other hand, molecular materials based on cyanido metal complexes are broadly exploited due to the extraordinary magnetic and optical properties, including chirality-related effects of magneto-chiral dichroism (MChD) or magnetization-induced second harmonic generation (MSHG).<sup>[3,4]</sup> In this regard, we decided to focus on the non-trivial combination of cyanide chemistry with organo-metallic approach to achieve a novel class of chiral dicyanidoiridate(III) complexes examining their potential for non-linear optics and luminescence functionalities such as molecular optical thermometry.<sup>[5]</sup> Here, we report a family of molecular materials based on dicyanidoiridates(III) with a chiral (*R,R*)-pinppy (2-phenyl-4,5-pineno-pyridine) ligand. Such materials exhibits strong visible photoluminescence of a charge transfer character with the distinct luminescent thermometry effect originating from the thermal dependency of emission and the pronounced SHG phenomenon under the 1064 nm irradiation. The characteristics of the resulting SHG-active luminescent thermometers are enhanced in the coordination chains when compared with the supramolecular analogs.



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## Exciton-like luminescence in KCl:Na crystals exposed to thermoelastic, local and uniaxial elastic deformation

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In the X-ray luminescence spectra of KCl:Na crystals, the emission band with a maximum at 2.8 eV has been detected for the first time at room temperature. The intensity of this luminescence is by about 50 times as high as that detected in the same spectral region in a pure KCl crystal.

The effect of the reduced local lattice symmetry of alkali halide crystals on the efficiency of recombination formation of bound excitons in these lattice regions has experimentally been revealed on the example of KCl:Na crystals. The reduction of a local lattice symmetry has been performed via several factors, such as thermoelastic (thermal quenching), local (crystal doping with light impurity cations) and uniaxial elastic deformation. A significant enhancement of the luminescence band peaked at 2.8 eV and related to exciton-like formations has been detected in KCl:Na crystals exposed to (i) thermal quenching up to 400-700°C, (ii) rise in sodium impurity concentration (from 10 to 1000 ppm) and (iii) uniaxial elastic deformation applied along  $\langle 100 \rangle$  and  $\langle 110 \rangle$  crystallographic directions (see also [1]).

In a heavily doped KCl:Na (1000 ppm) crystal, the additional intense (and even dominating over the 2.8-eV one) emission band with a maximum at 3.1 eV and tentatively ascribed to exciton-like formations nearby  $\text{Na}^+-\text{Na}^+$  impurity pairs has also been detected. In our opinion, all types of lattice symmetry lowering applied for KCl:Na crystals investigated (in particular, thermoelastic, local, and uniaxial elastic deformation) cause the increase of the mean free path of unrelaxed (hot) holes before their transition into a self-trapped state. As a result, the probability of bound exciton formation in the process of electron-hole recombination in the vicinity of sodium impurity strongly increases and the subsequent radiative decay of such electronic excitation leads to the appearance of a typical luminescence.

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## **The influence of the post-irradiation heat treatment on the photoluminescence of lithium fluoride crystals**

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Lithium fluoride (LiF) is a very well-known and widely used luminescent material. One of the most interesting phenomenon that occurs in this material is related to radiation-induced color centers and their photoluminescence. Ionizing radiation produces in LiF crystals mostly F centers, which often aggregate into more complex defects, like  $F_2$  and  $F_3^+$  color centers. When these centers are excited with blue light (wavelength near 445 nm), they emit photoluminescence peaked at about 670 nm (related to  $F_2$ ) and about 525 nm (related to  $F_3^+$ ). Concentrations of various color centers in LiF and their photoluminescence spectra were found to be significantly influenced by temperature. One of the newly developed application of LiF crystals is Fluorescent Nuclear Track (FNTD) technique. This method enables direct visualization of the paths of ionizing particles with fluorescence microscope using the photoluminescence of color centers. Although this method has a great potential of becoming a powerful tool in modern dosimetry, it suffers due to low signal-to-noise ratio. The thermal treatment of LiF crystals seems to be the most feasible way to enhance a measuring capabilities of those track detectors. In our studies, we focused on the application of the post-irradiation annealing. We tested different times and temperatures of applied heat treatment. Microscopic images for low fluences of alpha particles were taken, as well as absorbance and emission spectra for higher doses of radiation. We observed that there are some serious differences between the effects observed for high doses and for single tracks. While intensities of single tracks may be enhanced by using proper heat treatment after sample's irradiation, such effect was not observed when crystals were irradiated with fluences higher than  $3 \cdot 10^7 \text{ cm}^{-2}$ .

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# Effect of Ga<sup>3+</sup> doping on the up-conversion of Lu<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Pr<sup>3+</sup>

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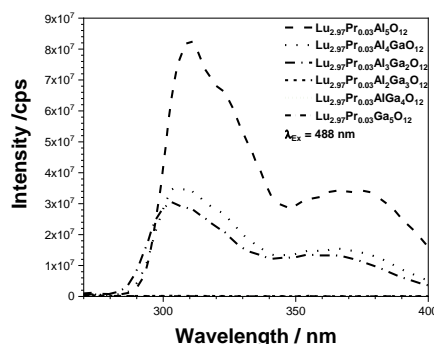


Fig. 2 Up-conversion emission of different members of the Lu<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Pr<sup>3+</sup> solid solution

This work deals with the photoluminescence (PL) and up-conversion of the solid solution Lu<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Pr<sup>3+</sup>. The replacement of Al<sup>3+</sup> by Ga<sup>3+</sup> leads to an increase of the covalent character, while the band gap declines at the same time. It turned out that the up-conversion luminescence in Lu<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Pr<sup>3+</sup> is strongly dependent on the Ga<sup>3+</sup> concentration. Temperature and time dependent measurements were performed and the results of the up-conversion PL spectra will be compared with those of the down-conversion PL spectra.

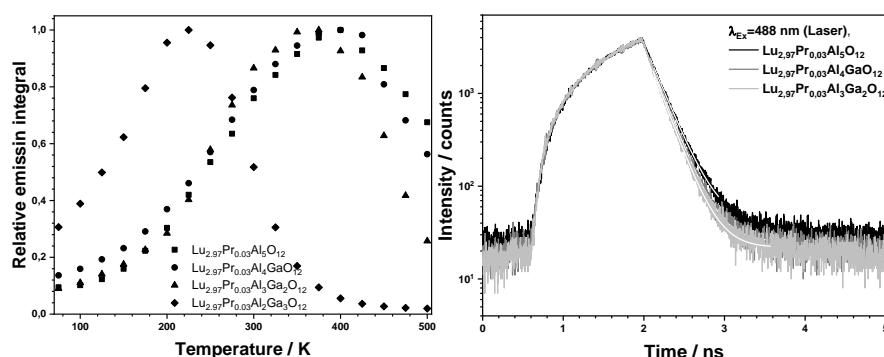


Fig. 3 Temperature and time dependence up-conversion measurements of the different Lu<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Pr<sup>3+</sup> microparticles

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## **Luminescence of micropowder phosphors based on the Ce<sup>3+</sup> and Mn<sup>2+</sup> doped Ca<sub>3</sub>Sc<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> garnets**

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Nowadays white LEDs (WLEDs) are widely used for lighting applications due to their high efficiency, long lifetime and ecologically friendliness compared to conventional light sources. Currently, the most known WLED type is the combination of blue LED chip and yellow-emitting Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce (YAG:Ce) photoconverters (pc) [1,2]. However, the lack of the red-emitting component in YAG:Ce pc hinders the realization of warm white light. Due to bright Ce<sup>3+</sup> luminescence and higher thermal stability, the green-emitting Ca<sub>3</sub>Sc<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>:Ce (CSSG:Ce) phosphor is considered now for pc-WLED application instead YAG:Ce pc [3]. However, CSSG:Ce has lacks emissive components in yellow-red ranges. For this reason, Mn<sup>2+</sup> codopant was applied for adding the yellow/red components in CSSG:Ce pc [4]. Namely, <sup>4</sup>T<sub>1</sub>(G)→<sup>6</sup>A<sub>1</sub>(G) d-d transitions of Mn<sup>2+</sup> give to a broad emission, ranging from green to red, depending on the crystal field strength [3]. Despite the fact that excitation of Mn<sup>2+</sup> d-d transitions is forbidden, it can be realized efficiently by Ce<sup>3+</sup>–Mn<sup>2+</sup> energy transfer [4].

The Ce<sup>3+</sup> and Mn<sup>2+</sup> doped Ca<sub>3</sub>Sc<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> MPs were obtained by conventional solid-state synthesis with use of Ba<sub>2</sub>O<sub>3</sub> flux in concentration of 5 weight % of the total charge content. The thermal treatment of MPs was performed in the air atmosphere firstly at 900°C and then in reducing atmosphere (N<sub>2</sub>/H<sub>2</sub>) at 1350°C. The morphology of grains is improved by using a flux at solid-state preparation of MPs, what results in an increase of their PL intensity [5]. For characterization of the MP properties, the cathodo- (CL) and photo- (PL) luminescence spectra, PL decay kinetics and photoconversion (PC) spectra were used.

The PL spectra of CSSG:Ce MPs show the dominant Ce<sup>3+</sup> emission broad bands with peaked at 507 and 546 nm. The PL spectra for CSSG:Ce,Mn MPs exhibit not only the Ce<sup>3+</sup> emission band at 506 nm but also the Mn<sup>2+</sup> emissions bads at 564 and 663 nm. We have supposed that Mn<sup>2+</sup> ions may either substitute for Ca<sup>2+</sup> of CSSG host and generate the yellow emission band at 564 nm and/or substitute for Sc<sup>3+</sup> to generate the red emission band at 663 nm. As a result, combining Ce<sup>3+</sup> and Mn<sup>2+</sup> in CSSG host could allow for the production of phosphors with a wide emission ranging from blue to red ranges.

The application possibility of the developed CSSG:Ce and CSSG:Ce,Mn MP phosphors was demonstrated as well. The planar WLED prototypes were fabricated by the coating of GaN 450 nm blue LED chip with several ~100-120 μm thick layers, containing CSSG:Ce and CSSG:Ce,Mn MP phosphors mixed with epoxy resin. The WLED prototype, which is based on the six CSSG:Ce pc-layer, emits the cold white light with color coordinates x=0.29; y=0.38. Meanwhile, the photoconversion properties of the WLED with CSSG:Ce,Mn pc show quate warmer white light with color coordinates x=0.32; y=0.29. For this reason, tuning of the Ce<sup>3+</sup> and Mn<sup>2+</sup> content in the CSSG:Ce,Mn MP phosphor, gives the possibility to fabricate WLED with different thons and temperature of white light.

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# Remote activation of photon avalanche up-conversion in $\text{Tm}^{3+}$ -doped nanocrystals via surface plasmon polaritons propagating in a single silver nanowire

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This work presents microscopic luminescence studies on hybrid nanostructure consisting of a single silver nanowire and  $\text{Tm}^{3+}$ -doped fluoride nanocrystals. The nanostructure is organized in such a manner that a small, femtolitre volume of the nanocrystals is deposited only at one end of about 15  $\mu\text{m}$  long and 100 nm thin single nanowire. Due to high crystalline quality, the nanowire supports light-activated surface plasmon polaritons (SPPs), propagating on the metal-air interface for distances reaching even tens of micrometers. In particular, polaritons launched at the free end of such nanowire can reach its opposite end and interact with thulium-doped nanocrystals. In other words, phonons (instead of photons) can activate the luminescence process.

We used an infrared laser operating at 1050 nm, focused by a high numerical aperture ( $\text{NA}=1.49$ ) microscope objective, and illuminated the free end of the nanowire. Consequently, we detected anti-Stokes luminescence at 800 nm, released from the same end of the nanowire, where no NCs were present. We assigned this emission to the  $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transition in  $\text{Tm}^{3+}$ . Its presence proves that the whole process is mediated by the plasmon polaritons, transporting (in the first step) the excitation energy from the free NW end to the NCs, and (in the second step) the up-converted luminescence from NCs back to the free end of the nanowire where the excitation/detection objective operates. The excitation wavelength matches the  $^3\text{F}_4 \rightarrow ^3\text{F}_2$  excited state absorption transition in  $\text{Tm}^{3+}$ , and no ground state absorption transition at this wavelength is observed. Thus, the observed luminescence was identified as photon avalanche upconversion (PAU). Indeed, we noticed a drastic increase in the up-conversion emission intensity with increasing laser power. Furthermore, the unique role of the SPPs in the whole process is analyzed, and the influence of the PAU on the subdiffraction luminescence imaging is discussed.

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## High pressure studies of near infrared luminescence of $\text{LiGaO}_2\text{:Fe}^{3+}$

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Transition metal-doped, near infrared (NIR) luminescent lithium gallate ( $\text{LiGaO}_2$ ) materials have potential applications in the biological field, GaN crystal growth, and energy storage devices [1, 2]. In this work, we study the NIR features of lithium gallate ( $\text{LiGaO}_2$ ) phosphor material doped with iron ( $\text{Fe}^{3+}$ ), under high-pressure and low-temperature conditions. The oxide phosphor was characterized utilizing XRD, ambient and high-pressure luminescence, and decay measurements using diamond anvil cells (DAC), etc.

The powder X-ray analysis shows that at room temperature the phosphor has an orthorhombic crystal structure and has a space group of  $\text{Pna}2_1$ . It suggests that the sample has a stable  $\beta\text{-LiGaO}_2$  phase [2]. The particle size was calculated from XRD data using the Debye-Scherrer formula and it is around 32nm. The photoluminescence measurement at ambient conditions shows that it has a broad and high intense NIR luminescent band centered at 746nm when excited from different peaks of excitation spectra. The intensity of this main band increases with decrease in temperature and also red shifted towards longer wavelength. When the sample was subjected to a low temperature below 100K, a sharp phonon band also started appearing around 710nm, which pointing towards the relatively weak interaction between dopant  $\text{Fe}^{3+}$  ions and the host lattice. That means the  $\text{Ga}^{3+}$  ions in the host material were effectively replaced by the  $\text{Fe}^{3+}$  ions during doping.

The high-pressure luminescence and high-pressure decay measurements were done with a diamond anvil cell setup at helium temperature. The sample was illuminated using a 275nm laser excitation source. During the high pressure luminescence (up to 14 Gpa) spectra measurement, we observed a phase change was happening around 3Gpa by the disappearance of the main phonon line at 710nm. It suggests that the initial orthorhombic phase changed to the trigonal phase at 3Gpa [3]. Also, the luminescence was almost quenched out around 14Gpa with an irreversible phase transition. The high pressure and low temperature decay profile of both main band and phonon band were also measured and fitted with a three exponential equation, obtained results showing that both peaks have around 13ms lifetime at 0.44Gpa pressure, and it decreases with the increase of pressure.

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## Photo- and radio-luminescent properties of halide perovskite nanocrystals embedded into a polymer film

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The development of novel scintillation materials and modern applications of scintillation detectors require a cheaper scintillator manufacturing process at the same time with more stringent requirements in terms of their light output and fast decay. One of the ways to meet these requirements is to apply excitonic materials with bright and fast luminescence like semiconductor nanocrystals. It has recently been shown that nanoscale halide perovskite crystals like CsPbBX<sub>3</sub>, where X anions: Cl, Br, or I, can be effectively used in different optoelectronic applications [1]. Despite the short history of their studying, perovskite materials already recommended themselves as perspective materials for ionizing radiation detection [2-4].

In the present report, we demonstrate the results of photo- and radioluminescence of CsPbBr<sub>3</sub> nanocrystals embedded in PMMA polymer films. It is shown that the lifetime of the perovskite nanocrystals decreases to about 1 ns when embedded into polymer films compared to 30-40 ns in toluene. A radio-luminescent signal from perovskite nanocrystals in PMMA film under  $\alpha$ -excitation was obtained even for thin films containing low nanocrystals concentrations. It was found that the decay time of radioluminescence at  $\alpha$ -excitation is approximately 1 ns, as at photoexcitation. Thus, the obtained results are quite reassuring in terms of fast scintillators development.

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## **Interdiffusion investigation in ZnO/Zn<sub>1-x</sub>Cd<sub>x</sub>O heterostructures on a and r oriented Al<sub>2</sub>O<sub>3</sub>**

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The wide gap II–VI semiconductors have become of increasing technological importance, in particular for the development of light-emitting diodes [1] and lasers [2] operating in the visible to ultraviolet region. Such devices contain heterojunctions and active areas based on quantum structures. Because of the large concentration of dopants, the gradients are present, and, therefore, interdiffusion of the matrix components during growth and processing is of inevitable concern as it can lead to composition changes of the interface and quantum structure profiles and the strain distribution, modifying the bandgap configuration and consequently the device parameters.

In this work, the results of a photoluminescence and Rutherford backscattering study of the temperature-induced inter-diffusion in ZnO/ZnCdO structures. Three series of samples were grown by the Molecular Beam Epitaxy technique of various arrangements, and Cd content in the range of 1.5 to 8%. Comparison of results for as-grown and annealed structures suggest that disturbed lattice structure, due to the presence of Cd, was partly recovered after thermal treatment. Chosen annealing temperatures and time were enough to induce low-range inter-diffusion of Cd ions into neighboring ZnO layer. The effect of the inter-diffusion was well visible in the RBS depth profiles and confirmed with NDF simulations.

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## Post-synthesis modification of well-defined cesium lead halogenide QDs

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The first all-inorganic perovskites synthesis was published in 2015 [1], and the demand to develop such unique nanoscale materials has increased significantly over the past few years. Due to high absorption and luminescence efficiency, adjustable excellent optical and electronic properties, the metal perovskites became the most promising materials in photovoltaics, optoelectronics, and photocatalysis [1]. Moreover, variation of halides in perovskite composition allows to obtain the QDs with tunable emission over the full range of visible spectrum [2,3].

Within this study, we demonstrated that all-inorganic lead perovskite QDs could easily be synthesized by employing a novel ultrasound-induced synthesis method. The synthesis approach that combines both hot-injection and sonochemical synthesis routes allowed to obtain the highly reproducible all-inorganic lead perovskite QDs in less than 30 minutes. Moreover, we also showed that the post-synthesis modification of the synthesized QDs had benefited from several points of view: firstly, the reduction of surface defects resulted in better quantum efficiencies of QDs; secondly, the simple post-synthesis ion exchange using various trimethyl silyl halogenides (TMS-X) allowed the simple tuning of perovskite's emission color. The effects of TMS-X on the change of perovskite emission color, quantum efficiency, and photoluminescence lifetimes were determined and described.

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## **FRET in TiO<sub>2</sub>@SiO<sub>2</sub> nanoparticles**

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We present the synthesis and characterization of new core-shell material designed for Förster Resonance Energy Transfer (FRET) studies. As a donor and an acceptor of excitation energy, strongly fluorescent rhodamine 110 and rhodamine 101 were selected and covalently bounded to the shell surface. In the first type of nanoparticles, the number ratio of donors to acceptors is low, which means that energy transfer takes place directly from donor to acceptor; in the second type of nanoparticles the number ratio of donors to acceptors is high, which means that multistep energy migration among donors precedes energy transfer to acceptors. These two different systems are analyzed by measurements and analysis of fluorescence intensity decay. The analysis is based on analytical model presented by us previously as well as on Monte-Carlo simulations [1].

As a result the ratio of donors to acceptors number attached to the shell and/or size distribution of core-shell nanoparticles can be determined.

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## Energetic structure of $\text{Sm}^{3+}$ luminescence centers in $\text{Sr}_2\text{TiO}_4$

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The functional materials based on  $\text{Sr}_2\text{TiO}_4$  matrix (the first member of Ruddlesden-Popper family of compounds) have gained intense attention in optoelectronic, solar cell, and photocatalytic technologies due to their unique properties attributed to two-dimensional, layered perovskite-like crystal structure as well as to presence of easily reducible titanium ions. Moreover, these compounds are interesting due to their low-cost production, easy preparation, and excellent physical and chemical stabilities. There are studies describing various physical features of the  $\text{Sr}_2\text{TiO}_4$  material, such as superconductivity, magnetoresistance, extensive electrical and electrochemical characteristics, catalytic activity, magnetic and optical properties

In this contribution a luminescent properties of the material based on the strontium orthotitanate matrix doped with 1% of a mole of samarium, obtained using the typical solid-state synthesis method under a neutral atmosphere of nitrogen are presented. The sample was investigated using powder X-ray diffraction (XRD) and several luminescence techniques to study the phase composition, luminescence as well as to determine the position of the energetic states of  $\text{Sm}^{3+}$  in relation to the valence and conduction bands of  $\text{Sr}_2\text{TiO}_4$ . The PL spectra show that the phosphor can be effectively excited at 409 and 342 nm to get significantly different emissions. The luminescence obtained under 409 nm excitation is typical of  $\text{Sm}^{3+}$  in  $\text{Sr}_2\text{TiO}_4$  and attributed to the nonsymmetrical luminescent center (A-center). In contrast, the luminescence obtained under excitation at 342 nm originates from the symmetrical center (B-center) and has not been reported in the literature so far. The presence of the two emission centers related to  $\text{Sm}^{3+}$  ions in the  $\text{Sr}_2\text{TiO}_4$  matrix characterized by only one crystallographic site of  $\text{Sr}^{2+}$  can be explained by considering the different ways of charge compensation:  $\text{Sm}^{3+}$  in the A-center *via* strontium vacancy ( $V_{\text{Sr}}''$ ), and  $\text{Sm}^{3+}$  in the B-center *via*  $\text{Ti}^{3+}$  ( $\text{Ti}_{\text{Ti}}'$ ).

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# Optical spectroscopy of $\text{Li}_6\text{Y}(\text{BO}_3)_3$ single crystal doped with thulium

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Lithium yttrium borate (LYB) crystal with monoclinic structure having the  $P2_1/c$  space group is an excellent optical material with wide UV transmittance range. It is also a good candidate for laser host and for scintillation material due to its flexibility and the easy incorporation of rare earth dopants into the yttrium sites. Thulium doped LYB single crystals have not been studied yet, only the isostructural  $\text{Li}_6\text{Gd}(\text{BO}_3)_3:\text{Tm}$  crystal [1] and  $\text{Li}_6\text{Lu}(\text{BO}_3)_3:\text{Tm}$  polycrystalline phosphor [2] have been investigated.

In the present work the results of luminescence, Fourier transform infrared and UV/Vis absorption spectroscopic measurements on  $\text{Li}_6\text{Y}(\text{BO}_3)_3:\text{Tm}$  single crystal doped with 1% thulium grown by the Czochralski method [3] will be presented.

Electronic transitions of the incorporated  $\text{Tm}^{3+}$  ions were successfully identified by absorption measurements in the  $5000\text{--}40000\text{ cm}^{-1}$  wavenumber range. The effect of crystal-field splitting in this low-symmetry crystal was investigated in details by temperature and polarization dependent absorption (see Fig. 1.) and luminescence measurements.

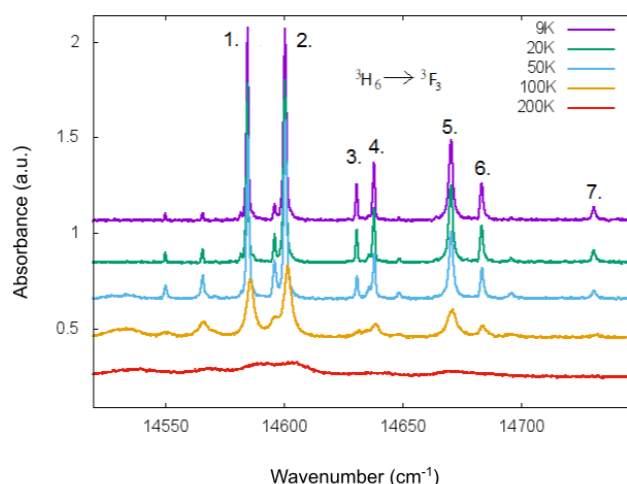


Fig. 1. Temperature dependence of the  $^3\text{H}_6 \rightarrow ^3\text{F}_3$  electronic transition of  $\text{Tm}^{3+}$  ions in LYB crystal.

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## Picoseconds kinetics direct and back intramolecular energy transfer in Thulium (III) -porphyrins

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One of the main physical factors determining wide applications of lanthanide complexes as luminescence materials is the efficiency sensibilization of narrow  $f$ - $f$  emissions in  $\text{Ln}^{3+}$  ions by organic ligands (antennas). Their luminescence properties are determined by a balance between the rates of a ligand to  $\text{Ln}^{3+}$  ion intramolecular direct and back energy transfer (ET), multiphonon relaxation and for some ions by radiationless degradation through ligand-to-metal charge transfer states. Experimentally, the determination of fast ET rates in lanthanide systems is difficult, largely due to the inability of luminescence methods for direct monitoring of non-emissive ligand and lanthanide ion excited states. To measure the intramolecular ET rate constants, the time evolution of the antenna excited states can be observed by the ultrafast transient absorption spectroscopy.

Time evolution studies of the of the antenna excited electronic states of porphyrin ligand has been performed. The picosecond transient absorption technique has been used to three Tm-porphyrins with different relative position of  $T_1$  electronic level to  $^3H_4$  level of the chelated  $\text{Tm}^{3+}$  ion. The energy of the  $^3H_4$  and  $^3H_5$  levels of  $\text{Tm}^{3+}$  is 12680 and 8320  $\text{cm}^{-1}$ , respectively. It was found that for Tm(III)-3,8,13,18-tetraethyl-2,7,12,17-tetramethylporphyrin ( $E_{T_1}=12180\text{cm}^{-1}$ ) and Tm(III)-tetrabenzoporphyrin ( $E_{T_1}=14140\text{cm}^{-1}$ ) there is a monoexponential decay related to transient  $T_1 \rightarrow T_n$  absorption with lifetimes of 230 ps, and 1.5 ns respectively. The main channel for the deactivation of the  $T_1$  state of this Tm-porphyrins is an irreversible ET from the  $T_1$  level of the porphyrin to the lower levels of  $^3H_4$  and  $^3H_5$  of the  $\text{Tm}^{3+}$  ion.

For Tm(III)-5,10,15,20-tetrakis(p-tolyl)porphyrin (TmTTP) the following components are observed in the decay kinetics of the  $T_1$ -state: clearly non-exponential decay in the initial region ( $\sim 200$  ps), later on, it becomes monoexponential with a lifetime of 2 ns. The two-component kinetics observed in TmTTP is apparently related to the fact that, in addition to the irreversible energy transfer from the  $T_1$  ( $E_{T_1}=12600\text{cm}^{-1}$ ) level to the lower  $^3H_5$  level of  $\text{Tm}^{3+}$ , a reversible energy transfer to the  $^3H_4$  level located near 100  $\text{cm}^{-1}$  above  $T_1$  is also possible. The direct and back intramolecular ET ( $T_1 \rightarrow ^3H_4, ^3H_5$ ) rate constants have been determined and dynamics of Intramolecular energy transfer in lanthanide complex compounds is discussed.

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## **Transparent barium silicate ceramics for optical memory purposes**

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Optical information storage demands materials suitable for optical write-in and read-out. Here we report the synthesis of a series of transparent BaSi<sub>2</sub>O<sub>5</sub>:Eu ceramic material, that has been recently offered as a perspective material for optical memory applications, however we offer an improvement of the material, as transparency allows excitation and emission in the volume of the material, not only on the surface [1]. The optical properties of the material have been investigated (transmission, PLE, decay kinetics), as well as structure analysis. Optical write-in and read-out has been tested. Thermally stimulated luminescence measurements have been conducted for the determination of trapping depths. The optimal synthesis parameters are discussed for the optical stimulation purposes.

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# Radioluminescence and low temperature thermoluminescence of $\text{MgGa}_2\text{O}_4$ and $\text{ZnGa}_2\text{O}_4$ semiconductor scintillators

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The ultra-wide bandgap (UWBG) transparent semiconducting oxides (TSO) in various forms (bulk single crystal, crystalline, polycrystalline, films, ceramics and nanocrystals) have already found a lot of various electronic and optoelectronic applications, such as flat panel displays, solar-/visible blind photodectors, high power and mobility electronics, phosphors and scintillators [1].

In this Communication we focus our attention on two materials belonging to the UWBG TSO class, i.e.  $\text{ZnGa}_2\text{O}_4$  and  $\text{MgGa}_2\text{O}_4$  spinels [1-3]. Three crystal samples of each compound, grown at Leibniz-Institut für Kristallzüchtung by the Vertical Gradient Freeze and Czochralski method, respectively, and differing in the values of free electron concentration, have been investigated by measurements of their X-ray excited emission spectra (at various temperatures between 10 and 350 K), and thermoluminescence glow curves below and above room temperature. The radio- and thermoluminescent properties of the studied  $\text{ZnGa}_2\text{O}_4$  and  $\text{MgGa}_2\text{O}_4$  samples are discussed with relation to their free electron concentrations, and compared to those of  $\beta\text{-Ga}_2\text{O}_3$ , already recognized as a very promising semiconductor scintillator [1,4].

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# Comparison of luminescent and scintillation properties of $\text{Gd}_3\text{Al}_{5-x}\text{Ga}_x\text{O}_{12}:\text{Ce}$ single crystals with different Ga content

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$\text{Ce}^{3+}$  doped  $\text{Gd}_3\text{Al}_{5-x}\text{Ga}_x\text{O}_{12}:\text{Ce}$  ( $x=2.5-3$ ) (GAGG $x$ :Ce) single crystals (SC) belong today to list of most efficient scintillators with light yield (LY)  $\sim 50$  ph/KeV under  $\gamma$ -quanta ( $^{137}\text{Cs}$ ) excitation [1]. For these reasons, SCs of these garnets are a good choice as substrate for enhanced composite scintillators based on the epitaxial structures of garnet compounds. The successful crystallization of the single crystalline films (SCF) of TbAG:Ce and mixed (Gd, Tb,Lu) $_3$ (Al,Ga) $_5\text{O}_{12}:\text{Ce}$  garnets onto GAGG:Ce substrates open wide possibilities for development of *new types of composite scintillators based on the SCF of mixed garnets and GAGG:Ce with different Ga content*. Scintillation decay kinetics of SCF and SC parts of composite scintillators based on the mentioned mixed garnets can be specially optimized and fitted due to different Ga content both in the SCF and SC scintillators. This will lead to better separation of scintillation signals for the detection of different types of ionizing radiation.

In this work, the comparison of luminescent and scintillation properties of GAGG $x$ :Ce SCs with different gallium content  $x=2.3, 2.5$  and  $3.0$  were performed. GAGG2.5:Ce crystal was produced in ISMA (Kharkiv, Ukraine). The GAGG2.3:Ce and GAGG3:Ce crystals were produced by IMR Tohoku University (Sendai, Japan). For investigation of the properties of GAGG $x$ :Ce crystals with different Ga/Al content the absorption, cathodo-, photo-, and thermoluminescence spectroscopy were used. The scintillation properties (LY and decay kinetic) of these crystals were measured under excitation by  $\alpha$ -particles ( $^{239}\text{Pu}$  and  $^{241}\text{Am}$ );  $\beta$ -particles ( $^{90}\text{Sr}+^{90}\text{Y}$ ) and ( $^{137}\text{Cs}$ ) sources. Furthermore, the luminescent spectroscopy of GAGG $x$ :Ce ( $x=2.3, 2.5, 3$ ) SCs were performed at 10 and 300K under excitation by synchrotron radiation at new Superlumi station at DESY (Germany) (Fig.1).

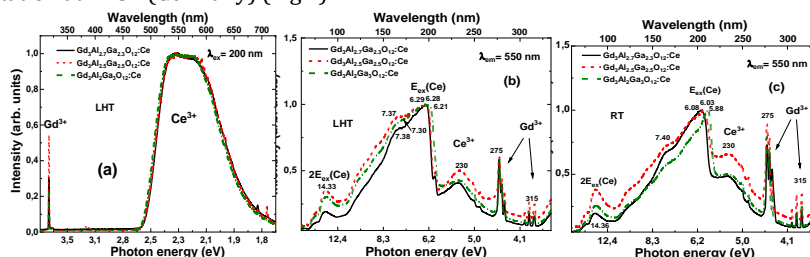


Fig.1. Emission (a) and excitation (b, c) spectra for  $\text{Ce}^{3+}$  luminescence in GAGG $x$ :Ce SCs at 10 K (a, b) and 300 K ©.

The most intensive bands in the exciton range peaked at 6.08-5.88 eV at 300K and 6.29-6.21 eV at 10K corresponds to the energy creation  $E_{\text{ex}}(\text{Ce})$  of excitons bound with  $\text{Ce}^{3+}$  ions. The positions of these bands show low energy shift with increasing Ga content in GAGG $x$ :Ce SCs, mostly at RT (Fig.1c). The bumps in the excitation spectra at 10K and 7.4 eV at 300K presumable correspond to the second excitation level of excitons. The peaks at 4.36 eV at RT corresponds to the multiplication of electronic excitation, e. g. to  $2E_{\text{ex}}(\text{Ce})$  energies.

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## Power-dependent dynamics of the up-conversion process in $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped single nanocrystals

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This work analyzes the dynamics of the up-conversion process observed in  $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped single fluoride nanocrystals (NCs). We focus on the red emission of erbium ions ( $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ ), which can be activated by a laser operating at 980 nm. Results of time-dependent luminescence microscopy show a strong dependence of the luminescence transients character on the excitation laser power. For low laser power (c.a. 100  $\mu\text{W}$ ), the acquired transients feature distinct and relatively slow rising part preceding the main decay profile. However, the transient intensity peaks immediately for higher excitation power (c.a. 1 mW), and no rising part is observed. Additionally, we noticed a decrease in the average decay time with increasing excitation power.

To understand this phenomenon, we solved the set of time-dependent rate equations of the  $\text{Er}^{3+}/\text{Yb}^{3+}$  system. Our computations show that for low laser power, the up-conversion luminescence is activated mainly by the nonradiative energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  ions. Instead, erbium is excited primarily due to the direct absorption of photons in the excited state absorption process for high laser power. We also identified an additional nonradiative decay channel depopulating the red-emitting level. We attributed this channel to the presence of surfactants stabilizing nanocrystal. Indeed, the channel activity can be reduced by coating NCs with an additional optically passive shell insulating the active core from surfactants. The efficiency of this channel requires overcoming a potential barrier and depends on the local temperature. The latter, however, is controlled by the laser. Eventually, we extracted the radiative decay rate of the red emission level regardless of the excitation laser power. We found the presented approach valuable for the dynamics of the up-conversion processes analysis.

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