8th International Workshop on

Photoluminescence in Rare Earths: Photonic Materials and Devices

4-6 September 2019 | Nice, France

Book of abstracts

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Welcome

PRE’19 is the eighth event in the series of International Workshops covering a wide range of research topics concerning the properties and applications of rare-earth ions in optoelectronics and photonics. The series begun in Trento, Italy in May 2005 (PRE’05), followed by PRE’07 again in Trento, PRE’10 in Firenze (Italy), PRE’12 in Kyoto (Japan), PRE’14 in San Sebastián (Spain), PRE’16 in Greenville (USA) and PRE'17 in Roma (Italy).

The Photoluminescence in Rare Earths: Photonic Materials and Devices (PRE) workshop aims to provide a global forum for material scientists, chemists and physicists to discuss and debate the state of the art and future perspectives of rare earth based materials for optoelectronic and photonic applications. Fundamental aspects, properties, and applications of photoluminescent materials are considered.

More than 700 scientists and students from more than 30 countries, in total, have attended the previous Workshops. The average size of each event, around 100 people, makes for a collegial environment where students and world experts can mingle and talk in an informal and effective way.

We welcome you in PRE'19, to be held on 4-6 September 2019 in Nice, France, to discuss on your most recent findings and join the community of scholars advancing the field of light emission based on rare-earth doped materials.

Looking forward to meeting you in the French Riviera !

Wilfried Blanc, Pieter Dorenbos, Fiorenzo Vetrone, *PRE'19 Co-chairs*

Giancarlo C. Righini, *PRE'19 Honorary chair*

https://pre19.sciencesconf.org/

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Tuesday, 3 Sept.	Wednesday, 4 Sept.		Thursday, 5 Sept.		Friday, 6. Sept.	
	8:30-9:00 **Opening Session**		*8:00-9:30* **Nanoparticles and phosphors I**	*8:00-9:30* **Organic and inorganic II**	*8:30-10:30* **Phosphors**	*8:30-10:30* **Glass and applications**
	9:00-10:00 **Plenary**		*10:00-11:10* **Lasers and applications**	*10:00-11:10* **Persistent and phosphors**	*11:00-12 :50* **Nanocomposite glasses**	*11:00-12:50* **Scintillators**
	10:30-12:00 **Structure and properties**	*10:30-12:00* **Thermometry and scintillators**	*11:10-12:30* **Plenary**		*12:50-13:10* **Best paper award ceremony & Closing session**	
	Lunch		Lunch		Lunch	
15:00-19:00 **Registration**	*13:30-15:00* **Fibers ang glasses I**	*13:30-15:00* **Fundamentals and theory**	*14:00-15:30* **Nanoparticles and phosphors II**	*14:00-15:30* **Sustainability**		
	15:15-16:15 **Energy transfer and clustering**	*15:15-16:15* **Organic and inorganic I**	*16:00-17:30* **Fibers and glasses II**	*16:00-17:30* **Nanoparticles and bio-applications**		
	16:30-19:30 **Poster session**					
			20:00 **Diner**			

Wednesday, 4 September 2019

8:30-9:00 **Opening Ceremony** | Room: Chagall

9:00-10:00 **Plenary |** Chair: Pieter Dorenbos | Room: Chagall

Non-luminescent defects in solids: enemies or friends?
Philippe F. SMET - LumiLab, Department of Solid State Sciences, Ghent University, Belgium

Coffee Break

10:30-12:00 **Structure and properties |** Chair: Dominik Dorosz | Room Chagall

10:30-11:00 *Rare earth elements in glasses, a multiscale approach* - invited
Maria Rita CICCONI - Institut de Physique du Globe, Paris, France

11:00-11:20 *Optical sensing properties based on a reversible redox process*
Véronique JUBERA - ICMCB - Université de Bordeaux, CNRS, Pessac, France

11:20-11:40 *Evidence of Ce^{4+} ions by XANES spectroscopy in the new fast scintillator crystal: Ce^{3+}-Mg^{2+} -co-doped $Gd_3Al_2Ga_3O_{12}$ garnet*
Georges BOULON - Institut Lumière Matière, CNRS- Université Claude Bernard Lyon 1, Université de Lyon, Villeurbanne, France

11:40-12:00 *Towards tetravalent praseodymium*
Mathias WICKLEDER - University of Cologne, Department of Chemistry, Germany

10:30-12:00 **Thermometry and scintillators** | Chair: Jumpei Ueda | Room: Dufy - Renoir

10:30-11:00 *Nd^{3+} doped garnet-type nanocrystals for temperture sensing at the nanoscale* - invited
Géraldine DANTELLE - Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, Grenoble, France

11:00-11:20 *Primary luminescent thermometer in the visible range based on Er,Yb:$GdVO_4$ microcrystals and its excitation power dependence*
Maria CINTA PUJOL - Universitat Rovira i Virgili, Departament de Química Física i Inorgànica, Física i Cristal·lografia de Materials i Nanomaterials (FiCMA-FiCNA) and EmaS, Tarragona, Spain

11:20-11:40 *Cerium concentration effect on scintillation properties and temperature dependence of $(Gd, La)_2Si_2O_7$ scintillator*
Masao YOSHINO - Institute for Materials Research, Tohoku University, Japan

11:40-12:00 *Difference of Mg^{2+} and Mo^{6+} co-doping effects on luminescence and scintillation properties of Ce:LuAG single crystal scintillators*
Kyoung JIN KIM - Institute for Materials Research, Tohoku University, Sendai, Japan

Lunch

13:30-15:00 **Fibers and glasses I** | Chair: Daniele Milanese | Room: Chagall

13:30-14:00 *Towards laser cooling in rare earth doped silicate glass fibers* - invited
Peter DRAGIC - Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, IL, USA

14:00-14:20 *Local field effect in structured optical fiber co-doped with noble metal nanoparticles and lanthanide ions*
Jacek ZMOJDA - Bialystok University of Technology, Faculty of Electrical Engineering, Bialystok, Poland

14:20-14:40 *Multicolor emission of polymer optical fibers co-doped with RE and fluorescent dyes*
Piotr MILUSKI - Bialystok University of Technology, Department of Electrical Engineering, Bialystok, Poland

14:40-15:00 *All optical methane sensor based on rare-earth doped fibers*
Imen HAFIENNE - CIMAP, CEA-CNRS-ENSICaen, Université de Caen Normandie, France

13:30-15:00 **Fundamentals and theory** | Chair: Mathias Wickleder | Room: Dufy - Renoir

13:30-14:00 *Nephelauxetic effect on the binding energy in the lanthanide $4f^q$ ground states* - invited
Pieter DORENBOS - Delft University of Technology, Faculty of Applied Sciences, Delft, The Netherlands

14:00-14:20 *Pauli antisymmetry interactions between active center and host: The R1-line of Cr^{3+} in garnets*
Luis SEIJO - Departamento de Química, Instituto Universitario de Ciencia de Materiales Nicolás Cabrera, and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, Madrid, Spain

14:20-14:40 *Evidence for intervalence charge-transfer (IVCT) states in Eu-doped phosphors*
Jonas JOOS - LumiLab, Dept. of Solid State Sciences, Ghent University, Ghent, Belgium

14:40-15:00 cancelled

15:15-16:15 **Energy transfer and clustering** | Chair: Géraldine Dantelle | Room: Chagall

15:15-15:35 *Luminescence properties of Eu^{2+}-Mn^{2+} co-doped $Ba_2MgSi_2O_7$*
Atul SONTAKKE - Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, the Netherlands

15:35-15:55 cancelled

15:55-16:15 *Luminescence and energy transfer in fluoroindate glasses co-doped with Er^{3+}/Ho^{3+}*
Marcin KOCHANOWICZ - Bialystok University of Technology, Bialystok, Poland

15:15-16:15 **Organic and inorganic I** | Chair: Animesh Jha | Room: Dufy - Renoir

15:15-15:35 *Molecular logical arrays through Ln^{3+}-ions using exclusively physical inputs*
Carlos BRITES - CICECO-Institute of Materials, Physics Department, Universidade de Aveiro, Portugal

15:35-15:55 *Cellulose fibres and paper modified by nanophosphors based on rare earth elements activated by UV and IR radiation*
Agata SZCZESZAK - Adam Mickiewicz University in Poznan, Poznan, Poland

15:55-16:15 *RE^{3+} based phosphors embedded into organic polyethylene films*
Salvador CARMONA-TELLEZ - Cátedras CONACyT/Benemérita Universidad Autónoma de Puebla, Facultad de Ciencias Físico-Matemáticas, Puebla Mexico

Coffee break

16:30:19:30 **Poster session** | Room: “Lunch”

Thursday, 5 September 2019

8:00-9:30 **Nanoparticles and phosphors I** | Chair: Claudia Wickleder | Room: Chagall

8:00-8:30 *Inorganic nanomaterials and doping strategies for future perspectives in scintillation applications and biomedicine* - invited
Irene VILLA - Department of Materials Science, University of Milano-Bicocca, Milano, Italy

8:30-8:50 *Structural modification of nanohydroxyapatite* $Ca_{10}(PO_4)_6(OH)_2$ *related to* Eu^{3+} *and* Sr^{2+} *ions doping and its spectroscopic and antimicrobial properties*
Katarzyna SZYSZKA - Institute of Low Temperature and Structure Research PAS, Wroclaw, Poland

8:50-9:10 *Novel Microemulsion approach for the synthesis of* Eu^{2+} *doped nanoparticles*
Adrian MATTNER - Inorganic Chemistry, Faculty of Science and Technology, University of Siegen, Germany

9:10-9:30 *Controlled synthesis and photoluminescence properties of hexagonal* Eu^{3+} *activated* $Na(Y,Gd)F_4$ *microphosphors*
Suryanarayan DASH - Dept. of Physics and Astronomy, National Institute of Technology Rourkela, Odisha, India

8:00-9:30 **Organic and inorganic II** | Chair: Ciro Falcony | Room: Dufy - Renoir

8:00-8:30 *Metal-organic frameworks as near-infrared emitting materials based on lanthanide cations: from fundamental science to biological imaging* - invited
Stéphane PETOUD - Centre de Biophysique Moléculaire CNRS, Orléans, France & Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, USA

8:30-8:50 *Mixed* Eu^{3+}*-*Tb^{3+} *metal-organic frameworks built on isophtalic acid ligand as ratiometric luminescent thermometer*
Hélène BRAULT - Institut des Matériaux Jean Rouxel, Université de Nantes, CNRS, Nantes, France

8:50-9:10 *Microwave assisted synthesis of Tb-metal-organic frameworks with luminescent properties*
Gilberto ALARCÓN-FLORES - Instituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Ciudad de México, México

9:10-9:30 *Lanthanide-doped organic-inorganic materials for downshifting layers in solar cars*
Sandra CORREIA - Department of Physics and CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal

Coffee break

10:00-11:10 **Lasers and applications** | Chair: Peter Dragic | Room: Chagall

10:00-10:30 *Erbium doped GaN for Laser Applications* – invited
John ZAVADA - Tandon School of Engineering, New York University, New York, USA

10:30-10:50 *Rare earth doped transparent ceramics for laser gain medium*
Simon GUENE-GIRARD - ICMCB - Université de Bordeaux, CNRS, Pessac, France

10:50-11:10 *Numerical investigation of simultaneous lasing at three different wavelengths in an Yb:Er:Tm:Ho co-doped germanate glass*
Francesco PRUDENZANO - Department of Electrical and Information Engineering, Politecnico di Bari, Bari, Italy

10:00-11:10 **Persistent and phosphors** | Chair: Luis Seijo | Room: Dufy - Renoir

10:00-10:30 *Traps with controllable depths in persistent luminescence phosphors* – invited
Yixi ZHUANG - College of Materials, Xiamen University, China

10:30-10:50 *Hexagonal* $Sr_{1-x/2}Al_{2-x}Si_xO_4{:}Eu^{2+},Dy^{3+}$ *transparent ceramics exhibiting white persistent luminescence excitable by visible light*
Victor CASTAING - PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, Paris, France

10:50-11:10 *Afterglow phosphors based on lanthanide-doped germanates in the system* $CaO–GeO_2–Y_2O_3$
Ivan LEONIDOV - Institute of Solid State Chemistry, UB RAS, Ekaterinburg, Russia

11:10-11:30 **Plenary** | Chair: Wilfried Blanc | Room: Chagall

In memory of Marc De Micheli - Contribution to rare-earth doped Lithium Niobate integrated devices
Pascal BALDI – Institut de Physique de Nice, Université Côte d'Azur, CNRS, Nice, France

11:30-12:30 **Plenary** | Chair: Fiorenzo Vetrone | Room: Chagall

Lanthanide-based thermometers at the cutting-edge of luminescence thermometry: from biomedical applications to the Internet of Things
Luis CARLOS - Physics Department and CICECO-Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal

Lunch

14:00-15:30 **Nanoparticles and phosphors II** | Chair: Bruno Viana | Room: Chagall

14:00-14:30 *New directions in luminescent nanoparticles* – invited
Claudia WICKLEDER - Inorganic Chemistry, School of Science and Technology, University of Siegen, Siegen, Germany

14:30-14:50 *Precursor-directed synthesis of upconverting* $LiYF_4:Yb^{3+}$, Tm^{3+} *nanoparticles and their composites designed for near infra-red driven photocatalysis*
Bhagyesh PUROHIT - Univ Lyon, ILM CNRS-Univ Lyon 1, Villeurbanne, France

14:50-15:10 *Rare earth based nanomaterials; dopant variations and its luminescent properties*
Rajesh KOMBAN - Fraunhofer Center for Applied Nanotechnology CAN (Fraunhofer CAN)*, Hamburg, Germany

15:10-15:30 Bi^{3+} *influence on physicochemical properties of* $Ba_2REV_3O_{11}$ *upconverting nanoparticles*
Nina KACZOROWSKA - Adam Mickiewicz University in Poznań, Faculty of Chemistry, Department of Rare Earths, Poznań, Poland

14:00-15:30 **Sustainability** | Chair: Franck Mady | Room: Dufy - Renoir

14:00-14:30 *Rare earth elements and urban mines: critical stategies for sustainable development* – invited
Maurizio FERRARI -IFN-CNR CSMFO Lab. and FBK Photonics Unit, Trento, Italy

14:30-14:50 *Spectroscopic Analysis of Rare-Earth-ion* (RE^{3+}) *and* Mn^{2+} *ions in CdS Q-Dot bearing Silicate Glasses*
Animesh JHA - School of Chemical and Process Engineering, University of Leeds, Leeds, U.K.

14:50-15:10 *Advances in Rare Earth characterization by optical spectroscopy*
Célia OLIVERO, Horiba Scientific

15:10-15:30 cancelled

Coffee break

16:00-17:30 **Fibers and glasses II** | Chair: Luiz Jacobsohn | Room: Chagall

16:00-16:30 *Specific mechanisms associated with rare-earth dopants (Yb, Er, Ce) in the radiation-induced attenuation of silica-based optical fibers* – invited
Franck MADY - Université Côte d'Azur, CNRS, INPHYNI, Nice, France

16:30-16:50 *New insights into the spectroscopic properties of Yb-doped YAG-derived all-glass optical fibers*
Magnus ENGHOLM - Mid Sweden University, Sundsvall, Sweden

16:50-17:10 *Electrons and protons irradiation of* Er^{3+}, Yb^{3+} *codoped phosphate glasses*
Laeticia PETIT - Photonics Laboratory, Tampere University, Tampere, Finland

17:10-17:30 *Drawing of glass containing rare-earth-doped oxide nanoparticles : A study by Molecular dynamics simulations*
Jorel FOURMONT - Laboratoire de Photonique d'Angers (LPhiA), Université d'Angers, Angers, France

16:00-17:30 **Nanoparticles and bio-applications** | Chair: Maria Cinta Pujol Baiges | Room: Dufy - Renoir

16:00-16:30 *Lanthanide ions activated optical nanothermometers* - invited
Adolfo SPEGHINI - NRG, Department of Biotechnology and INSTM, RU Verona, University of Verona, Verona, Italy

16:30-16:50 *Dye-sensitized blue-to-UVB upconversion nanocrystals for phototherapy*
Yu DECHAO - Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht, University, Utrecht, The Netherlands

16:50-17:10 *Rare-Earth codoped nanocrystals* $Cr^{3+},RE^{3+}:ZnGa_2O_4$ *for bioimaging applications*
Bruno VIANA - PSL Research University, Chimie ParisTech – CNRS, Institute de Recherche de Chimie Paris, France

17:10-17:30 *Up-conversion luminescence of nanoparticles sensitized by* Nd^{3+}, Ho^{3+}, Er^{3+} *and* Tm^{3+} *ions*
Tomasz GRZYB - Adam Mickiewicz University in Poznań, Faculty of Chemistry, Department of Rare Earths, Poznań, Poland

19:30-23:30 Conference diner

Friday, 6 September 2019

8:30-10:30 **Phosphors** | Chair: Francesco Prudenzano | Room: Chagall

8:30-8:50 cancelled

8:50-9:10 *Spectroscopic investigation of the $YV_xAs_{1-x}O_4$ doped with Tb^{3+} ions*
Rafael WIGLUSZ - Institute of Low Temperature and Structure Research PAS, Wroclaw, Poland

9:10-9:30 *Highly-transparent efficient sol–gel-derived silica–$(Gd,Pr)PO_4$ glass-ceramic narrow-band UVB phosphors*
Koichi KAJIHARA - Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences,Tokyo Metropolitan University, Tokyo, Japan

9:30-9:50 *Optical properties of novel nitridic and oxidic phosphors doped with Eu^{2+}*
Jasmin SCHMIDT - Inorganic Chemistry, Faculty for Science and Technology, University of Siegen, Siegen, Germany

9:50-10:10 *Effect of post-preparation annealing on powder and pulsed laser deposited thin film phosphors of oxyorthosilicate doped with rare-earths*
Martin NTWAEABORWA - School of Physics, University of the Witwatersrand, Johannesburg, South Africa

10:10-10:30 *Synthesis of orange emitting Sm^{3+} doped sodium calcium silicate phosphor by sol-gel method for photonic device applications*
M. JAYASIMHADRI - Luminescence Materials Research Lab (LMRL), Department of Applied Physics, Delhi Technological University, Delhi, India

8:30-10:30 **Glass and applications** | Chair: Laeticia Petit | Room: Dufy - Renoir

8:30-8:50 *Luminescence performance of Eu^{3+} ions doped Alkaline-Earth Boro Tellurite glasses*
Koneru SWAPNA - Department of Physics, Koneru Lakshmaiah Education foundation, Green Fields, Vaddeswaram, Guntur, Andhra Pradesh, India

8:50-9:10 *Up-conversion luminescence of erbium ion in sodium-germanate glasses*
Vladimir ASEEV - ITMO University, Saint-Petersburg, Russia

9:10-9:30 *Radiative analysis of orange emitting silica borate glasses for photonic applications*
Allam S. RAO - Department of Applied Physics, Delhi Technological University, Shahbad Daulatpur, New Delhi, India

9:30-9:50 *Er^{3+}/Yb^{3+} doped 1-D Microcavity based on alternating aluminosilicate glass and titania sol-gel layers for visible emission and efficient up-conversion*
Rojas HERNANDEZ ROCIO - Department of Materials Engineering, Tallinn Univ. of Technology, Tallinn, Estonia

9:50-10:10 *Tb^{3+} and Sm^{3+} doped $Ga_5Ge_{20}Sb_{10}Se_{65}$ fibers long-wave IR luminescence around 8µm*
Florent STARECKI - CIMAP, CEA-CNRS-ENSICAEN, Université de Caen, Caen, France

10:10-10:30 *Fabrication, structural and spectroscopic characterizations of first translucent ceramics from cubic nano-crystalline La_2MoWO_9 activated by Nd^{3+} ions*
Malgorzata GUZIK - Faculty of Chemistry, University of Wrocław, Wrocław, Poland

Coffee break

11:00-12:50 **Nanocomposite glasses** | Chair: Véronique Jubera | Room: Chagall

11:00-11:30 *Progress on the preparation of glass-based phosphate materials for photonics* – invited
Laeticia PETIT - Photonics Laboratory, Tampere University, Tampere, Finland

11:30-11:50 *Transparent oxyfluoride glass-ceramics prepared by Spark Plasma Sintering (SPS) for optical applications*
Singarapu BABU - Dept.of Coating Processes, FunGlass, Alexander Dubcek Univ. of Trencín, Trencín, Slovakia

11:50-12:10 *Chemical Characterization of* LaF_3*:*Tm^{3+} *Doped Phase-Separated Dielectric Nano- Particles (DNPs) via Secondary Ion Mass Spectrometry (SIMS) Imaging*
Wilfried BLANC - Université Côte d'Azur, CNRS, INPHYNI, Nice, France

12:10-12-30 *Crystallization study of* Er^{3+} *doped glasses in* $NaPO_3$*-*CaF_2*-*TiO_2*/MgO/ZnO system*
Nirajan OJHA - Photonics Laboratory, Tampere University, Tampere, Finland

12:30-12:50 cancelled

11:00-12:50 **Scintillators** | Chair: Georges Boulon | Room: Dufy - Renoir

11:00-11:30 *Understanding the luminescence properties of* Ce^{3+}*-doped garnet phosphors on the basis of composition, crystal and electronic structure* - invited
Jumpei UEDA - Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan

11:30-11:50 *Comparison of Mo ion co-doping effects in Ce:*$Y_3Al_5O_{12}$ *and Ce:YAlO3 single crystal scintillators*
Mutsumi UENO - Institute for Materials Research, Tohoku University, Sendai, Japan

11:50-12:10 *Melt growth and luminescence properties* Lu_2O_3 *based high dense single crystals grown by indirect heating method using arc plasma*
Kei KAMADA - New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan

12:10-12-30 *Characterization of* Ce^{3+} *or* Pr^{3+}*- single doped type III KGd*$(PO_3)_4$ *bulk crystals as scintillator materials*
Maria CINTA PUJOL - Universitat Rovira i Virgili, Departament Química Física i Inorgànica, Física i Cristal·lografia de Materials i Nanomaterials (FiCMA-FiCNA) - EMaS, Tarragona, Spain

12:30-12:50 *Optical study on garnet-type scintillator with longer-wave-emitting*
Shunsuke KUROSAWA - New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan

12:50-13:10 **Best paper award ceremony and closing session** | Chair: Giancarlo Righini | Room: Chagall

Lunch

List of posters

P1 *The pathway to an optimum luminescent thermometer – Bending the Boltzmann distribution*
Markus SUTA, Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Department of Chemistry, Utrecht University, Utrecht, Netherlands

P2 *Luminescence investigation of Ln^{3+} -doped inorganic materials in high-pressure*
Przemysław WOŹNY, Adam Mickiewicz University in Poznań, ul. Uniwersytetu Poznańskiego 8, Poznań, Poland

P3 *Up-conversion luminescence and energy transfer mechanism of $ZnTiO_3$: Er^{3+},Yb^{3+} phosphor*
Mokhotjwa DHLAMINI, Department of Physics, College of Science Engineering and Technology, University of South Africa, Johannesburg, South Africa

P4 *Influence of the synthesis route on the structural and spectroscopic properties of Nd^{3+}-doped YPO_4 nano and micro-powders*
Jakub PAWLOW, Faculty of Chemistry, University of Wrocław, Wrocław, Poland

P5 *Site selective spectroscopy as an efficient tool for structural and spectroscopic studies of Nd^{3+} -doped $LuPO_4$ nano/micro-powders*
Kacper PROKOP, Faculty of Chemistry, University of Wrocław, Wrocław, Poland

P6 *$Tb_2(BDC)_3$ high-quality luminescent metal-organic framework films*
Ciro FALCONY, Centro de Investigación en Materiales Avanzados, Unidad Monterrey, Apodaca, Nuevo León, México

P7 *Dy^{3+} ions as optical probes for structural study of $K_4SrGe_3O_9$*
Ivan LEONIDOV, Institute of Solid State Chemistry, UB RAS, Ekaterinburg, Russia

P8 *Core-Shell architecture to enhance RE doped UC NanoCrystals Luminescence Emissions for Photocatalytic Applications*
Pablo ACOSTA-MORA, Departamento de Física, Universidad de La Laguna, Tenerife, Spain

P9 *Structural and optical characterization of Tm^{3+}-doped apatite related $NaLa_9(GeO_4)_6O_2$ phosphors*
Olga A. LIPINA, Institute of Solid State Chemistry, UB RAS, Ekaterinburg, Russia

P10 *Synthesis and spectroscopic properties of red-emitting lithium tantalate garnet phosphors for solid state lighting*
Olga A. LIPINA, Institute of Solid State Chemistry, UB RAS, Ekaterinburg, Russia

P11 *Rare earth-doped phosphate and germanate glasses for near-infrared power amplifiers and laser sources*
Daniel Milanese, DIA and RU INSTM, Università di Parma, Parma, Italy

P12 *Insight into the effect of Li^{+} concentration on the structure and photoluminescence properties of $Ca_{10}(PO_4)_6(OH)_2$: Sm^{3+} intended for theranostic application*
Paulina SOBIERAJSKA, Institute of Low Temperature and Structure Research, PAS, Wroclaw, Poland

P13 *Study of luminescence properties of Eu^{2+} ion depending on changes of Eu^{3+} ion concentration in the silicate-substituted apatite*
Sara TARGOŃSKA, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland

P14 *The effects of local symmetry on the upconversion emission intensity, color and dynamics under ns pulsed excitation*
Daniel AVRAM, Faculty of Physics, University of Bucharest, Magurele, Ilfov, Romania

P15 *Spectral, luminescent, laser and holographic properties of photo-thermo-refractive glass doped with rare earth ions*
Nikolay NIKONOROV, ITMO University, Saint Petersburg, Russia

P16 *Praseodymium-doped Type III $KGd(PO_3)_4$ nanocrystals: synthesis and characterization*
Maria Cinta PUJOL BAIGES, Universitat Rovira I Virgili, Departament Quimica Fisica I Inorganica, Física i Cristal.lografia de Materials i Nanomaterials-EMaS, Campus Sescelades, Tarragona, Spain

P17 *The changes of the photoluminescence properties caused by ion implantation of erbium into single-crystalline and nano-crystalline ZnO*
Pavla NEKVINDOVÁ, Department of Inorganic Chemistry, University of Chemistry and Technology, Prague, Czech Republic

P18 *Experimental and theoretical study of erbium incorporation in various crystal materials – ZnO, $LiNbO_3$ and Al_2O_3*
Jakub CAJZL, Department of Inorganic Chemistry, University of Chemistry and Technology, Prague, Czech Republic

P19 *beta-NaYF4 nanoparticles with core@shell morphology doped with Er^{3+}, Tm^{3+} and Yb^{3+} ions: their synthesis, characterisation and photoluminescence study*
Piotr KAMINSKI, Adam Mickiewicz University in Poznań, Faculty of Chemistry, Department of Rare Earths, Poznań, Poland

P20 *Detailed analysis of Nd^{3+},X^{3+} (X=Gd, Y, Sc, Lu, Ce, La) codoped CaF_2 laser crystals for broadband laser operation*
Cesare MERONI, Centre de recherche sur les Ions, les Matériaux et la Photonique (CIMAP), UMR 6252 CEA-CNRS-ENSICAEN, Université de Caen, 6 Blvd Maréchal Juin, 14050 Caen, France

P21 *Concentration dependence of spectroscopic properties and energy transfer analysis of the fluorophosphate glasses with small phosphates additives doped with Er^{3+}/Yb^{3+} ions*
Elena KOLOBKOVA, ITMO University, Saint-Petersburg, Russia

P22 *Study of persistent luminescence in $SrSi_2N_2O_2$:Eu^{2+}, M (M=Ce, Cr, Er, Dy, Nd)*
Natalia MAJEWSKA, Institute of Experimental Physics, Faculty of Mathematics, Physics and Informatics, University of Gdansk, Gdansk, Poland

P23 *Tm^{3+} photoluminescence in $Si_{0.75}xAl_{1-x}N$ libraries grown by combinatorial magnetron sputtering*
Giacomo BOSCO, Delft University of Technology, Faculty of Applied Sciences, Delft, The Netherlands

P24 *Up-conversion emission in strontium fluoride doped with erbium ions upon 1532 nm excitation*
Sylwia WASILEWSKA, Department of Rare Earth, Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego, Poznań, Poland

P25 *Radioluminescence of $Lu_3Al_5O_{12}$:Ce single crystal and transparent polycrystalline ceramic at high temperatures*
Luiz JACOBSOHN, Department of Materials Science and Engineering, Clemson University, Clemson, SC, USA

P26 *Up-conversion phenomenon of core@shell nanoparticles based on SrF_2, doped with Yb^{3+}, Er^{3+} and Nd^{3+} ions excited at 808 nm and 975 nm wavelength*
Dominika PRZYBYLSKA, Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University in Poznań, ul. Uniwersytetu Poznańskiego, Poznań, Poland

P27 *Scintillation properties of Tm-doped $GdAlO_3$ crystals doped with different Tm concentrations*
Masaki AKATSUKA, Nara Institute of Science and Technology, Nara, Japan

P28 *A NIR emitting scintillator material $YAlO_3$:Re^{3+} (Re=Er, Ho, Pr, Tm)*
Masaki AKATSUKA, Nara Institute of Science and Technology, Nara, Japan

P29 *Rare-earth doped optical fiber employing in-situ metal oxidation*
Courtney KUCERA, Center for Optical Materials Science and Engineering Technologies (COMSET) and the Department of Materials Science and Engineering, Clemson University, Clemson, SC, 29625, USA

P30 *Photoluminescence and photoluminescence excitation spectra of Eu and Si co-doped AlN films for visible light-emitting devices*
Hiroshi KATSUMATA, School of Science and Technology, Meiji University, Kawasaki, Japan

P31 *Luminescent properties of Titania doped with nanoparticles of Gadolinium oxide and Europium*
Pablo Marco TREJO GARCÍA, Facultad de Ciencias Físico Matemáticas, Benemerita Universidad Autonoma de Puebla, C.P. 72570 Puebla, México

P32 *Synthesis and characterization of an hybrid SiO_2-PMMA material doped with luminescent Eu doped Gd_2O_3 nanoparticles*
Pablo Marco TREJO GARCÍA, Facultad de Ciencias Físico Matemáticas, Benemerita Universidad Autonoma de Puebla, C.P. 72570 Puebla, México

P33 *The effect of Zn, Al and Ge on the phonon energy and Er^{3+} photoluminescence in silicate glasses*
Petr VARAK, Department of Inorganic Chemistry, University of Chemistry and Technology, Prague, Czech Republic

P34 *Surface modification of $NaYF_4$: Yb^{3+}, Er^{3+}@NaYF4 up-conversion nanoparticles for biological applications*
Natalia JURGA, Adam Mickiewicz University in Poznań, Faculty of Chemistry Department of Rare Earths Uniwersytetu Poznańskiego, Poznań, Poland

P35 *How to tune the UC luminescence in YPO_4 nanoparticles doped with lanthanide ions?*
Artur TYMIŃSKI, Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego, Poznań, Poland

P36 *Photoluminescence and scintillation properties of Cs_3PrCl_6 crystal*
Yutaka FUJIMOTO, School of Engineering, Tohoku University, Aramaki, Aoba-ku, Sendai, Japan

P37 *Luminescence characteristics of Cs_3ScCl_6:Ce crystals*
Takahashi KEISUKE, Department of Engineering, Tohoku University, Miyagi, Japan

P38 *Tb^{3+}- and Dy^{3+}-doped $CaO–Al_2O_3–B_2O_3$-based glasses for neutron detection*
Ichiro KAWAMURA, Tohoku University, Miyagi, Japan

P39 *Photoluminescence and scintillation properties of $Al(PO_3)_3 - CeCl_3 - CsCl - CsPO_3$ – based glass scintillators*
Kei KAGAMI, Department of Engineering, Tohoku University, Miyagi, Japan

P40 *Optical, Scintillation and Dosimetric Properties of $Ca_3(PO_4)_2$ Transparent Ceramics Doped with Rare Earth Ions*
Takumi KATO, Division of Materials Science, Nara Institute of Science and Technology (NAIST), Nara, Japan

P41 *Emission Properties of Dy-doped $MgAl_2O_4$ Transparent Ceramics*
Takumi KATO, Division of Materials Science, Nara Institute of Science and Technology (NAIST), Nara, Japan

P42 *Model-Free Sliding Mode Control For Shaping 800 nm Pulses Of Yb/Tm Co-Doped Laser*
Maison CLOUATRE, Department of Electrical and Computer Engineering, Mercer University, Macon, GA, USA

P43 *$SrAl_2O_4$:Eu^{2+}, Dy^{3+} ultra-small particles obtained by pulsed laser ablation in liquid and their luminescent features*
Hongli DU, PSL Research University, Chimie ParisTech – CNRS, Institute de Recherche de Chimie Paris, France

P44 *Photoluminescence and scintillation properties of Ce-doped barium silicate glasses synthesized by the FZ method*
Daiki SHIRATORI, Nara Institute of Science and Technology, Nara, Japan

P45 *Evaluation of optical and X-ray induced Scintillation properties in Ce-doped Gd_2O_3-BaO-Al_2O_3-SiO_2 glasses*
Daiki SHIRATORI, Nara Institute of Science and Technology, Nara, Japan

P46 *Effect of La^{3+} and Gd^{3+} concentration on the NIR emission of $XNbO_4$:Tm^{3+} for bio-labelling application*
Susane B. MOSCARDINI, Universidade De Franca, Av. Armando Salles Oliveira, Franca, SP, Brazil

P47 *Luminescent properties of nanosized $LiYF_4$:Eu modified with gold nanoparticles assisted by atmospheric plasma jet*
J. M. GONCALVES, University of São Paulo, Ribeirão Preto, Brazil

P48 *Evaluation of photoluminescence and scintillation properties of Ce-doped $Ca_3Hf_2SiAl_2O_{12}$ crystals*
Hiroyuki FUKUSHIMA, Nara Institute of Science and Technology (NAIST), Nara, Japan

P49 *Photoluminescence and scintillation properties of Eu-doped CaZrO3 single crystals synthesized by the floating zone method*
Hiroyuki FUKUSHIMA, Nara Institute of Science and Technology (NAIST), Nara, Japan

P50 *Optical and radiation induced luminescence properties of* $SrBr_2$ *transparent ceramics doped with different Eu concentrations*
Hiromi KIMURA, Division of Materials Science, Nara Institute of Science and Technology (NAIST), Nara, Japan

P51 *Photostimulated luminescence properties of Eu-doped Cs(Cl, Br) transparent ceramics*
Hiromi KIMURA, Division of Materials Science, Nara Institute of Science and Technology (NAIST), Nara, Japan

P52 *Scintillation and dosimetric properties of Eu-doped* $BaCaBO_3F$ *ceramics*
Naoki KAWANO, Akita University, Akita, Japan

P53 *Scintillation properties of Nd-doped* TeO_2-Al_2O_3-WO_3 *glasses*
Naoki KAWANO, Akita University, Akita, Japan

P54 *Examination of luminescence initiated by ultrashort pulse excitation in* $Gd_3Al_{2.5}Ga_{2.5}O_{12}$*:Tm, Yb crystals*
Radosław LISIECKI, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland

P55 *Direct femtosecond laser printing of rare earth-doped silk microstructures*
Moliria SANTOS, São Carlos Institute of Physics, University of São Paulo, São Carlos, SP-Brazil

P56 *Exploring the tunneling luminescence process in strontium aluminate phosphors*
Virginija VITOLA, Institute of Solid State Physics, University of Latvia, Riga, Latvia

P57 *Dynamic tunability of upconverting* $NaYF_4$ *colloidal nanoparticles by* Ce^{3+} *co-doping*
Aleksandra PILCH-WRÓBEL, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland

P58 *Photoluminescence properties of coumarins containing copolymers*
Beata DERKOWSKA-ZIELINSKA, Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland

P59 *Microscopic parameters characterizing thermoluminescence in Ce-doped garnets*
Vasilii KHANIN, Utrecht University, Utrecht, the Netherlands

P60 *Alkali cations effects on structural, morphological and photoluminescence properties of zinc oxide materials (ZnO) synthesized from seed growth by hydrothermal process*
Widad BEKHTI, Laboratoire des Sciences de la Matière Condensée, Département de physique, Faculté des Sciences, Université d'Oran I Ahmed Ben bella, Oran, Algeria,

P61 *Visualizing the infection dynamics of pathogenic bacteria labelled by upconverting nanoparticles inside mouse gut*
Gokhan DUMLUPINAR, Tyndall National Institute, IPIC, Biophotonics, Lee Maltings Complex, Cork, Ireland

P62 *Upconversion emission studies of structural phase flips in* Er^{3+}/Yb^{3+}*:* $KLaF_4$ *bio-compatible nanoparticles*
Rajat BAJAJ, Delhi Technological University, New Delhi, India

P63 *Structural and spectroscopic properties of thermally stable* Eu^{3+} *doped barium zinc orthophosphate phosphor for w-LEDs*
Mukesh K. SAHU, Luminescent Materials Research Lab (LMRL), Department of Applied Physics, Delhi Technological University, Delhi, India

P64 *Photoluminescence studies on* Er^{3+}*-doped sodium-bismo-phosphate glasses for optoelectronic applications*
A.S. RAO, Department of Applied Physics, Delhi Technological University, New Delhi, India

Plenary presentations

Non-luminescent defects in solids: enemies or friends?

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This talk deals with a specific class of luminescent materials, or phosphors, which are able to store excitation energy in their lattice, in such a way that the time between excitation and emission can be extended up to minutes, hours or even many thousands of years [1]. They find applications in geological dating and as x-ray storage phosphors (involving optically stimulated luminescence), in persistent phosphors (driven by thermally driven release) or in mechanoluminescent phosphors (where the application of pressure leads to emission of light [2]). Rare earth ions turn out to be versatile in that respect, both as dopants, creating the appropriate emission and excitation behavior, and as co-dopants, influencing or creating the trapping centers.

Quite surprisingly, the nature of the defect(s) responsible for the energy storage is for many materials still unknown or assignments are speculative. Advanced analytical techniques (such as XANES or EPR) or quantum mechanical calculations are required to probe their exact role [3-5]. Especially when multiple techniques are combined, puzzles can be solved.

Those defects are often playing a role which goes beyond the mere energy storage reservoir which a phosphor designer has in mind. Different types of defects present in energy storage phosphors can interact with each other and with disturbances (be it light, heat and/or pressure), thereby influencing the storage and release conditions. Finally, we make the connection between situations when the same defects are considered friends – in order to increase the storage capacity – or are treated as enemies, i.e. when reducing quantum efficiency of phosphors [6].

Acknowledgements

This talk is a result of more than ten years of research activities on energy storage phosphors at the LumiLab research group and through research collaborations. Hence, many more people than listed as author have contributed to the current understanding, by painstakingly optimizing materials, bringing up inspiring ideas and overthrowing wild hypotheses by dedicated experiments. Thanks to all for countless hours of darkness - inherent to research on persistent phosphors - and many sparks of brightness!

References

[1] K. Van den Eeckhout, P.F. Smet, D. Poelman, *Materials*, **3**, 2536 (2010)
[2] A. Feng, P.F. Smet, *Materials*, **11**, 484 (2018)
[3] K. Korthout et al., *Phys. Rev. B*, **84**, 085140 (2011)
[4] D. Gourier et al., *Journal of Physics and Chemistry of Solids*, **75**, 826 (2014)
[5] A. De Vos et al., *Inorganic Chemistry*, **55**, 2402 (2016)
[6] D. Van der Heggen et al, *ACS Photonics*, **5**, 4529 (2018)

Lanthanide-Based Thermometers at the Cutting-Edge of Luminescence Thermometry: From Biomedical Applications to the Internet of Things

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The emergence of luminescent nanothermometry during the last decade opened up the possibility of measure thermal flows at spatial scales below 1 μm, unreachable by conventional electrical methods [1]. In fact, diverse phosphors capable of providing a contactless thermal reading through their light emission properties have been examined, e.g., polymers, DNA or protein conjugated systems, organic dyes, quantum dots, and trivalent lanthanide ions incorporated in organic-inorganic hybrids, multifunctional heater-thermometer nanoplatforms, upconverting, downconverting and downshifting nanoparticles.

In the last couple of years, the focus of luminescence thermometry has gradually shifted from the fabrication of more sensitive nanoarchitectures towards the use of the technique as a tool for thermal bioimaging and for the unveiling of properties of the thermometers themselves and of their local surroundings [2-4].

After a general perspective of the work done on ratiometric luminescent nanothermometers since the explosion of the field at one decade ago, the lecture will be focused on recent examples illustrating the potential of the technology on biomedical and mobile-based Internet of Things (IoT) applications.

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References

[1] C. D. S. Brites, S. Balabhadra, L. D. Carlos, *Adv. Opt. Mater.*, **7**, 1801239 (2019).

[2] R. Piñol, C. D. S. Brites, R. Bustamante, A. Martínez, N. J. O. Silva, J. L. Murillo, R. Cases, J. Carrey, C. Estepa, C. Sosa, F. Palacio, L. D. Carlos, A. Millán, *ACS Nano* **9** 3134–3142 (2015).

[3] C. D. S. Brites, X. Xie, M. L. Debasu, X. Qin, R. Chen, W. Huang, J. Rocha, X. Liu, L. D. Carlos, *Nature Nanotech.*, **11** 851–857 (2016).

[4] C. D. S. Brites, M. C. Fuertes, P. C. Angelomé, E. D. Martínez, P. P. Lima, G. J. A. A. Soler-Illia, L. D. Carlos, *Nano Lett.*, **17**, 4746-4752 (2017).

Invited presentations

Invited

Rare earth elements in glasses, a multiscale approach

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Rare-Earth Elements (REE) have very unique optical, magnetic and electronic properties because of the particular electronic configuration. The use of these elements has increased exponentially with the development of cutting-edge technologies, and besides the attractiveness for their applications in materials science, REE are particularly important as well in geosciences, and for biomedical applications.

To exploit REE characteristic properties, there is the need to derive the structure-property relationships, and then, it is required to bridge atomistic and macroscopic scales. Element selective techniques, such as X-Ray Absorption Spectroscopy (XAS) coupled with Raman, Optical Absorption, Photoluminescence spectroscopy, and thermoanalytical techniques provide the information needed to successfully link the macroscopic behavior to the microscale properties.

Examples on the study of REE-doped glasses and melts and on the parameters influencing their speciation will be provided.

Invited

Nd^{3+} doped garnet-type nanocrystals for temperature sensing at the nanoscale

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Accurate and non-invasive techniques allowing for temperature measurements at the nanoscale have widely spread out with the major development of nanotechnologies and, more specifically, of nanomedicine [1]. Luminescent nanoprobes (quantum dots, dyes, fluorescent polymers, rare-earth doped nanoparticles, etc) have ever since competed to ensure the best thermal sensitivity in the 20 to 50°C temperature range, as well as high biocompatibility and appropriate size (below 100 nm) for *in vivo* applications. Due to their high chemical stability and intrinsic luminescence in the near infrared (NIR) region, overlapping with the biological optical transparency window, rare-earth doped oxide nanoparticles (NPs) are promising candidates for in vivo nanothermometry.
In this work, Nd^{3+}-doped $Y_3Al_5O_{12}$ (YAG:Nd^{3+}) and $Gd_3Sc_2Al_3O_{12}$ (GSAG:Nd^{3+}) NPs are investigated as luminescent nanothermometers. The development of a new solvothermal synthesis method, combining high temperature (400°C) with high external pressure (200 bar), allows for the elaboration of luminescent YAG:Nd^{3+} and GSAG:Nd^{3+} NPs with an average size of 80 nm [2]. The liquid-based solvothermal reaction induces the adsorption of hydroxyl and alcoholic molecules onto the NP surface, leading to the stabilisation of the NPs in water. Typical Nd^{3+} emission was observed under a 808-nm excitation, with two emission bands centred at 938 and 945 nm, corresponding to the electronic $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition split by the crystal field effect. Thermal sensing properties of Nd^{3+}-doped GSAG NPs were found to be excellent for contactless NIR temperature measurements with even higher relative thermal sensitivity as compared to the conventional Nd^{3+}-doped YAG NPs [3,4]. Additionally, the presence of Gd^{3+} ions in the GSAG structure offers a further property (MRI contrast), defining GSAG:Nd NPs as multifunctional nanoprobes.

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References

[1] C. D. S. Brites, P. P. Lima, N. J. O. Silva, Angel Millan, V. S. Amaral, F. Palacio, L. D. Carlos, *Nanoscale*, **4**, 4799 (2012)
[2] G. Dantelle, D. Testemale, E. Homeyer, A. Cantarano, S. Kodjikian, C. Dujardin, J.L. Hazemann, A. Ibanez, *RSC Advances* **8**, 26857 (2018)
[3] A. Benayas, B. del Rosal, A. Pérez-Delgado, K. Santacruz-Gómez, D. Jaque, G. A. Hirata, F. Vetrone, *Adv. Opt. Mater*. **3**, 687 (2015)
[4] G. Dantelle, M. Matulionyte, D.Testemale, A. Cantarano, A. Ibanez, F. Vetrone, *Phys. Chem. Chem. Phys.* **21**, 11132 (2019)

Invited

Towards laser cooling in rare earth doped silicate glass fibers

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Laser cooling in solids can be achieved by pumping a rare earth (RE) element at an energy less than its average spontaneous emission energy. Phonons then can be extracted from the host material; under proper conditions giving rise to temperatures reaching the cryogenic range [1]. Since laser cooling efficiency usually is only on the order of a few percent, the material system must be free of parasitic heating processes, such as non-radiative decay, impurity absorption, etc. This places particularly strict requirements on the quality of the host and the local environment of the RE [2]. Owing in part to its simple two-level *f-f* transition diagram, possessing only one excited state (and therefore lacking upconversion or excited state absorption processes), and a relatively high concentration quenching limit, Yb^{3+} is a preferred RE ion for the cooling application. While laser cooling has been demonstrated in several Yb-doped crystalline materials [1,3], laser cooling of Yb-doped glass has been most successful in fluorides, namely ZBLAN [4,5], whereas the observation of cooling in silicate hosts has remained elusive. Due to its being physically robust, and having a relatively high optical damage threshold, doped silica is the material of choice for high power fiber lasers in the near infrared. Demonstration of fluorescence cooling in these materials could therefore enable, for example, lasers that generate no internal heat [6]. As stated, meeting the requirements of laser cooling necessitates the consideration of a wide range of physical characteristics associated with the RE and its host. Ideally the host will possess neither absorbing impurities nor defects and render a relatively low average emission wavelength. The RE^{3+} will remain unquenched, emitting with 100% quantum efficiency from the preferred valency (3+). The correlated efforts to tailor the host to achieve cooling in silicate glass fibers will be presented. Both conventional (including nanoparticle doped) and unconventional fabrication methods, as well as procedures to measure and quantify glass properties and cooling, will be discussed.

Acknowledgements

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References

[1] D.V. Seletskiy, S.D. Melgaard, S. Bigotta, A. Di Lieto, M. Tonelli, and M. Sheik-Bahae, *Nat. Photon.*, **4**, 161-164 (2010)
[2] M.P. Hehlen, R.I. Epstein, and I. Hiroyuki, *Phys. Rev. B*, **75**, 144302 (2007)
[3] L. Cheng, L. Andre, and S.C. Rand, *Laser Science*, paper JW3A.46 (2018)
[4] C.E. Mungan, M.I. Buchwald, B.C. Edwards, R.I. Epstein, and T.R. Gosnell, *Phys. Rev. Lett.*, **78**,1030–1033 (1997)
[5] J. Knall, A. Arora, M. Bernier, S. Cozic, and M.J.F. Digonnet, *Opt. Lett.* **44**, 2338-2341 (2019).
[6] S.R. Bowman, *IEEE J. Quant. Electron*., **35**, 115-122 (1999)

Invited

Nephelauxetic effect on the binding energy in the lanthanide $4f^q$ ground states

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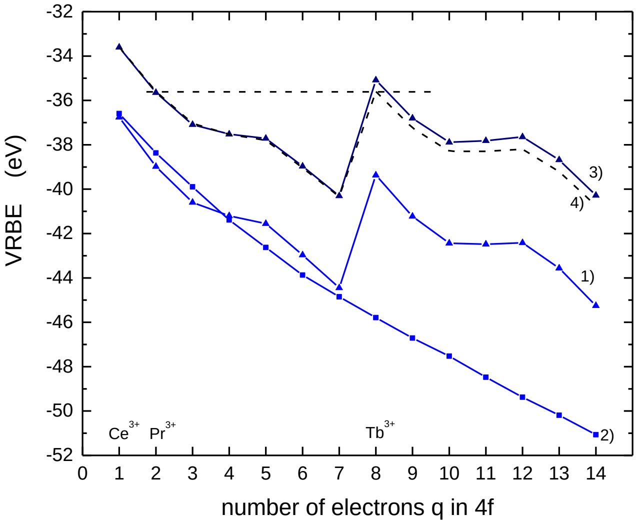
Curve 1) in the figure shows the vacuum referred binding energy (VRBE) of a 4f-electron in the ground state of the trivalent lanthanides. In a compound the curve is shifted upward and due to the lanthanide contraction it is also slightly tilted as illustrated by curve 3). In the construction of a VRBE diagram with the lanthanide $4f^q$ ground states, the shift is compound dependent but otherwise the shape of the curve is always assumed to be compound independent. Experimental data will be presented that indicates that a few 0.1 eV compound dependence does exist. To explain its origin we will first apply Jörgensen spin pairing theory to determine the 4f-4f inter-electron repulsion as function of q from the free lanthanide Racah E^1, Racah E^3, and spin orbit coupling ζ_{ff} parameters. Subtracting that repulsion energy from curve 1) yields curve 2) representing the binding of a 4f-electron to the nucleus and the [Xe] closed shell electron configuration. Racah and spin-orbit parameter values in compounds are reduced by the nephelauxetic effect. In this work the effect of such reduction on the ground state VRBE is evaluated. It turns out that the effect on the lanthanides with $q<8$ is barely significant but for $q>7$ it increases the binding energy by 0.1 to 0.5 eV depending on type of compound. In other words, there is a compound dependent lowering of the right hand branch ($q>7$) of the zigzag curve as illustrated by the dashed curve 4).



The few 0.1 eV compound dependent lowering of the right hand branch has escaped attention in lanthanide emission and excitation spectroscopy. With much more sensitive thermoluminescence (TL) spectroscopy the few 0.1 eV energy changes between Pr^{3+} and Tb^{3+} ground state level locations will be demonstrated.

Invited

Inorganic nanomaterials and doping strategies for future perspectives in scintillation applications and biomedicine

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Luminescent materials have found a wide variety of applications as phosphors for fluorescent lighting, display devices, X-ray monitoring and imaging, scintillators, and in biomedical imaging. The research on nanostructured materials resulted in the development of novel synthetic methods to control their structure, morphology, and doping. When the size of crystalline powders is tailored down to the nanoscale, several advantages are achieved, like enhanced tunability of the physico-chemical properties and reduction of the emitted light scattering when fabricating optical nanocomposites. For instance, the realization of high density optical ceramics by nanoparticles (NPs) compaction can be pursued, especially with materials that possess cubic crystalline structure, leading to the fabrication of a new class of luminescent materials. Nanoscale dimensions are also necessary in biotech applications where the material is required to travel in blood vessels and penetrate into cells.

Recently, hafnium oxide (HfO_2) has gained interest as an attractive nanophosphor because of its excellent physical and chemical properties, especially when doped by rare earth (RE) or transition metal ions. In particular, we have investigated the luminescence properties of RE doped HfO_2 NPs with a diameter below 5 nm, obtained through a purposely designed doping strategy. The tuning and the optimization of HfO_2 optical features have been pursued by multiple RE doping (such as trivalent Tb and Eu), while deputing the NP cubic structural stabilization both to optically inert Lu^{3+} and to Eu^{3+} ions at concentration higher than 5 mol%. [1] Besides the doping strategy, also the intrinsic luminescence of HfO_2 NPs, due to optically active intrinsic defects and self-trapped excitons, can be controlled by annealing treatments and defect engineering, resulting in crystal growth, rearrangement of lattice defects, structural modifications, and surface restructuring. In this framework, we have explored the suitability of an intrinsic blue scintillation emission of HfO_2, with a decay time in the ns range, for future purposes as new fast scintillator nanomaterial. [2-3]

In parallel, we have investigated the use of emitting NPs for biological applications. In the *in vitro* imaging field, we have demonstrated that $Eu:HfO_2$ NPs can be effectively used as non-toxic, highly stable probes for cell optical imaging and, potentially, as radiosensitive materials for clinical treatments. [4] In turn, novel *in vivo* fluorescence imaging approaches are based on infrared-emitting NPs working in the biological window from 1000 to 1400 nm. In this spectral range, the partial transparency of human skin allows for the acquisition of high resolution, deep tissue images, and the reduction of auto-fluorescence from tissues and specimen's diet. We have proved the feasibility of performing auto-fluorescence free, high contrast fluorescence images by using Nd^{3+} doped SrF_2 emitting at 1.3 μm. The strong brightness, the chemical and physical stability as well as high biocompatibility make these NPs very promising infrared nanoprobes for *in vivo* imaging and real-time bio-distribution studies. [5]

References

[1] A. Lauria et al., *ACS Nano*, **7**, 7041 (2013)
[2] I. Villa, et al., *Phys. Chem. Chem. Phys.*, **20**, 15907 (2018)
[3] I. Villa, et al., *Chem. Mater*, **28**, 103245 (2016)
[4] I. Villa, et al., *Nanoscale*, **10**, 7933 (2018)
[5] I. Villa, et al., *Nano Res*, **8**, 649 (2015)

Invited

Metal-organic Frameworks as Near-infrared Emitting Materials Based on Lanthanide Cations: from Fundamental Science to Biological Imaging

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Fluorescence and luminescence are detection techniques that possess important advantages for bioanalytical applications and biologic imaging: high sensitivity, versatility and low costs of instrumentation. A common characteristic of biologic analytes is their presence in small quantities among complex matrices such as blood, cells, tissue and organs. These matrices emit significant background fluorescence (autofluorescence), limiting detection sensitivity.

The luminescence of lanthanide cations has several complementary advantages over the fluorescence of organic fluorophores and semiconductor nanocrystals, such as sharp emission bands for spectral discrimination from background emission, long luminescence lifetimes for temporal discrimination and strong resistance to photobleaching. In addition, several lanthanides emit near-infrared (NIR) photons that can cross important depths of tissues for non-invasive investigations and that result in improved detection sensitivity due to the absence of native NIR luminescence from tissues and cells (autofluorescence). The main requirement to generate lanthanide emission is to sensitize them with an appropriate chromophore ("antenna effect")[1].

We have proposed few years ago an innovative concept for such sensitization of NIR-emitting lanthanides is proposed herein. The current limitation of low quantum yields experienced by most mononuclear lanthanide complexes is compensated for by using a large number of lanthanide cations and by maximizing the absorption of each discrete molecule, thereby increasing the number of emitted photons per unit of volume and the overall sensitivity of the measurement. To apply this concept, we have created several metal-organic frameworks and succeeded in generating highly emissive NIR MOF reporters.[2,3] We will discuss their structures, photophysical properties and examples of applications for biological imaging in cells with NIR microscopy.

Acknowledgements

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References

[1] I. Martinic, S. V. Eliseeva, S. Petoud, *J. lumin.*, **189**, 19-43 (2017)

[2] K. A. White, D. A. Chengelis, K. A. Gogick, J. Stehman, N. L. Rosi, S. Petoud, *J. Am. Chem. Soc.*, **131**, 18069-18071 (2009)

[3] A. Foucault-Collet, K. A. Gogick, K. A. White, S. Villette, A. Pallier, G. Collet, C. Kieda, T. Lib, S. J. Geib, N. L. Rosi, S. Petoud, *Proc. Natl. Acad. Sci. USA*, **110**, 17199-17204 (2013)

Invited

Title: Erbium doped GaN for Laser Applications

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The interest in doping semiconductor materials with rare earth elements is largely due to the possibility of forming electrically pumped light emitters integrated with silicon microelectronics. In this regard, erbium (Er) has been the prime candidate as it has an optical emission at 1.5 µm, which is important for telecommunications. However, there is strong thermal quenching of light emission from Er-doped silicon. Research has shown that thermal quenching of 1.5 µm emission in Er-doped III-nitride semiconductors is greatly reduced. We review MOCVD synthesis of Er-doped gallium nitride (GaN:Er) thin films and progress in the formation of laser gain media. Initially, a p-i-n light emitting diode based on GaN:Er was fabricated and emission at 1.5 µm and in the green spectral region was observed [1]. Subsequently, optical gain in GaN:Er thin films in an optically pumped configuration was demonstrated. Experiment data indicated that optical gain was enhanced through growth of multi-quantum well (MQW) structures that included GaN:Er layers. Recently, stimulated emission was achieved through optical pumping of specific Er centers in the MQWs [2]. We also discuss the optical properties of bulk GaN:Er layers grown by HVPE and the prospects for achieving high power lasing.

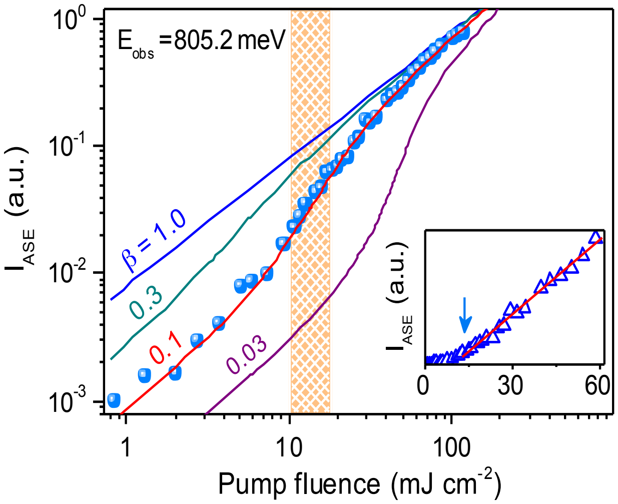

Figure 1: L-L data showing the dependence of the edge-emission intensity at 805.3 meV on the pump fluence. Linear behavior is observed below threshold and superlinear at higher pump fluences.

References

[1] R. Dahal, C. Ugolini, J.Y. Lin, H.X. Jiang, J.M. Zavada, Appl. Phys. Lett., Vol. 93, 033502-033505 (2008).
[2] V.X. Ho, T.M. Al Tahtamouni, H.X. Jiang, J.Y. Lin, J.M. Zavada, and N Q. Vinh, ACS Photonics Vol. 5, 1303-1309 (2018).

Traps with controllable depths in persistent luminescence phosphors

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Persistent luminescence materials have attracted much attention due to their unique delayed luminescence properties. Composition/structure design, regulation of afterglow properties, discussion of afterglow mechanism, and exploration of new applications of persistent luminescence materials are the main research topics in this field. This report summarizes our efforts to design new persistent luminescence materials based on trap depth control in recent years, explores the possibility of the obtained materials in new applications such as optical information storage and bio-optical imaging [1-3], and analyses the future development trend.

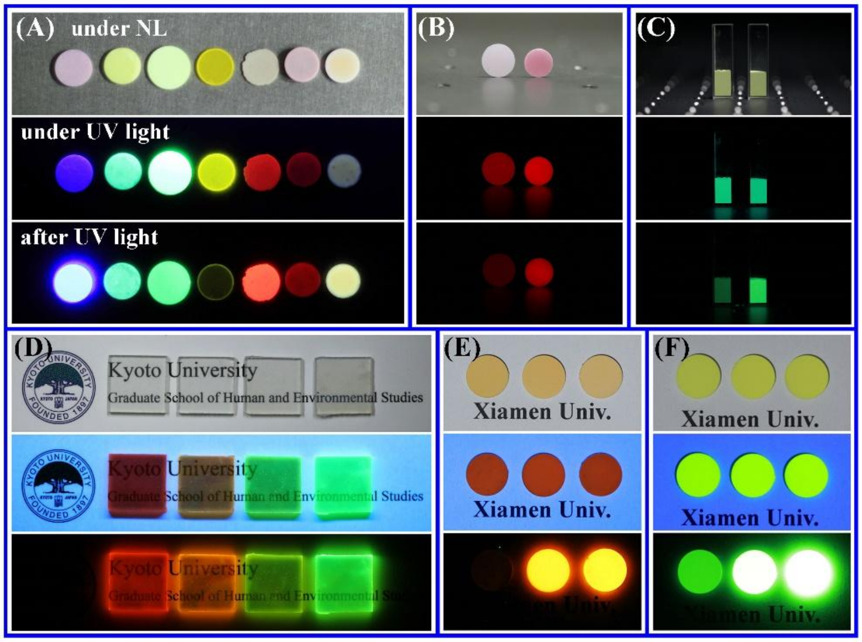

Figure 1: Photographs of persistent luminescent materials prepared by our groups..

Acknowledgements

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References

[1] Y. Zhuang, L. Wang, Y. Lv, T.-L. Zhou, R.-J. Xie, *Adv. Funct. Mater.,* **28**, 1705769 (2018)
[2] Y. Zhuang, Y. Lv, L. Wang, W. Chen, T.-L. Zhou, T. Takeda, N. Hirosaki, R.-J. Xie, *ACS Appl. Mater. Interfaces,* **10**, 1854-1864 (2018)
[3] W. Li, Y. Zhuang, P. Zheng, T.-L. Zhou, J. Xu, J. Ueda, S. Tanabe, L. Wang, R.-J. Xie, *ACS Appl. Mater. Interfaces,* **10**, 27150-27159 (2018)

Invited

New Directions in Luminescent Nanoparticles

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Due to the continuous miniaturization of electronic and optical devices, the importance of functionalized nanoparticles (NPs) has drastically increased in the past few years. In contradiction to the analogous bulk samples, lanthanide doped luminescent NPs present several advantages as high packing density, low light scattering effects, energy saving synthesis (with shorter preparation time and lower sintering temperatures) and are easily suspendable in liquid media [1-3]. Due to the small size, nanophosphors are able to build thinner films simply by printing e.g. on the surface of light emitting diodes (LEDs) and are less subjected to concentration quenching effects, in comparison to doped micron-sized phosphors. Moreover, core-shell NPs can be functionalized on their surface and are therefore suitable as biological sensors or medical markers [3].

In this talk, we present several nanocrystalline materials doped with divalent lanthanides. However, the common preparation methods using water as solvent in general do not work due to the oxidation behavior of Ln^{2+} ions [4]. Therefore, two fast and mild synthesis routes for luminescent nanoparticles (NPs) are presented for the first time. On one hand, Eu^{2+} containing NPs of varying host lattices can be obtained even in aqueous solution using Zn as reducing agents for Eu^{3+}. On the other hand, ionic liquids can serve as solvent as well as fluorine source for fluoride NPs, which are not available by common melting methods. In detail, we were successful preparing phase pure samples of several flouridic Eu^{2+} doped materials with small sizes and low size distributions (30-40 nm) with extremely high luminescence quantum yields. Using this method we were successful to prepare Yb^{2+} containing NPs for the first time, which are very promising candidates for nanothermometry applications. Finally, some applications in biological and medical fields and also multifunctional magnetic, afterglow NPs (Fig. 1, right) are presented, showing their large benefits compared to common materials due to their higher stability at extremely low toxicity.

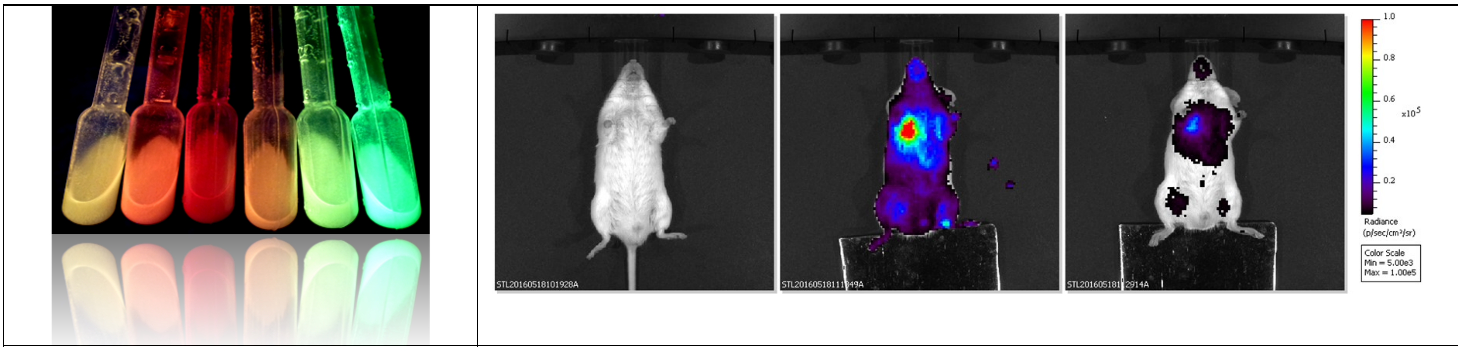

Figure 1: **Left: emission of several Eu^{2+} containing nanoparticles suspended in water, right: Eu^{2+} containing afterglow nanoparticles injected in mice, with excitation of the luminescence before emission.**

References

[1] H. Cerqueira Streit, J. Kramer, M. Suta, C. Wickleder, Materials 2013, 6, 3079.

[2] H. Terraschke, M. Suta, M. Adlung, S. Mammadova, N. Musayeva, R. Jabbarov, M. Nazarov, C. Wickleder, J. Spectroscopy 2015, Article ID 541958.

[3] H. Terraschke, M. F. T. Meier, Y. Voss, H. Schönherr, C. Wickleder, J. Cer. Proc. Res. 2015, 16, 59.

[4] H. Terrasche, C. Wickleder, Chem. Rev. 2015, 115, 11352.

Invited

Rare earth elements and urban mines: critical strategies for sustainable development

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The production of waste electrical and electronic equipment (e-waste, WEEE) is continuously increasing. Consequently, there is strong demand of suitable policies to manage the situation and find effective mitigating solutions [1]-[3]. Many economically interesting materials can be recovered from this kind of waste. Rare earth elements are one of them. Therefore, it is necessary to develop new technologies that enable to obtain rare earths from e-waste in order to increase the recycling capabilities in the countries without rare earth reserves. The overall objective is to change the strategic material recovery procedure in a way that will allow economic benefits without affecting the environment. This communication will give an outline of the current situation regarding e-waste, rare earths availability, and recycling policy and techniques.

Acknowledgements

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References

[1] www.industry.gov.au/sites/default/files/2019-03/australias-critical-minerals-strategy-2019.pdf
[2] Roderick G. Eggert *Nature Chemistry* 3 pp. 688-691 (2011)
[3] Alan J. Hurd, Ronald L. Kelley, Roderick G. Eggert, and Min-Ha Lee *MRS Bulletin* 37 pp. 405-410 (2012)

Invited

Specific mechanisms associated with rare-earth dopants (Yb, Er, Ce) in the radiation-induced attenuation of silica-based optical fibers

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We report on an original approach enabling an in-depth investigation of the mechanisms of the radiation-induced attenuation (RIA) development and annealing in silica-based fiber preforms [1]. The experimental protocol combines temperature- and spectrally-resolved TSL measurements with the characterization of the RIA annealing in TSL conditions. TSL allows the identification of those dopant- or defect-related centers that capture free carriers under irradiation (to form color centers responsible for RIA) and that are restored by recombination during the thermal annealing induced by the TSL readout. The simultaneous monitoring of the RIA bleaching reveals correlations between these reformation processes and the recovery of radiation-induced optical absorption bands attributed to well-known color centers. Such correlations bring decisive indications on RIA mechanisms in terms of trapping, detrapping and recombination for both electrons and holes.

Our protocol is applied in a systematic manner to glass compositions of increasing complexity to elucidate the specific role played by each dopant. Silicate, aluminosilicate, Yb-doped silicate, Er-doped silicate, Yb-doped and Yb,Ce-codoped aluminosilicate preform samples are notably examined. For each composition, annealing processes can be described in detail as a function of temperature and their non-monotonic character is demonstrated. They indeed pass through various stages along heating, where color centers are well destructed or transitorily created due to the thermally-stimulated transformation of less stable radiation-induced states. In the main, temperature effects on the color-center stability and enhancement are thus resolved. Temperature ranges at which trapped carriers forming intrinsic or dopant-related color centers are released are highlighted, thus enabling the assessment of their thermal activation energies.

Specific attention is paid on the way rare-earth ions take part in RIA processes. Trivalent Yb and Er ions capture electrons very efficiently, then preventing from the formation of other trapped-electron states at oxygen deficient centers (the formation of AlE' centers is notably quenched in Al-containing samples). Electrons trapped into Yb^{2+} or Er^{2+} ions are thermally stable, at least up to 600 °C in TSL conditions. Their recovery is then due to their recombination by thermally-released holes. Ce^{3+} ions are shown to trap even more efficiently both electrons and holes to form Ce^{2+} and Ce^{3++} ions, respectively. Both contribute to the reduction of the RIA: holes captured into Ce^{3++} ions do not form other trapped-hole centers (notably Al-OHC centers, harmful to the NIR-VIS RIA in Al-containing samples), whereas electrons captured into metastable Ce^{2+} ions do not contribute to the formation of much more stable Yb^{2+} or Er^{2+} species. Electrons at Ce^{2+} states can be readily released, even at room temperature (RT). Part of them recombine at trapped-hole color centers, including Al-OHC, thus strengthening their mitigation. This explains why Ce enhances the isothermal recovery of RIA, *after* but also *during* irradiations conducted close to RT. Thus, the RIA mitigation brought by Ce should be enhanced if the ionizing dose is delivered through long irradiations, i.e. at low dose rates.

References

[1] Franck Mady, Angela Guttilla, Mourad Benabdesselam, and Wilfried Blanc, *Opt. Mat. Express*, **9** (6), 2466-2489 (2019)

Invited

Lanthanide ions activated optical nanothermometers

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Lanthanide doped nanofluorides have been the subject of many investigations for their possible use as diagnostic probes in nanomedicine. In this presentation, we focus on binary (e.g. CaF_2 or SrF_2) and ternary (e.g. KY_3F_{10}) nanofluorides, activated with several lanthanide ions (such as Yb^{3+}, Er^{3+}, Nd^{3+}, Tm^{3+}, Eu^{3+}), prepared by hydrothermal synthesis[1-2]. Upon infrared excitation in the first biological window, the lanthanide activated nanofluorides exhibit strong luminescence, in the ultraviolet, visible and near infrared optical regions. The emission intensities show significant variations with temperature changes, suggesting that their thermometric properties can be exploited for estimating the temperature at the nanoscale. The thermal sensitivities have been evaluated using a ratiometric approach, by considering the ratio of emission bands in different optical regions. The binary and ternary nanofluorides show relevant sensitivities in the biological window. A core@shell architecture is also described, pertinent to enhance the emission efficiency of the nanoparticles and to tune the thermometric performance.

Acknowledgements

The authors thank the University of Verona for funding in the frame of the project named “Ricerca di Base 2015”.

References

[1] Cortelletti, P.; Skripka, A.; Facciotti, C.; Pedroni, M.; Caputo, G.; Pinna, N.; Quintanilla, M.; Benayas, A.; Vetrone, F.; Speghini, A., Tuning the sensitivity of lanthanide-activated NIR nanothermometers in the biological windows. *Nanoscale* **10**, 2568-2576 (2018).

[2] Pedroni, M.; Cortelletti, P.; Cantarelli, I. X.; Pinna, N.; Canton, P.; Quintanilla, M.; Vetrone, F.; Speghini, A., Colloidal nanothermometers based on neodymium doped alkaline-earth fluorides in the first and second biological windows. *Sensor Actuat B-Chem* **250**, 147-155 (2017).

Progress on the preparation of glass-based phosphate materials for photonics

Invited

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Phosphate glasses have created a lot of research interest for optical applications because of their high rare earth solubility and good chemical, mechanical and optical properties. Phosphate glasses containing rare-earth (RE) ions are therefore good candidates to be used in applications like optical amplifiers and laser sources.

Rare-earth doped phosphate glass–ceramics (GCs) have been also of great interest as they can exhibit significantly enhanced optical properties (such as absorption and emission cross-section and energy transfer rates) compared to their glassy counterparts, if the crystalline phase of the desired nature and structure precipitates around the rare-earth ions. Indeed, due to the crystalline environment surrounding the RE ions, the RE-doped glass-ceramics have shown to combine glass properties (large flexibility of composition and geometry) with some advantages of the RE-doped single crystals (higher absorption, emission and lifetimes). The GCs are usually prepared by conventional melting followed by a thermal treatment. However, the heat treatment does not necessarily lead to the bulk precipitation of rare-earth doped crystals. Therefore, a new route was developed in order to prepare glasses, which contain rare-earth doped crystals. In this technique called direct doping method, the crystals doped with RE are first synthetized and then added in the glass batch after the melting. The main challenge with this novel route of preparing glasses is to balance the survival and dispersion of the particles in the glasses.

In this presentation, we will review our work on the development of new phosphate glasses, glass-ceramics and glasses which contain particles. First, we explain how these materials are prepared and characterized. We discuss the challenges related to preparation of the glasses which contain crystals.

Acknowledgements

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Invited

Understanding the luminescence properties of Ce^{3+}-doped garnet phosphors on the basis of composition, crystal and electronic structure

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The series of Ce^{3+}-doped garnet luminescent materials with 5d-4f emission is a fascinating group of compounds from the viewpoints of optical application and scientific interest. However, unsolved mysteries for the 5d energy positions of Ce^{3+} and the quenching process with respect to different compositional garnets still remains. In order to understand these optical properties in the series of Ce^{3+}-doped garnet, we analyzed the optical data on the basis of composition, crystal and electronic structure.

Firstly, the absorption and luminescence properties (centroid shift and crystal field splitting of 5d orbitals) of Ce^{3+}-doped garnets are summarized from the viewpoints of chemical composition (electron negativity and optical basicity) and the local crystal structure of the Ce^{3+} ion (bond length and distortion). It is found that clear trends exist between (1) the centroid shift of 5d energy (ε_c) and the optical basicity of the host garnets and between (2) the crystal field splitting of the lowest $5d_1$-$5d_2$ levels (Δ_{12}) and a new distortion parameter obtained from the crystal structure data.

Secondary, the data of quantum yield and quenching temperatures of Ce^{3+}-doped garnets are also considered, indicating the thermal ionization process as the main mechanisms for the quenching process. Based on our recent experimental results, to prove the thermal ionization process, the principle and the most important features of the photocurrent excitation (PCE) and thermoluminescence excitation (TLE) spectra measurements are summarized. Finally, a general trend for the quenching temperature of Ce^{3+} luminescence in the garnets is discussed in terms of the energy gap between the lowest $5d_1$ level and the conduction band bottom obtained from the vacuum referred binding energy (VRBE) diagram.

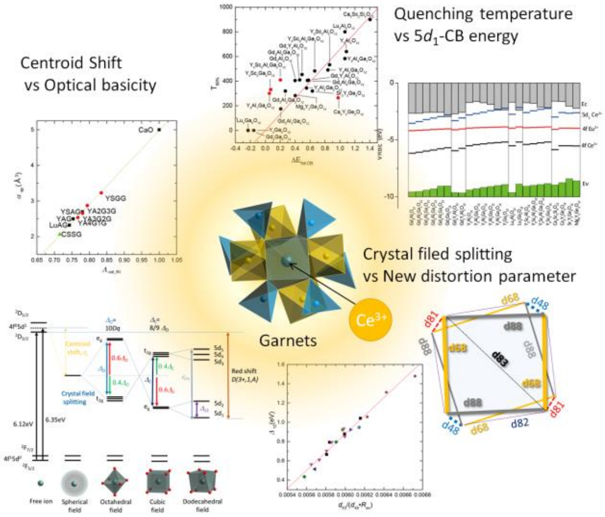

Figure 1: Analysis of Ce^{3+}-doped garnet optical properties based on composition, crystal and electronic structure.

References

[1] Jumpei Ueda and Setsuhisa Tanabe, *Optical Materials X*, in press (2019)

Oral presentations

Optical Sensing Properties Based on a Reversible Redox Process

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Development of selective and specific sensor has been attracted considerable attention for a decade. Optical sensing systems are compatible with distance testing keeping the excitation and detection system out of the sensing zone. They are suited to the on board technologies and multiple light sources and detectors are now available for the obtaining of compact and robust systems. To detect an event means that a significant change of the optical properties has to occur.

We focus this work on interesting luminescent materials that present reversible redox phenomena under irradiation or temperature. The ignition and the extinction of a blue and red emission is related to the oxidation and reduction processes between trivalent cerium and a p element under UV irradiation. The specific crystallographic packing and the location of the doping element seem to be a key point to observe such luminescent properties. DFT calculation is proposed to support the assignation of the optical properties performed between 10 K and 300 K. Cycling of the materials also illustrates the capability of these materials to be used as optical sensors.

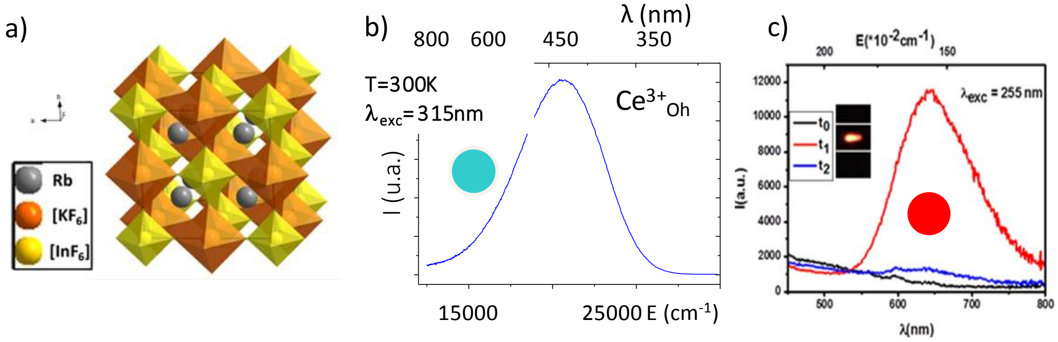

Figure 1: Ce doped Elpasolite structure : crystal structure (a) Crystal structure, Emission of Ce^{3+} (b), Emission resulting from the redox processus (cycling) (c)

Acknowledgements

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References

[1] L. Cornu, M. Gaudon, P. Veber, A. Villesuzanne, S. Pechev, A. Garcia, V. Jubera, *Chem. Eur. J.*, **21** (13), 5242-5251 (2015)
[2] L. Cornu, M. Gaudon, O. Toulemonde, P. Veber, V. Jubera, *Dalton Trans.*, **45,** 3380 – 3387 (2016)

Evidence of Ce^{4+} ions by XANES spectroscopy in the new fast scintillator crystal: Ce^{3+}-Mg^{2+}-co-doped $Gd_3Al_2Ga_3O_{12}$ garnet

Oral

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There is a strong demand of scintillator materials combined to detect high energy photons and accelerated particles in many fields. As a result, great R&D effort brought several new single crystals, namely the Ce^{3+}-doped orthosilicates as Gd_2SiO_5 (GSO), Lu_2SiO_5 (LSO), $(Lu1\_xYx)_2SiO_5$ (LYSO), pyrosilicates based on $RE_2Si_2O_7$ (RE = Lu, Y,Gd), LaX_3 (X = Cl,Br) and $Lu_3Al_5O_{12}$, $Gd_3Ga_3Al_2O_{12}$ garnet single crystals.

Indeed, garnet single crystals are well mastered technology developed before for laser, phosphor and magneto-optic hosts. Recently, $Lu_3Al_5O_{12}$ [1,2] and $Gd_3Al_2Ga_3O_{12}$ [3,4] single crystals have been demontrated to be efficient scintillators exceeding the light yield values achieved for the best Ce^{3+}-doped orthosilicate scintillators. Among hypothesis of scintillation mechanisms, it has been claimed that Ce^{4+} ions are stabilized by the addition of Mg^{2+}/Ca^{2+} divalent impurities. The sequential charge capture of an electron hole pair by Ce^{3+} has been described as [5]:

1) $Ce^{3+} + hole^{+} \rightarrow Ce^{4+}$ (hole trapping)
2) Ce^{4+} + e- $\rightarrow (Ce^{3+})^{*}$ (electron trapping leading to Ce^{3+} in an excited state)
3) $(Ce^{3+})^{*} \rightarrow Ce^{3+} + h\nu$ (radiative de-excitation followed by photon emission)
4) $Ce^{3+} + hole^{+} \rightarrow Ce^{4+}$ (hole trapping again for another cycle)

It means the skipping of the first hole trapping stage could result in acceleration of the decay by suppression of slow components.

The presence of Ce^{4+} in Ce^{3+}-doped single crystals has always been a big issue. If the crystal growth and the spectroscopic properties have been deeply analyzed by Yoshikawa's group in Sendai [3,4], the confirmation of Ce^{4+} concentration from quantitative values of the Ce^{3+}/Ce^{4+} ratio in the new scintillator Ce^{3+}-Mg^{2+}-co-doped $Gd_3Al_2Ga_3O_{12}$ garnet host has never been done before. Consequently, the main goal of this communication is to report this ratio measured by XANES spectroscopy at the Ce L3 threshold of the ESRF-BM16 in Grenoble and to compare it with Ce^{3+}-doped YAG and Ce^{3+}-doped $Gd_3Al_2Ga_3O_{12}$ crystals without any Mg^{2+} cation.

References

[1] J. Pejchal & al, Optical Materials 86, 213–232 (2018)
[2] M.V. Derdzyan, & al, Cryst Eng Comm, DOI: 10.1039/c7ce02194a, 17 (2018)
[3] K. Kamada & al, Optical Materials 41, 63–66 (2015)
[4] M. Yoshino & al, Journal of Crystal Growth 491, 1–5 (2018)
[5] S. Blahuta & al, IEEE Trans. Nucl. Sci., 60, 3134–3141 (2013)

Towards tetravalent praseodymium

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The chemistry of the Rare Earth Elements (REE) is strongly stamped by the oxidation sate +III. However, some of the metals are also known in their divalent (Eu, Sm, Yb, Tm) or tetravalent (Ce, Pr, Tb). Compared to divalent rare earth compounds, which have been reported in a great variety especially for Eu^{2+}, the knowledge of tetravalent rare earth compounds is still limited. They are essentially known in the form of oxides and fluorides, e.g. with the most electronegative elements as bonding partners.[1,2] Indeed, the oxidation potentials are high and elaborated preparation techniques, often involving elemental fluorine, are mandatory.

The work in our research group has a strong focus on metals compounds displaying unusual oxidation states. However, in contrast to literature findings we are especially interested in stabilizing the high-valent metal ions by complex oxoanions. The preparation of the first oxoanionic compound of tetravalent palladium, $K_2[Pd(S_2O_7)_3]$, by oxidizing palladium with a mixture of SO_3 and XeF_2 may serve as a striking example.[3] Accordingly, we attempted to transfer similar reaction to the element praseodymium. It appears that Pr^{4+} would be a worthwhile ion for fundamental investigations. It exhibits an electronic f^1-configuration and is isoelectronic to the well-investigates Ce^{3+} ion. As a potential starting material for our investigations we have chosen the Pr(IV) oxide Li_8PrO_6 which has been prepared according to literature reports from P_6O_{11} and Li_2O_2 in sealed gold ampoules.[4] However, subsequent reactions of this compound with SO_3 did not lead to a sulfate but afforded well-shaped single crystal of the oxides. It is interesting, that SO_3 acts as a solvent here without taking part in the reaction. Further results and ideas for the formation of defined oxoanionic Pr(IV) compounds will be discussed in the lecture.

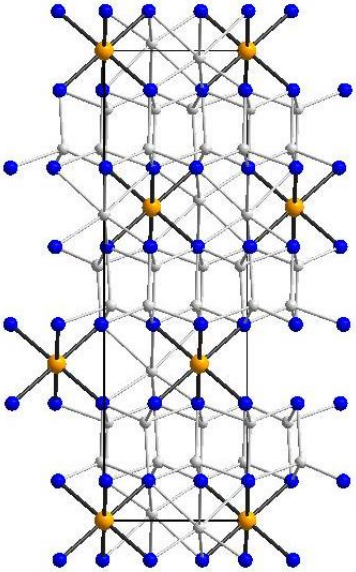

Figure 1: Crystal structure of Li_8PrO_6 with octahedral Pr^{4+} coordination

References

[1] J. Soriano, M. Givon, J. Shamir, *Inorg. Nucl. Chern. Letters* **2**, 13 (1966).
[2] L. B. Asprey, J. S. Coleman, M. J. J. S., Reisfeld, *Adv. Chem. Ser.* **71**, 122 (1967).
[3] J. Bruns, D. van Gerven, T. Klüner, M. S. Wickleder, *Angew. Chem. Int. Ed.* **128(28)**, 8121 (216).
[4] K. Feldner, R. Hoppe, R., *Rev. Chim. Min.* **20**, 351 (1983).

Primary luminescent thermometer in the visible range based on Er,Yb:$GdVO_4$ microcrystals and its excitation power dependence

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Fluorescence intensity ratio (FIR) thermometry based on lanthanide ion (Ln^{3+}) spectroscopy was already reported by Kusama *et al.* in 1976 [1]. From then until now, this field of research has been largely growing due to their multiple applications, the increasing availability of new Ln^{3+} doped nanocrystalline materials and the demonstrated potential of these noncontact thermal nanoprobes [2].

In the present work, it is obtained the primary calibration of the Er,Yb:$GdVO_4$ microcrystals as luminescent thermometers based on the erbium green emission by upconversion mechanism. Besides, it is known that the FIR performance can depend on the excitation power of the source used to excite the crystals, so, the effect of this excitation power dependence on the FIR parameters of the Er,Yb:$GdVO_4$ is evaluated. As expected, as lower is the excitation power, higher thermal relative sensitivity was obtained, and the values describing the dependency of the green emission as function of the temperature are more similar to the ones obtained solely taking into account Boltzmann mechanism for describing the electronic population ratio of the two thermally coupled Erbium emitting states.

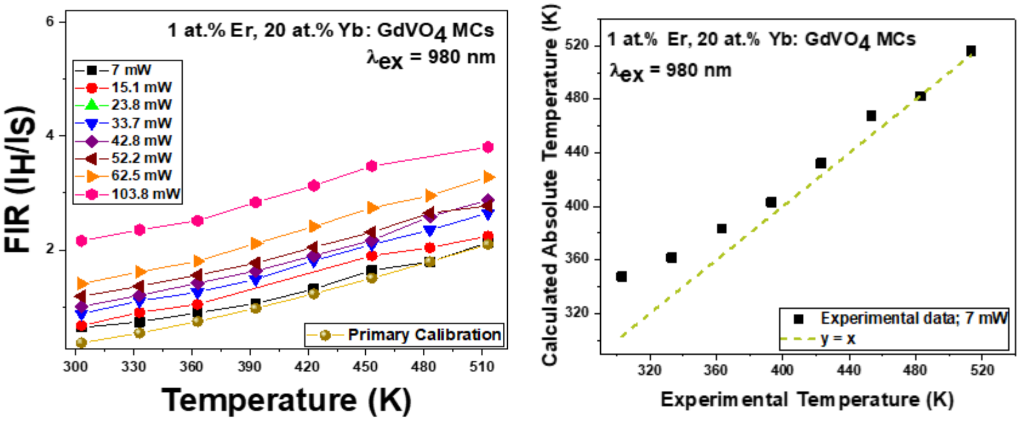

Figure 1: a) FIR for the Erbium emission from the $^2H_{11/2}$ (I_H) and $^4S_{3/2}$ (I_S) levels in Er,Yb:$GdVO_4$ MCs under 980 nm diode laser excitation. Primary calibration was obtained by measuring the emission at RT under different excitation powers. b) Calculated absolute temperature using the primary calibration versus the experimental temperature.

Acknowledgements

The authors acknowledge the support from Spanish Government Projects MAT2016-75716-C2-1-R (AEI/ FEDER,UE) and from Catalan Government under Project 2017 SGR 755.

References

[1] H. Kusama, O. J. Sovers, T. Yoshioka, *Jpn. J. Appl. Phys.* **15**, 2349-2358 (1976)
[2] C. D. S. Brites, S. Balabhadra, L. D. Carlos, *Adv. Optical Mater.***7**, 1801239 (2019)

Cerium concentration effect on scintillation properties and temperature dependence of (Gd, La)$_2$Si$_2$O$_7$ scintillator

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Scintillation materials are applied to detect high energy photons and particles. The oxide materials in the form of the single crystal are promising candidates for the next generation of the ultra-efficient scintillators. Cerium-doped (Gd, La)$_2$Si$_2$O$_7$ (LaGPS:Ce) are potentially interesting scintillators due to their high light yield. Kurosawa et al. [1] has reported the scintillation properties of LaGPS:Ce at high temperature (150 °C). However, the knowledge of the Ce concentration effects on the luminescence properties of LaGPS:Ce single crystal is still not well studied nor understood.

The aim of this research is to improve the understanding of Ce concentration effect on the scintillation properties of LaGPS single crystals. To improve the understanding, we prepared the LaGPS single crystals with Ce 0.1, 0.5, 1.0, 1.5 % concentration by Cz method. The samples are characterized by absorption, PL / PLE, decay kinetics and light yield measurements. We found that the LaGPS with Ce 1.5% sample shows the highest light yield. To reveal the mechanism responsible for light yield improvement, we will also present the temperature dependence measurements of photoluminescence decay time and PL in the range 77-500 K.

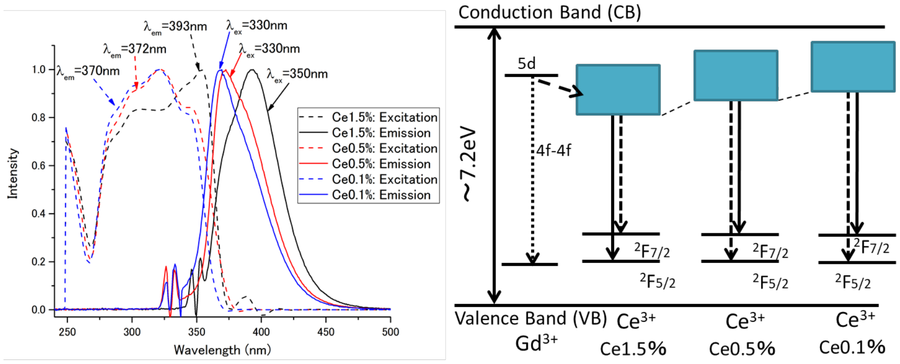

Figure 1: (left) PL/PLE spectra of LaGPS with various Ce concentration, (right) The energy level scheme in LaGPS with Ce 1.5%, 0.5%, and 0.1% concentration

References

[1] S. Kurosawa, T. Shishido, A. Suzuki, J. Pejchal, Y. Yokota, A. Yoshikawa, Performance of Ce-Doped (La,Gd)$_2$Si$_2$O$_7$ Scintillator with an Avalanche Photodiode. Nucl. Instrum. Methods Phys. Res. A, 744, 30–34, (2014)

Difference of Mg^{2+} and Mo^{6+} co-doping effects on luminescence and scintillation properties of Ce:LuAG single crystal scintillators

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In the last two decades, a number of excellent scintillators based on the Ce^{3+} and Pr^{3+} doped materials were discovered and studied in depth. Recent studies have shown that the divalent ion Me^{2+} (Me=Ca, Sr, Mg) co-doping could improve both the light yield and scintillation decay of $Ce:Lu_2SiO_5$ (Ce:LSO) and $Ce:LaBr_3$ single crystals [1,2]. Some light yield decrease was also observed in the Mg^{2+}/Ca^{2+} co-doped $Ce:Gd_3Al_2Ga_3O_{12}$ (Ce:GAGG) garnet single crystals [3].

In this study, the Mg^{2+} or Mo^{6+} ion co-doped Ce:LuAG single crystals were prepared by micro-pulling down (μ-PD) method with various co-dopant concentrations. Co-doping effect on the luminescence and scintillation properties were systematically investigated. Optical absorption, radioluminescence spectra, PLE and PL spectra, light yield and scintillation decay times were measured and compared with those of the non co-doped Ce:LuAG single crystal sample. The Mg^{2+} co-doped sample showed higher light yield value and accelerated scintillation decay time compared to that of the non co-doped one as reported in Ref. [4]. Positive effect of Mo co-dopant consists mainly in the significant increase of light yield. The light yield values of Ce,Mo:LuAG increase with increasing of Mo concentration and the highest light yield value of about 120% compared to the non co-doped LuAG sample is observed with Mo 3000 ppm co-doping. However, the Mo^{6+} ion co-doped Ce:LuAG samples show slightly slow scintillation decay time than that of the non co-doped one and the relative weight of the fast decay component decrease in all Mo co-doped samples.

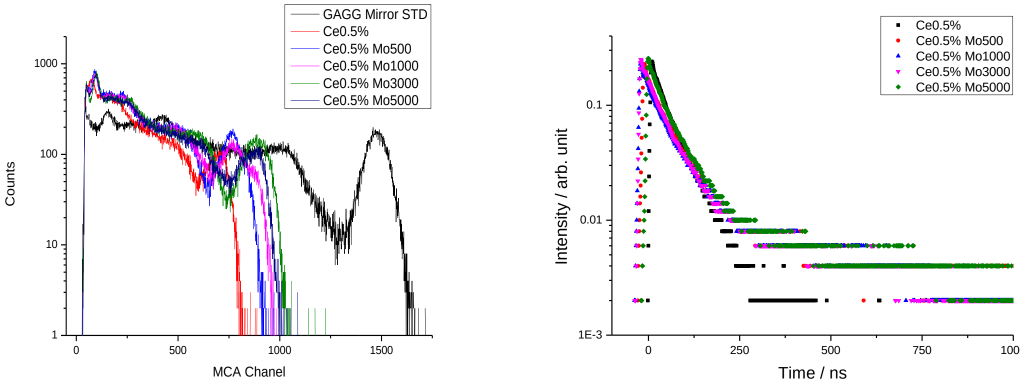

Figure 1: The pulse height spectra and scintillation decay curves of non co-doped and Mo co-doped Ce:LuAG crystals. (Excited by 662 keV gamma-ray of ^{137}Cs at R.T. and measured using the APD photodetector)

References

[1] M.A. Spurrier et al, *J. Cryst. Growth*, **310**, 2110-2114 (2008)
[2] M.S. Alekhin et al., *Appl. Phys. Lett.*, **102**, 161915, (2013)
[3] K. Kamada, A. Yoshikawa et al., *Opt. Mater.*, **41**, 63-66 (2015)
[4] K. Kamada, A. Yoshikawa et al., *Nucl. Instrum. Methods Phys Res. A*, **782**, 9-12 (2015)

Local field effect in structured optical fiber co-doped with noble metal nanoparticles and lanthanide ions

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Nanocomposite optical glasses and fibers give a novel way to manage luminescent properties of lanthanides ions, mainly due to their unique properties, obtained as a result of the interaction of metallic nanoparticles with photons [1-3]. The most advanced systems are found in the currently used waveguide structures, characterized by sophisticated optical properties and an excellent thermal stability parameter required in modern optical fiber technology. State-of-art is a combination of noble metals properties, ie. silver (Ag^+), gold (Au^+) and technology of rare earth (RE) ions doped glassy materials. Modification of emission properties of glassy materials doped with lanthanide ions, which is obtained by co-doping with nano-sized metal particles, is an innovative research area. One of the reasons of introducing nanoparticles of noble metal to glassy materials is the possibility of increasing the luminescence signal in the visible range by energy transfer between metal nanoparticles and rare earth elements and by enhancement of electric field within rare earth ions that results from the surface plasmon resonance.

Studies concerning interaction mechanisms of noble metal nanoparticles on luminescent properties of active glasses are currently the subject of research being carried out by many scientific centers around the world. This will lead to new possibilities in the production of optoelectronic devices, including optical fibers sensors and sources currently being used in medicine, optics and nanophotonics (SERS - Surface-Enhanced Raman Scattering, LSPR - Local Surface Plasmon Resonance sensors).

In this paper, an effect of silver ions on luminescent properties of europium ions in antimony-germanate-borate SGB structured optical fiber is presented. The glass was synthesized by standard melt-quenching technique and glass fiber was drawn at the temperature of 580°C. In the experiment, the interaction mechanism was investigated in terms of localized SPR in each step of the glass fiber fabrication process. Moreover, we demonstrate that self-assembling of silver nanoparticles on internal capillary surface of SGB fiber exist only for fiber co-doped with $AgNO_3$ ions. The non-conventional bottom-up technique of thin film of Ag nanoparticles was analysed by SEM measurements.

Acknowledgements

The project was funded by National Science Centre (Poland) granted on the basis of the decision No. DEC-2016/21/D/ST7/03453. The COST Action MP1401 "Advanced fibre laser and coherent source as tools for society, manufacturing and lifescience" is also acknowledged.

References

[1] H. A. Atwater, and A. Polman, Nature Materials **9**, 205 (2010).
[2] P. Candeloro, E. Iuele, G. Perozziello *et al.*, Microelectronic Engineering **175**, 30-33 (2017).
[3] W. Q. Lim, and Z. Gao, Nano Today **11**, 168-188 (2016).

Multicolor emission of polymer optical fibers co-doped with RE and fluorescent dyes

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Luminescent compounds enable the development of new optical fibers. The technology of polymer optical fibers seems to be suitable for the production of optical fibers doped with organic and organometallic compounds, because the temperature of their extraction is usually lower than the decomposition temperature of organic molecules. There are a number of dyes with useful luminescent properties to obtain multicolor emission. The aromatic hydrocarbons, xanthene compounds and lanthanide complexes can be incorporated in the polymer matrix [1-4]. Their properties can be modified additionally be co-doping fabrication process. The high absorption cross section of organic dyes and antenna effect observed in organometallic complexes of lanthanides allow to efficient excitation and luminescence. Different mechanism of luminescence modification in polymeric fibers (e.g. reabsorption, energy transfer) will be presented to obtain specific luminescent properties in the visible spectrum range. The poly(methyl methacrylate) fibres co-doped with organic dyes lanthanides (Tb^{3+} - Eu^{3+}, Tb^{3+} - Rhodamine B) will be shown. The luminescence spectrum modification vs. the fibre length will be investigated. Finally the proposition of white light emission in co-coped fibers (Perylene – Rhodamine 6G, 1,4-Bis(2-methylstyryl) benzene - Rhodamine B) will be presented. The obtained wide emission band and mechanisms of modification of the fluorescence profile with the use of optical fiber structure indicate the possibilities of using the produced optical fibers in the constructions of miniature fluorescent fiber optic illuminators.

Acknowledgements

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References

[1] Bilro L., Alberto N., Pinto J.L., Nogueira R., *Sensors* **12(9)** 12184 (2012).

[2] Kakuichi M., Kasatani K., Morita Y., Okamoto H., Kawamata J., *Nano Studies* **7**, 177–184 (2013)

[3] Miluski P., Kochanowicz M., Zmojda J., Dorosz D. Chinese Optics Letters, 14(12), 121602–121607 (2016).

[4] Al-Hamdani A.H., Al-Ethawi A.S., Al-Hamdani R., *Journal of Materials Science and Engineering* **4(12)**, 57–61 (2010)

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All optical methane sensor based on rare-earth doped fibers

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Many radicals spectroscopic signatures associated to gases of interest are in the 2.5–15 µm spectral range (4000-350 cm^{-1}). This spectral range can be addressed by emissions from rare-earth ions embedded into chalcogenide glasses which are well-known for having low phonon energies. We will show our latest work on the development of an all-optical methane sensor at 3.5µm based on rare-earth doped chalcogenide glasses. The sensor concept (Fig. 1) comprises first an infrared source at 3.5µm based on Pr^{3+} doped fiber. The 3.5µm infrared signal is then sent to the gas cell to probe the methane absorption. After the gas cell, the transmitted IR probe signal at 3.5µm is converted to 660nm by excited state absorption within an Er^{3+} doped chalcogenide fiber which is simultaneously pumped at 804 nm. This frequency conversion makes possible the transport of the probe signal through silica optical fibers over large distances considerably increasing the scope of possible applications.

The optimization of the Pr^{3+} or Yb^{3+}, Pr^{3+} doped fibers as the IR source and the Er^{3+} doped chalcogenide fiber as wavelength converter, which will be presented, is based on a comparison between experimental data and the modeling of the different luminescent fibers. A special emphasis is made on the modeling of this original conversion process. The dependence of the converted signal with the pump and probe photon fluxes will be presented. We will also discuss, using experimental results and simulations, critical parameters for the energy conversion and the sensor itself such as the dopant concentrations, the fibers geometry or the impact of pump upconversion parasitic signals on the converted signal to noise ratio.

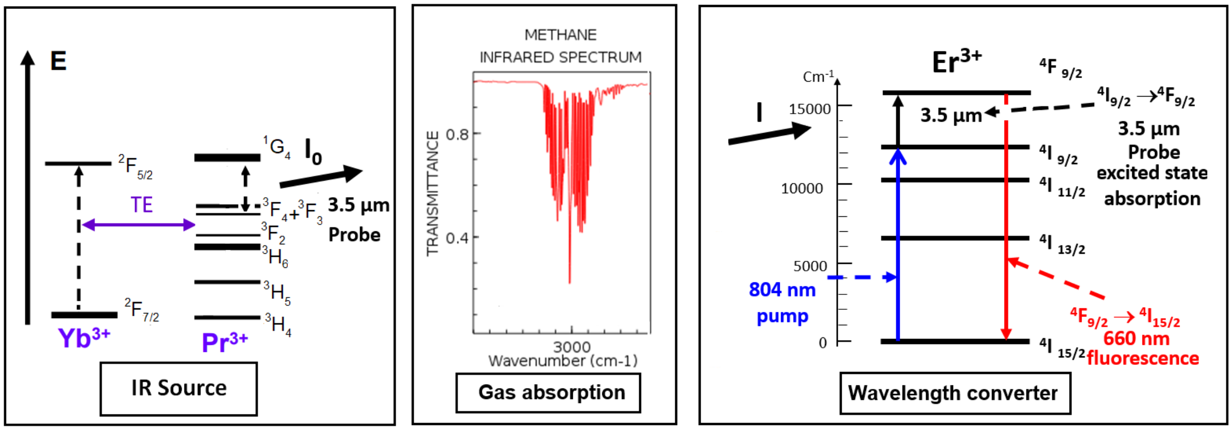

Figure 1: All optical methane sensor concept.

References

[1] F. Charpentier, F. Starecki, J. L. Doualan, P. Jóvári, P. Camy, J. Troles, S. Belin, B. Bureau, V. Nazabal, Mat. Letters, 2013.

[2] A.L. Pelé, A. Braud, J.L. Doualan, R. Chahal, V. Nazabal, C. Boussard-Plédel, B. Bureau, R. Moncorgé, and P. Camy, Optics Express, 2015.

Pauli antisymmetry interactions between active center and host: The R$_1$-line of Cr^{3+} in garnets.

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The shifts and multiplets of the Cr^{3+} R$_1$-line fluorescence (^{2}E-^{4}A$_2$) in the mixed LuAG/YAG and YAG/TbAG garnets $Lu_{3x}Y_{3-3x}Al_5O_{12}:Cr^{3+}$ and $Tb_{3z}Y_{3-3z}Al_5O_{12}:Cr^{3+}$ [1,2] cannot be associated with changes in the Cr-O covalency. This raises questions on the nature of the interactions between the CrO_6 active centre and its environment, hence on the impact of local disorder.

Multiconfigurational ab initio calculations show that Pauli antisymmetry interactions with next-nearest neighbour ions induce a nephelauxetic effect on the CrO_6 active centre that shifts the R$_1$-line. The strength of this *Pauli antisymmetry induced nephelauxetic effect* increases with the ionic radius and number of co-dopant ions, all of it resulting in controlled shifts and multiplets of R$_1$-lines [3].

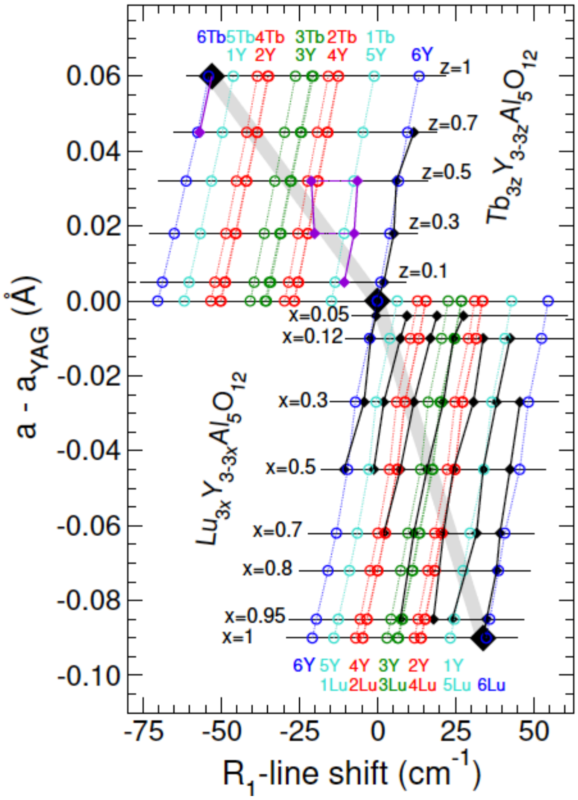

Figure 1: Cr^{3+} R$_1$-line multiplets: experiments and calculations. Shifts with respect to YAG:Cr^{3+} are shown.

References

[1] S. Feofilov, A. Kulinkin, K. Ovanesyan, A. Petrosyan, C. Dujardin, *Phys. Chem. Chem. Phys.*, **16**, 22583–22587 (2014).
[2] S. Feofilov, A. Kulinkin, K. Ovanesyan, A. Petrosyan, *Solid State Commun.*, **226**, 39–43 (2016).
[3] L. Seijo, S. Feofilov, Z. Barandiarán, *J. Phys. Chem. Lett.*, **10**, 3176–3180 (2019).

Evidence for intervalence charge-transfer (IVCT) states in Eu-doped phosphors

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Divalent europium is one of the most studied luminescence activators, due to its huge application potential thanks to its color tunability across the visible spectral range. This is reflected in the large-scale use of Eu-based phosphors in state-of-the-art white light emitting diodes (LEDs) [1]. Despite the large efforts that have been devoted to optimize phosphors, high efficiencies are often not been reached due to loss mechanisms of which the nature is often not known, yielding suboptimal quantum efficiencies or stronger thermal quenching.

The multivalent nature of Eu is yet another challenge, as Eu^{2+} and Eu^{3+} are both stable ions in many hosts. Distributions of both activators can be expected in Eu-doped materials, which enables intervalence charge transfer (IVCT) transitions, potentially drastically affecting luminescence properties. Indeed, it was recently shown that IVCT is responsible for the anomalous emission in Ce-doped elpasolites and Yb-doped fluorides [2,3].

Here, we show direct evidence of Eu^{2+}/Eu^{3+} IVCT states in a series of representative luminescent materials: Eu-activated CaF_2, SrF_2, and BaF_2. Evidence of IVCT states in Eu-doped materials was so far missing. Independently and unanimously, state-of-the-art relativistic multiconfigurational *ab initio* embedded cluster calculations and diffuse reflection spectroscopy show that the IVCT states intercalate between the ground ($4f^7$) and the luminescent ($4f^6 5d$) states of Eu^{2+}. We show how the location of IVCT levels is affected by changing the chemical composition of the host compound [4].

References

[1] Smet, P. F., Parmentier, A. B., Poelman, D. "Selecting Conversion Phosphors for White Light-Emitting Diodes." *Journal of the Electrochemical Society* 158, **2011,** R37-R54.

[2] Seijo, L., and Barandiarán, Z. "Intervalence Charge Transfer Luminescence: The Anomalous Luminescence of Cerium-Doped $Cs_2LiLuCl_6$ Elpasolite." *Journal of Chemical Physics* 141, **2014**, 214706.

[3] Barandiarán, Z., and Seijo, L. "Intervalence Charge Transfer Luminescence: Interplay between Anomalous and 5d-4f Emissions in Yb-Doped Fluorite-Type Crystals." *Journal of Chemical Physics* 141, **2014**, 234704.

[4] Joos, J. J., Seijo, L., Barandiarán, Z. “Direct Evidence of Intervalence Charge-Transfer States of Eu-Doped Luminescent Materials.” The Journal of Physical Chemistry Letters 10, **2019**, 1581-1586.

Luminescence properties of Eu^{2+}-Mn^{2+} co-doped $Ba_2MgSi_2O_7$

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Rare earths activated silicates exhibit excellent luminescent properties ideal for many commercial applications including illumination phosphors and radiation scintillators.[1] A rigid, stable crystalline network and easy synthesis are some of the advantages of silicate hosts. Among rare earths, the Eu^{2+} and Ce^{3+} ions can be ideal sensitizers for Mn^{2+} (and other weakly absorbing luminescent ions) owing to their allowed and therefore strong $4f\leftrightarrow5d$ absorption.[2] In present work, we investigated the Eu^{2+} sensitization to Mn^{2+} ions in $Ba_2MgSi_2O_7$. The Eu^{2+} shows intense bluish-cyan emission, whereas Mn^{2+} ions exhibit narrow band green emission in monoclinic $Ba_2MgSi_2O_7$.[3,4] On Mn^{2+} co-doping in $Ba_2MgSi_2O_7$:Eu^{2+}, the emission profile broadens and a red shift in peak position appears due to the contribution of sensitized Mn^{2+} emission (Figure 1). The peak shift occurs till 7 at.% Mn^{2+} co-doping, but the luminescence intensity also showed a monotonous decrease on Mn^{2+} co-doping in $Ba_2MgSi_2O_7$:Eu^{2+}. The intensity decrease may be obvious as the thermal quenching of Mn^{2+} luminescence in $Ba_2MgSi_2O_7$ starts below room temperature.[4] Among the different doping concentrations investigated, the 5 at.% Eu^{2+} and 7 at.% Mn^{2+} co-doped $Ba_2MgSi_2O_7$ showed a prominent Mn^{2+} emission contribution, and the Eu^{2+}-Mn^{2+} energy transfer efficiency is about 30% as obtained from the donor decay kinetics. For higher Mn^{2+} co-doping, the emission spectral profile remains nearly unchanged, and the quenching becomes more prominent.

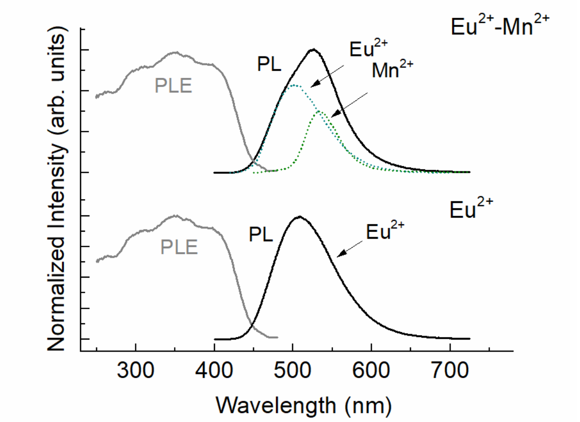

Figure 1: Room temperature photoluminescence (PL) and PL excitation (PLE) spectra of Eu^{2+} singly doped and Eu^{2+}-Mn^{2+} co-doped $Ba_2MgSi_2O_7$. The Eu^{2+} and Mn^{2+} concentrations are 5 at.% and 7 at.%, respectively.

Acknowledgements
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References

[1] G. Blasse, *et al., Philips Res. Rep.* **23**, 189-200 (1968); L. Pidol, *et al., IEEE Trans. Nucl. Sci.* **51**, 1084-1087 (2004); K. Toda, *et al., IEICE Trans. Electron.* **E89-C**, 1406-1412 (2006).
[2] W.-C. Ke *et al., J. Electrochem. Soc.* **157,** J307-J309 (2010); L. Liu, *et al., Inorg. Chem.* **54**, 5556-5565 (2015); X. Zhang, *et al., Inorg. Chem. Front.*, **6**, 1289-1298 (2019).
[3] J. Yan, *et al., J. Mater. Chem. C* **2**, 8328-8332 (2014).
[4] J. Yan, *et al., Opt. Mater.* **43**, 59-65 (2015).

Ion clustering in Tm^{3+}:CaF_2: Effect of doping concentration and buffer ions

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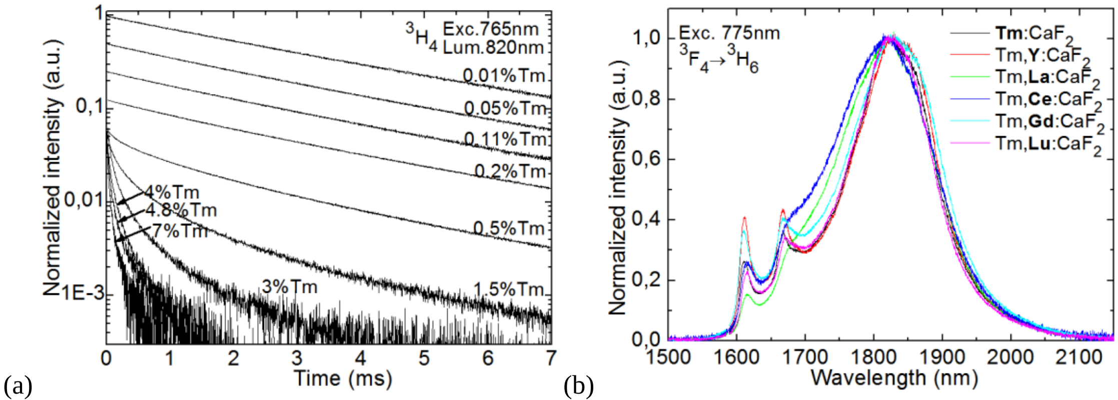
Cubic calcium fluoride crystals (CaF_2) are well-known optical materials. They are suitable for doping with trivalent rare-earth ions (RE^{3+}) such as Thulium (Tm^{3+}). The latter replace the Ca^{2+} cations, while the charge compensation is achieved by interstitial F^- anions entering the lattice. Therefore, RE^{3+}-doped CaF_2 exhibits a strong ion clustering [1] leading, even at low doping levels, to a glassy-like spectroscopic behavior. For Tm^{3+} ions, this is also revealed by a very efficient cross-relaxation (CR) process, $^3H_4 + {}^3H_6 \rightarrow {}^3F_4 + {}^3F_4$, leading to a strong depopulation of the $^3H_4$ state. CR can be an advantage for the ~2 µm ($^3F_4 \rightarrow {}^3H_6$) Tm laser emission and simultaneously a key limitation for the ~2.3 µm ($^3H_4 \rightarrow {}^3H_5$) one. Thus, a precise control of ion clustering and CR for Tm^{3+}:CaF_2 is important for its laser applications [2].

In the present work, we report on a detailed spectroscopic study of ion clustering in Tm^{3+}:CaF_2 crystals. Two types of crystals were studied: (i) singly-doped Tm^{3+}:CaF_2 crystals with a varied Tm^{3+} doping of 0.01–7 at.%) and (ii) crystals codoped with buffer ions, Tm^{3+},Ln^{3+}:CaF_2 (Ln = Y, Gd, Lu, etc.).

For singly doped crystals, the effect of the Tm^{3+} concentration on ion clustering and the CR rate was revealed. In Fig. 1(a), we show the luminescence decay curves from the $^3H_4$ state which were further analyzed within a model comprising distinct ion classes (isolated ions and ions with neighbors). For the Tm^{3+},Ln^{3+}:CaF_2 crystals, we studied the absorption spectra and analyzed the transition intensities using the Judd-Ofelt theory. Then, the effect of buffer ions on Tm^{3+} spectroscopy was studied. In Fig. 1(b), we show the spectra of ~2 µm ($^3F_4 \rightarrow {}^3H_6$) luminescence for the codoped Tm^{3+},Ln^{3+}:CaF_2 crystals.

As a result, we can determine the concentration-dependent fractions of ions forming clusters and the CR rates which are important to find the optimized conditions for laser operation.



(a) (b)

Figure 1: Spectroscopy of Tm^{3+}:CaF_2 crystals: (a) The effect of Tm^{3+} concentration on the decay of luminescence from the $^3H_4$ state; (b) luminescence spectra of Tm^{3+} ions in Tm^{3+},Ln^{3+}:CaF_2 crystals corresponding to the $^3F_4 \rightarrow {}^3H_6$ transition.

References

[1] V. Petit, P. Camy, J.L. Doualan, X. Portier, and R. Moncorgé, *Phys. Rev. B* **78**, 085131 (2008).
[2] P. Camy, J.L. Doualan, S. Renard, A. Braud, V. Menard, and R. Moncorgé, Opt. Commun. **236**, 395-402 (2004).

Luminescence and energy transfer in fluoroindate glasses co-doped with Er^{3+}/Ho^{3+}

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Keywords: *fluoroindate glass, RE-doped glass, energy transfer, infrared luminescence*

The wide photonic applications of rare - earth (RE) doped glasses and especially optical fibers emitting in the near and mid-infrared spectral region have attracted the interest of many scientific groups [1-3]. The key parameter of the host material in case of MID-IR emission is the phonon energy. Therefore, fluoroindate glass systems which are characterized by lower than ZBLAN glasses phonon energy (510 cm^{-1}), extended transparency in the infrared range, better thermal stability, mechanical rigidity and resistance to chemical corrosion [2-5] are very attractive glass host. Thus fluoroindate glasses with their excellent spectroscopic properties offer the possibility of using them as a host for RE-doping and emitting in NIR and especially MID-IR radiation. It's also known that under the specified, non-oxide technological conditions, it is possible to draw fluoroindate optical fibers.

This work reports the fabrication and the effect of optical pumping by laser diodes (@980 nm, 488 nm) on spectroscopic properties of the InF_3–ZnF_2–BaF_2–SrF_2–GaF_3–LaF_3 fluoroindate glasses co-doped with Er^{3+}/Ho^{3+} ions. Special attention will be paid on the analysis of donor-acceptor energy transfer mechanisms leading to the near infrared and mid-infrared luminescence. Analysis of the spectroscopic properties of the $0.8ErF_3/1.4HoF_3$ co-doped glass showed efficient $Er^{3+} \rightarrow Ho^{3+}$ energy transfer leading to the 1.2 μm and 2 μm emission under 980 nm laser diode excitation. Moreover, described sensitization mechanism of Ho^{3+} via energy transfer from Er^{3+} pumped by common 980 nm laser diode showed the possibility of obtaining strong, broadband luminescence in the (2.6-2.9) μm spectral range with FWHM=206 nm.

Acknowledgments

The project was funded by the National Science Centre (Poland) granted on the basis of the decision No. 2017/25/B/ST8/02530. The COST Action MP1401 "Advanced fiber laser and coherent source as tools for society, manufacturing and lifescience" is also acknowledged.

References

[1] D. Dong, Z. Bo, J. Zhu, F. Ma, , J. Non-Cryst. Solids **204,** 260 (1996),
[2] A. Akella, E.A. Downing, L. Hesselink, New fluoroindate glass compositions, J. Non-Cryst. Solids **161**, 213-214 (1997) ,
[3] J. Pisarska, J. Non-Cryst. Solids **382,** 345-346 (2004).
[4] M.A.S. de Oliveira, C.B. de Araujo, Y. Messaddeq, Opt. Express **19,** 5620 (2011),
[5] N. Rakov, G.S. Maciel, C.B. de Araujo, Y. Messaddeq, J. Appl. Phys. **91,** 1272 (2002).

Molecular logical arrays through Ln^{3+}-ions using exclusively physical inputs

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

Since the 80's molecular logic devices constituted by luminescent signalling molecules are being reported as an alternative approach towards molecular computing, showing that molecules can perform some of the computational functions achieved in semiconductor technology. The examples listed in the literature present molecules are actuated almost exclusively by chemical species.

In 2016 some of us reported a Eu^{3+}/Tb^{3+} based -self-assembled polymer monolayer functionalized Si surface is used as an optically active molecular demultiplexer[5], being until now the only example of a molecular logical device using Ln^{3+} ions and physical inputs. In this presentation we will discuss on our recent advances on molecular logic devices actuated exclusively by physical inputs (light and heat) and their implementation in logical gates and in logical operations.

Acknowledgements

CDSB thank the grant financed by the SusPhotoSolutions (CENTRO-01-0145-FEDER-00000) project.

References

1. B. Randell, in *The Origins of Digital Computers*, Springer, 1982, pp. 349-354.
2. M. a. Reed and J. M. Tour, *Scientific American*, 2000, **18**, 53-58.
3. J. M. Tour, *Accounts of Chemical Research*, 2000, **33**, 791-804.
4. L. Sun, Y. A. Diaz-Fernandez, T. A. Gschneidtner, F. Westerlund, S. Lara-Avila and K. Moth-Poulsen, *Chemical Society Reviews*, 2014, **43**, 7378-7411.
5. M. Rodrigues, R. Piñol, G. Antorrena, C. D. S. Brites, N. J. O. Silva, J. L. Murillo, R. Cases, I. Díez, F. Palacio, N. Torras, J. A. Plaza, L. Pérez-García, L. D. Carlos and A. Millán, *Advanced Functional Materials*, 2016, **26**, 200-209.

Cellulose fibres and paper modified by nanophosphors based on rare earth elements activated by UV and IR radiation

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Rare earth elements due to their exceptional spectroscopic features are very good candidate for anti-counterfeiting applications. Sharp and well-defined emission bands related to the f-f transitions, tunable color of the luminescence and many possibilities of excitation wavelength enable to create and produce materials which can prevent falsifying the important documents [1]. Fluorides matrices are suitable for doping with lanthanides ions due to their low phonon energy, which enable to avoid luminescence quenching. For this reason, nanomaterials based on fluorides doped with Yb^{3+}/Er^{3+} ions and Eu^{3+} ions were used to modify the Lyocell fibers cellulose fibers and paper. It resulted in green and red emission of the improved products under IR and UV excitation, respectively. Such modifications make possible to produce the luminescent ecological materials for documents and goods protection against counterfeiting.
The NMMO (N-Methylomorpholine-N-Oxide) method of fibers formation allows to modify them in the process of spinning dope preparation and as a result, the modifier nanoparticles are incorporated into polymer matrix of fibers, which provides durability and increases usability of the fibers [2,3]. Furthermore, modified fibers are used to prepare the series of luminescent papers with different concentration of luminescent Lyocell fibers in paper mass.

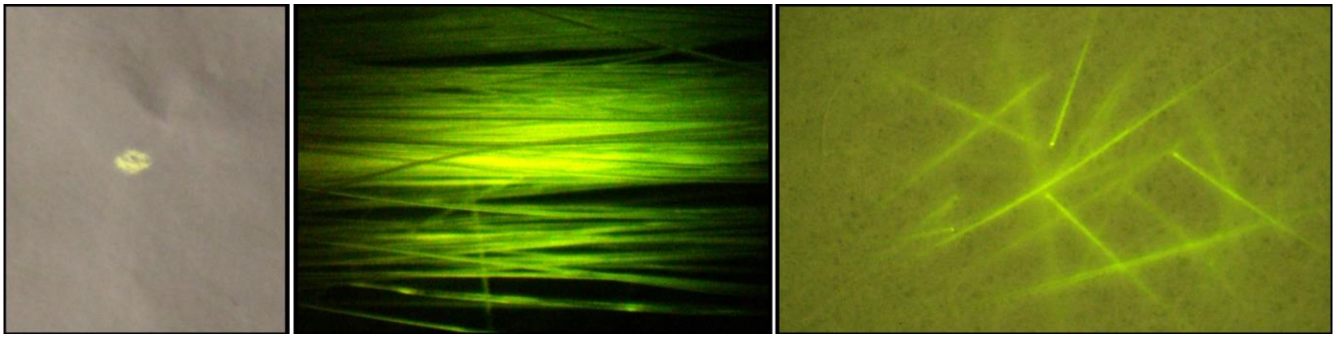

Figure 1: Green emission of the modified fibers and paper activated by IR radiation.

Acknowledgements
The presented results were financially supported by The National Centre for Research and Development, LIDER/39/0141/L-9/17/NCBR/2018 *Ecological cellulose fibers and paper modified with micro and nanoluminophores activated with ultraviolet and infrared radiation.*

References

[1] A. Szczeszak, M. Runowski, R.J. Wiglusz, T. Grzyb, S. Lis, *Opt. Mater.*, 1–7 (2017)
[2] A. Erdman, P. Kulpinski, T. Grzyb, S. Lis, *J. Lumin.* **169,** 520–527 (2016).
[3] P. Kulpinski, M. Namyslak, T. Grzyb, S. Lis, *Cellulose* **19** 1271–1278 (2012).

Oral

RE^{3+} based phosphors embedded into organic polyethylene films

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In the present work the synthesis and characterization of polyethylene/phosphors composites are studied. RE^{3+}-based inorganic phosphors were blended with the low-density polyethylene (LDPE) and then thin films were deposited by means of the dip coating technique. Their optical structural and luminescent properties were evaluated. All composites were made from virgin polyethylene, but easily scalable to waste-polyethylene and high volumes. FTIR measurements confirm the formation of polyethylene/phosphors composites, UV-Vis allows to characterize the transparency of the LDPE matrix after the incorporation of the phosphors. Finally, a complete luminescent study was carried out to characterize the optical properties of the composites and the possibility to use them in technological applications.

Acknowledgments

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References

[1] S. Carmona-Téllez, G. Alarcón-Flores, E. Zaleta-Alejandre, Z. Rivera-Alvarez, A. N. Meza-Rocha, R. Martínez-Martínezd, H. Murrieta S., M. Aguilar-Frutis and C. Falcony, Luminescent polystyrene films, a novel way to reduce styrofoam residues, Revista Mexicana de Física, 61, 2015, 323–329

[2] S. Carmona-Téllez, G. Alarcón-Flores, A. Meza-Rocha, E. Zaleta-Alejandre, M. Aguilar-Futis, H. Murrieta S. and C. Falcony, Polyethylene terephthalate thin films; a luminescence study, Optical Materials, 42, 2015, 99–105.

Oral

Structural modification of nanohydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ related to Eu^{3+} and Sr^{2+} ions doping and its spectroscopic and antimicrobial properties

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The calcium phosphates are the most important family to be used in biomedical applications due to high similarity to the inorganic part of hard tissues, their good biocompatibility, osteoconductivity, non-toxicity, non-immunogenicity and ability to prompt the direct chemical bond with living tissues[1,2]. The Eu^{3+} and Sr^{2+} ions co-doped hydroxyapatite nanopowders ($Ca_{10}(PO_4)_6(OH)_2$) were synthesized *via* a precipitation method and post heat-treated in 500°C per 3 h. The structural and morphological properties of the obtained materials were checked by the XRD (X-ray powder diffraction) and TEM (transmission electron microscopy) techniques and IR (infrared) spectroscopy. The average grain size of the obtained materials was calculated based on the Rietveld refinement method. The luminescence properties in dependence on dopant concentration and applied temperature of the Eu^{3+}/Sr^{2+} ions-doped $Ca_{10}(PO_4)_6(OH)_2$ were investigated. The antibacterial properties of the Eu^{3+} and Sr^{2+} ions doped and co-doped hydroxyapatite nanopowders were also determined against Gram-negative pathogens such as *Pseudomonas aeruginosa, Klebsiella pneumoniae* and *Escherichia coli*. The obtained results suggest that both europium and strontium ions may implement antibacterial properties for hydroxyapatites.

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References

[1] K. Zawisza, A. Strzep, R.J. Wiglusz, *New J. Chem.* **41**, 9990–9999 (2017).
[2] S. Targonska, K. Szyszka, J. Rewak-Soroczynska, R.J. Wiglusz, *Dalton Trans.* (2019) DOI:10.1039/c9dt01025d.

Novel Microemulsion approach for the synthesis of Eu^{2+} doped nanoparticles

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Nanoparticles become more and more important for different applications like medical sensing,[1] cosmetics[2] or even lightning in displays.[3] For this reason the research increases rapidly in the field of nanoscience. The advantages of inorganic nanoparticles are the high stability and low toxicity in comparison to other nanoparticles. In the context of luminescent materials, Eu^{2+} is the most promising dopant due to its very efficient and fast transitions and tunable emission energy.[4] The only disadvantage of Eu^{2+} ions is the unstable oxidation state which prevents the synthesis of non-agglomerated nanoparticles with an efficient luminescence by the common methods using water or alcohols as solvents. The often used strategy of doping Eu^{3+} into the particles with subsequent reduction at high temperature leads to an unwanted growth an aggregation of the nanoparticles. Therefore, the development of new synthesis methods for Eu^{2+} containing inorganic nanoparticles is necessary.

In this work we present a novel synthesis technique for these nanoparticles for the first time. In detail we adapted a modified microemulsion approach with prior reduction of Eu^{3+} to Eu^{2+} and subsequent stabilization give rise to direct Eu^{2+} doped nanoparticles with small sizes, showing efficient luminescence. The potential of this novel technique is shown for MSO_4: Eu^{2+} (M = Sr, Ba) and different fluorides, like CaF_2 $BaSiF_6$ and Ba_2ZrF_8. Moreover, the synthesis of $EuSO_4$ nanoparticles and their respective luminescence at low temperature will be presented.

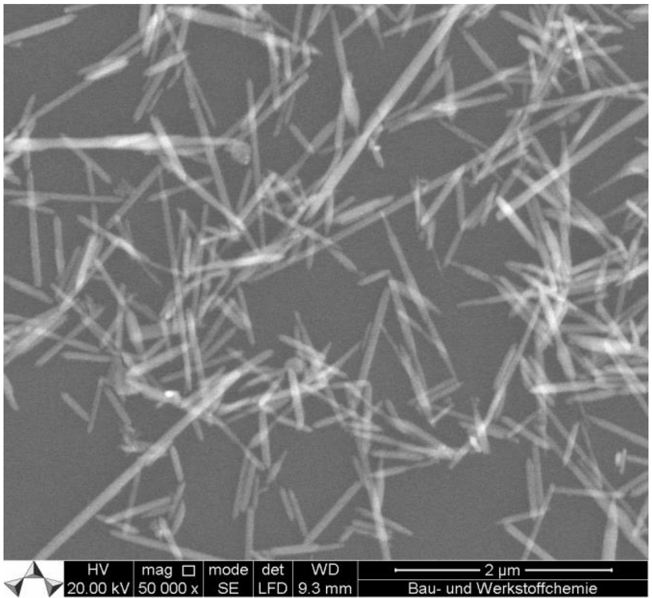

Figure 1: SEM image of $BaSiF_6$: Eu^{2+} nanorods.

References

[1] V. Biju, *Chem. Soc. Rev.*, **43**, 744 (2014).
[2] S. Raj, S. Jose, U. S. Sumod, M. Sabitha, *J. Pharm. Bioallied Sci.*, **4**, 186 (2012).
[3] M. K. Choi, J. Yang, T. Hyeon, D.-H. Kim, *npj Flex Electron*, **2**, 49 (2018).
[4] H. Terraschke, C. Wickleder, *Chem. Rev.*, **115**, 11352 (2015).

Controlled synthesis and photoluminescence properties of hexagonal Eu^{3+} activated Na(Y,Gd)F$_4$ microphosphors

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Rare earth (RE) doped upconversion materials capable of turning the incident NIR photons into UV–vis photons have shown promising potentials in the fields of solar cells [1], sensors [2], and so on. The efficient upconversion materials are based on fluorides specially NaYF$_4$, which are codoped with rare earth (RE) ions. These are generally exhibit multicolor fluorescence emission from ultraviolet to infrared (IR) because of the abundance of the 4f^N electronic states of the RE ions. Therefore, different technologies have been explored to obtain and tune fluorescence emission, which remains a considerable challenge for researchers. In this work, a series of hexagonal phase NaYF$_4$:Gd^{3+}/Eu^{3+} microcrystals have been successfully synthesized through controlled hydrothermal methods. The rietveld refinement of XRD and TEM SAED pattern has been employed to investigate the structure and morphology. Formation of single phase hexagonal microcrystals is detected for all the doping concentrations. Raman and FTIR spectra show the functional group and vibrational modes present in the system. The luminescence and excitation spectra of Eu activated NaYGdF$_4$ have been measured. From the emission spectra (Fig.1), the maximum intense peak observed at 612 nm excited at 394 nm may be assigned to the Eu^{3+} emission line $^5D_0$-$^7F_2$ under the influence of the host lattice [3]. The Eu^{3+} (3, 5, 7, 10 at %) co-doped Na(Y, Gd) F$_4$ show the CIE chromaticity coordinates transitions from blue region for low doping to red region for higher doping concentration of Eu^{3+} as shown in Fig.1 We would expect in such phosphors, mutual correlations and competitions among the lanthanides especially in this fluoride tuned the luminescent properties of the host. The current study suggests that the NaYF$_4$: Gd^{3+}/Eu^{3+} microcrystals with the strong red emission may have great potential applications in micro-fiber laser, multicolor display etc.

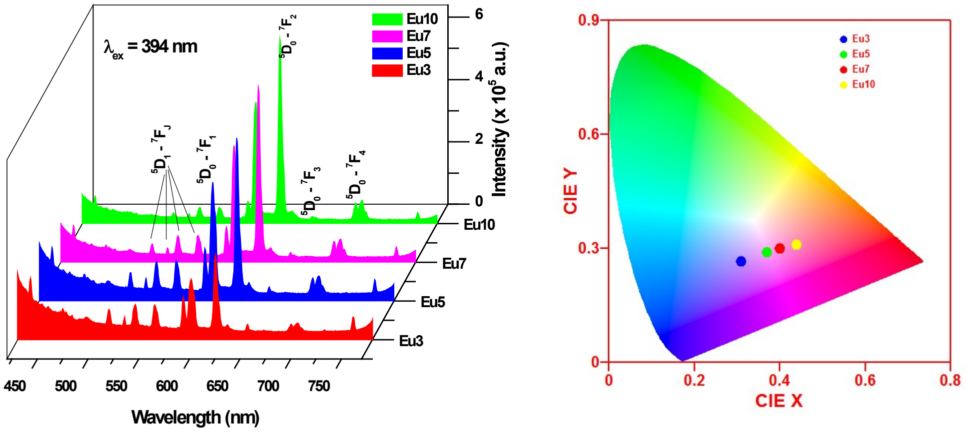

Figure 1: Emission spectra and CIE chromaticiity coordinates of NaYF$_4$: 5%Gd, x%Eu

References

[1] P. Ramasamy, P. Manivasakan, J. Kim, RSC Adv. **4,** 34873 (2014)
[2] U. Rocha etal, ACS Nano **7**, 1188 (2013).
[3] Ruoxue Yan and Y, Li, Advanced Functional Material, **15**, 763 (2005).

Mixed Eu^{3+}-Tb^{3+} Metal-Organic Frameworks built on Isophtalic acid ligand as Ratiometric Luminescent Thermometer

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Metal-Organic Frameworks (MOFs) are crystalline hybrid materials built-up from metal ions as nodes linked by bridging ligands. They have attracted great interest due to their versatile chemistry, high surface areas and chemical functionality. Recently, lanthanide-based luminescent MOFs (Ln-MOFs), whose optical properties may come from the organic or inorganic part, have emerged as luminescent thermometers.[1] Indeed, compared to conventional contact thermometers, luminescent thermometers have unique and distinct advantages of fast response, high accuracy, non-invasive nature, high spatial resolution characteristics at the submicron scale where traditional methods are ineffective. The most promising non-invasive technique to measure the temperature relies on ratiometric luminescent thermometers where the absolute temperature is directly linked to the intensities of two transitions of distinct emitting centers. In the case of mixed Ln-MOFs, the emitting centers are Ln^{3+} cations, generally the transitions $^5D_4$-$^7F_5$ of the Tb^{3+} and $^5D_4$-$^7F_2$ of the Eu^{3+}, respectively.[2]

In this work, we designed a series of mixed Eu-Tb MOF with isophthalic acid as principal ligand. We studied the impact of modifications in Ln^{3+} coordination sphere on the thermometric performances. Indeed, mixed Eu-Tb MOF synthetized with isophthalic acid gets a 2D structure and exhibit performance in the cryogenic range[3] but mixed Eu-Tb MOF synthetized with isophthalic acid and acetic acid exhibits a 3D structure and is sensitive in the physiological range (Fig.1).

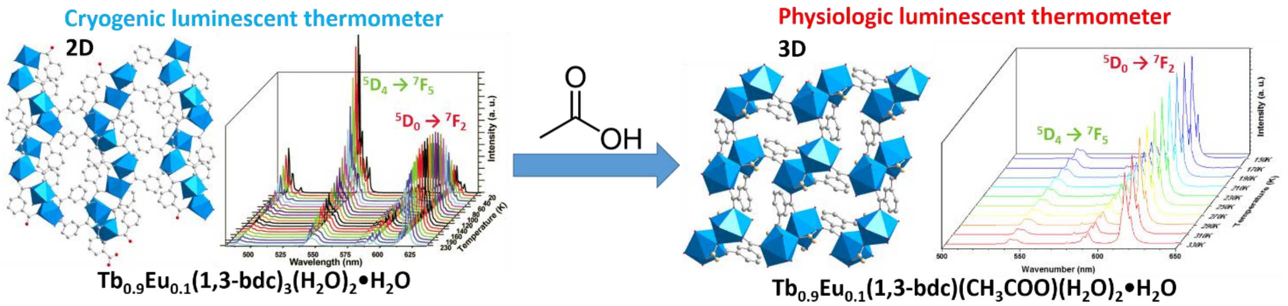

Figure 1: Left) Crystal structure and emission spectra of the thermometer in the 12-230 K range of the mixed Eu-Tb MOF with isophthalic acid. (Right) Crystal structure and emission spectra of the thermometer in the 150-330 K range of the mixed Eu-Tb MOF with isophthalic acid and acetic acid.

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References

[1] J. Rocha, C. D. S. Brites and L. D. Carlos, *Chem. Eur. J.*, **22**, 14782-14794 (2016).
[2] Y. Cui, H. Xu, Y. Yue, Z. Guo, J. Yu, Z. Chen, J. Gao, Y. Yang, G. Qian and B. Chen, *JACS*, **134**, 3979-1982 (2012).
[3] I. N'Dala-Louika, D. Ananias, C. Latouche, R. Dessapt, L.D. Carlos, H. Serier-Brault, *J. Mater. Chem. C*, **5**, 10933-10937 (2017).

Microwave assisted synthesis of Tb-metal-organic frameworks with luminescent properties

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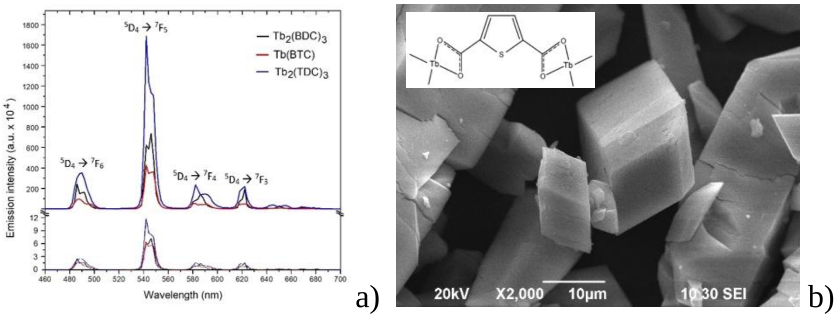
The structural and luminescent properties of Metal-Organic Frameworks (MOFs) derived from benzenecarboxylic acids with terbium such as $Tb_2(BDC)_3$, Tb (BTC) and $Tb_2(TDC)_3$ are reported. These MOFs were synthesized by the microwave-assisted solvothermal method and show the characteristic green emission of the Tb^{3+} ion. The photoluminescent emission is due to the antenna effect where the energy is transferred from the ligands, singlet levels in benzenecarboxylic acids, to the excited level $^5D_4$ of the Tb^{3+} from which the energy decays to its basal levels ^7F_J (J = 6, 5, 4, 3). Surprisingly, the emission intensity in all samples increases by two orders of magnitude (from 10^4 to 10^6), when they are thermally treated (Fig. 1a). The excitation spectra obtained by PL confirm that the excitation of the MOFs is by means of the organic sensitizers. XRD measurements confirm the presence of crystalline MOFs. By FTIR, the vibrations corresponding to the carboxylate functional groups were determined, in addition to the metal-oxygen bond. The Nitrogen adsorption isotherms denote the presence of porosity in the MOFs and a thermogravimetric analysis (TGA) was also carried out. SEM images are obtained for all samples indicating the formation of large crystals (Fig.1b).



a) b)

Figure 1. Luminescent emission of samples before and after the calcination process (a) and SEM image of the $Tb_2(TDC)_3$ sample

Acknowledgements

Authors acknowledge the partial financial support of projects: SIP-IPN #20181597, SIP-IPN #20181456, CB-2015/253342 and 871(2017) and 572(2018) of *Cátedras Conacyt*

Lanthanide-doped organic-inorganic materials for downshifting layers in solar cars

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The objectives of the United Nations stated the urgency in improving photovoltaic (PV) cells performance and integrate them into buildings, with the goal of attaining zero-energy buildings. The mismatch between the solar spectrum and the Si absorption is a crucial parameter that may be overcome by luminescent down-shifting (LDS) layers and luminescent solar concentrators (LSCs). Both devices are based on films which absorb the incident radiation complementary to that of the PV cell and re-emit it at a specific wavelength, posteriorly refracted (LDS) or guided through total internal reflection (LSC) towards the PV cell. The LSCs have an extra advantage of making possible the integration of PV elements in the built environment, as they could be embedded in façades or windows.

Lanthanide (Ln^{3+})-based materials have been used in the development of PV complementary devices due to their high absorption coefficient overlapping the AM1.5G spectrum, emission in the visible-NIR spectral range (Si PV cells absorption) with high emission quantum yield and large ligands-induced Stokes shifts.

Over the last years, our group developed several complementary PV devices, including LSCs with planar [1] and cylindrical geometry [2,3,4] and LDS layers [5], based on Ln^{3+}-doped organic-inorganic hybrid or polymeric matrices. Our top-performance devices presented optical conversion efficiency values of 2.3% [3] (Eu^{3+}-based hollow-core cylindrical LSC) and provided an absolute external quantum efficiency increase in the UV spectral region of ~25% compared to the bare PV cell in use (Tb^{3+} and Eu^{3+} based LDS layers) [5]. Here, we focus on latter mentioned work about Tb^{3+} and Eu^{3+} based LDS layers which provided a performance enhancement in the UV spectral region of all devices tested. Moreover, the Eu^{3+}-based LDS layer was successfully tested in a race between small solar vehicles with bare and coated PV cells, in which the solar car with the coated PV cell presented a relative increase in the velocity of ~ 9%, comparing with the one with the bare PV cell [5].

Acknowledgements

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References

[1] A.R. Frias, M.A. Cardoso, A.R.N. Bastos, S.F.H. Correia, P.S. Andre, L.D. Carlos, V. de Zea Bermudez, R.A.S. Ferreira, *Energies*, **12**, 451 (2019)

[2] S.F.H. Correia, A.R. Frias, L.S. Fu, R.Rondao, E. Pecoraro, S.J.L. Ribeiro, P.S. Andre, R.A.S. Ferreira, L.D. Carlos, *Advanced Sustainable Systems*, **2**, 1800002 (2018)

[3] S.F.H. Correia, P.P. Lima, E.Pecoraro, S.J.L. Ribeiro, P.S. André, R.A.S. Ferreira, L.D. Carlos, *Progress in Photovoltaics: Research and Applications*, **24**, 1178-1193 (2016)

[4] S.F.H. Correia, P.P. Lima, P.S. André, R.A.S. Ferreira, L.D. Carlos, *Solar Energy Materials and Solar Cells*, **138**, 51-57 (2015)

[5] S.F.H. Correia, A.R.N. Bastos, L. Fu, L.D. Carlos, P.S. André, R.A.S. Ferreira, *Opto-Electronic Advances*, **2**, 19006 (2019)

Oral

Rare earth doped transparent ceramics for laser gain medium

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Since two decades, transparent ceramics used as gain medium for high power laser have shown their efficiency [1]. Moreover, ceramic fabrication process are faster and more versatile than those of single crystals, allowing production of bigger and more complex pieces. Infrared lasers are useful for many applications, from surgery to telecommunications. However, for 4 or 5 µm laser sources, high optical quality materials are not available yet to produce high power laser. Consequently, development of transparent ceramics holmium doped will lead to gain medium capable of generating laser emission around 2 µm. Among eligible ceramics, we can list cubic oxide as YAG [1], LuAG, Lu_2O_3 and more recently promising results with Lu_3NbO_7. In this project isostructural compound Y_3NbO_7 [2] was chosen and doped with different rare earth, europium and holmium.

Europium ion is used as a local probe to study the crystalline structure of the synthetized powders and the nature of the sintered pellets. Different shaping techniques were performed and compared (pressure less process, SPS, vacuum sintering…). Crystalline structure, phase decomposition, migration and reduction of the elements were characterized by photoluminescence, micro-luminescence, XPS, EDX, EPR… The niobate phase is then doped with Holmium ions to study the effect of concentration on the crystalline structure and the infrared emission.

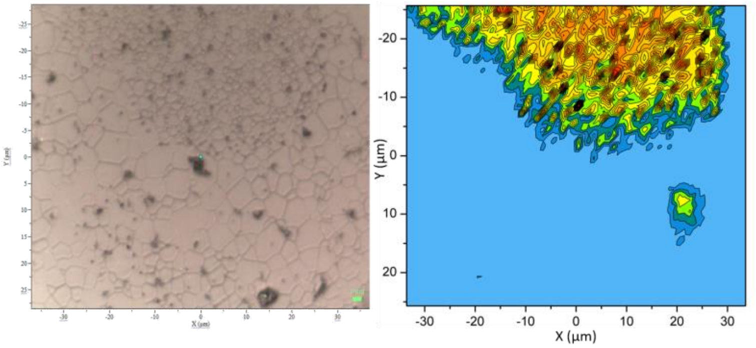

Figure 1: a) Surface of a pellet sintered in air, 1600 °C, 6h, thermally revealed and b) corresponding micro-luminescence cartography indicating local decomposition.

Acknowledgements

This investigation was supported by the CNRS and the Nouvelle Aquitaine region in the frame of the MISTRAL project. This study was carried out with financial support from the French State, managed by the French National Research Agency (ANR) in the frame of “the Investments for the future” Program IdEx Bordeaux – LAPHIA (ANR-10-IDEX-03-02) and PIXUFAST (ANR). The author would like to associate Alexandre Fargues, ICMCB for his contribution in the technical aspect of luminescence spectroscopy (calibration and correction file validation).

References

[1] Ikesue, A., Kinoshita, T., Kamata, K., & Yoshida, K. *Journal of the American Ceramic Society*, **78**, 1033-1040 (1995)

[2] K-Y Kim, U-C Chung, B. Mutulet, F. Weill, A. Demourgues, J. Rossit, J-M Heintz, A. Veillere, V. Jubera, *Inorg. Chem.*, **56 (8)**, 4495–4503 (2017)

Numerical investigation of simultaneous lasing at three different wavelengths in an Yb:Er:Tm:Ho co-doped germanate glass

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The development of broadband optical amplifiers and lasers relies on the availability of active media with an ultra-wide gain bandwidth. Glasses doped with multiple rare earth ions constitute an attractive solution for obtaining optical gain bandwidths spanning several hundreds of nanometers. In this work, a theoretical model of a quadruple-doped Yb:Er:Tm:Ho germanate glass [1] is developed in order to investigate simultaneous laser emission at three different wavelengths, i.e. 1550 nm, 1800 nm and 2050 nm. The system is pumped at 980 nm. The employed germanate glass exhibits some advantages with respect to both chalcogenide and fluoride glasses, such as high solubility of rare earth ions and high physicochemical stability. The performed simulations show that an appropriate concentration ratio between the different dopants is required in order to obtain a homogeneous optical gain at all the three operating wavelengths.

An accurate numerical code is implemented to solve for the rare earth populations and the optical powers inside the laser cavity [2–4]. The system is composed of 11 rate equations and 7 power propagation equations. In addition to the absorption and emission transitions, cross-relaxation and energy transfer processes are also included. Optical and spectroscopic parameters from experimental measurements reported in literature are used in the simulation. A step-index fiber with a 4 µm core diameter, which exhibits single mode propagation from 980 nm to 2050 nm, is considered. The rare earth doping profile is homogeneous and covers the entire fiber core.

By employing a fiber with a length of 0.3 m and an Yb:Er:Tm:Ho concentration ratio of 1:4.5:4.2:3.9, the ytterbium concentration being 1.5×10^{25} ions/m^3, the output powers of the three signals are 64 mW, 59 mW and 44 mW at 1550 nm, 1800 nm and 2050 nm, respectively, when the pump power is 0.5 W and the input and output couplers reflectivities are fixed to 99% and 50%, respectively, for all wavelengths. These results show that it is possible not only to obtain multi-wavelength laser emission, but also to balance the three output powers by varying the fiber parameters and the input pump power.

Future work will include the optimization of the performance of the system, e.g. obtaining three output powers as close as possible, by employing an evolutionary algorithm such as the particle swarm optimization (PSO) [3].

References

[1] A. Albalawi, M. Kochanowicz, J. Zmojda, P. Miluski, D. Dorosz, S. Taccheo, *Laser Congress 2018 (ASSL), OSA Technical Digest, Boston, United States*, paper ATu2A.4 (2018).

[2] G. Palma, M. C. Falconi, F. Starecki, V. Nazabal, J. Ari, L. Bodiou, J. Charrier, Y. Dumeige, E. Baudet, F. Prudenzano, *Optics Express*, **25**, 7014-7030 (2017).

[3] M. C. Falconi, G. Palma, F. Starecki, V. Nazabal, J. Trolès, J.-L. Adam, S. Taccheo, M. Ferrari, F. Prudenzano, *Journal of Lightwave Technology*, **35**, 265-273 (2017).

[4] M. C. Falconi, D. Laneve, M. Bozzetti, T. T. Fernandez, G. Galzerano, F. Prudenzano, *Journal of Lightwave Technology*, **36**, 5327-5333 (2018).

Hexagonal $Sr_{1-x/2}Al_{2-x}Si_xO_4$:$Eu^{2+}$,$Dy^{3+}$ transparent ceramics exhibiting white persistent luminescence excitable by visible light

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Rare earth doped aluminates, such as $SrAl_2O_4$:Eu^{2+},Dy^{3+} and $CaAl_2O_4$:Eu^{2+},Nd^{3+}, are among the best known materials for afterglow emission [1]. Numerous studies have been carried out on this strontium aluminate to find different elaboration ways and to elucidate its persistent luminescence mechanism [2]. It recently appeared that its hexagonal polymorph, which is the high temperature polymorph, should have promising properties too. However, an efficient way has been developed to elaborate the hexagonal $Sr_{1-x/2}Al_{1-x}Si_xO_4$:Eu^{2+},Dy^{3+} phases by glass crystallization. This elaboration method also takes its advantage to produce transparent materials particularly interesting due to volume effect. Here we report the optical studies on Eu^{2+}, Dy^{3+} co-doped $Sr_{1-x/2}Al_{1-x}Si_xO_4$ ($0 \leq x \leq 0.5$) transparent ceramics elaborated by this method. The experimental results show that the photoluminescence as well as the afterglow emissions shift from green to blueish white as x increases. This color change appears related to two effects: the blue shift of Eu^{2+} broad emission and the appearance of Dy^{3+} emission. Interestingly, the near white persistent emission can be activated using low power white LEDs. Advanced optical properties such as radiance decay, thermoluminescence and 2D afterglow excitation/emission measurements combined with theoretical calculations have been performed in order to learn more about the influence of the Si content on the optical properties and to try to elucidate the evolution of the persistent luminescence mechanism.

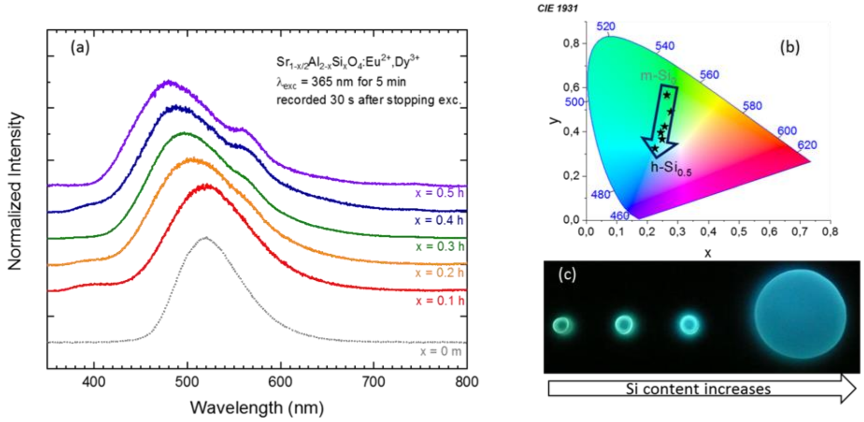

Figure 1: (a) Persistent luminescence spectra of monoclinic x = 0 (bottom) and hexagonal $Sr_{1-x/2}Al_{2-x}Si_xO_4$:$Eu^{2+}$,$Dy^{3+}$ x = 0.1 to x = 0.5 with λ_{exc} = 365 nm for 5 min. (b) CIE coordinates and (c) pictures of the samples.

Acknowledgements

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References

[1] T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama, *J. Electrochem. Soc.*, **143**, 2670-2673 (1996)
[1] P. Smet, *Handbook on the physics and chemistry of rare earths, including actinides*, **48**, 1-108 (2015)

Oral

Afterglow phosphors based on lanthanide-doped germanates in the system $CaO–GeO_2–Y_2O_3$

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Persistent luminescence materials which can emit light for several hours after removal of an irradiation source continue receiving considerable attention due to their applications in emergency signalization, micro defect sensing, optoelectronics for image storage, thermal sensors, optical bioimaging, etc. [1]. Germanates are less widely studied for further development of white afterglow phosphors, in contrast to silicates, aluminates, phosphates and other inorganic hosts doped with lanthanide and transition metal ions [2]. To enlarge our view of persistent luminescence in germanate-based compounds, we have focused on thermoluminescence and afterglow properties of several lanthanide-doped germanate hosts. Ca_2GeO_4 (E_g = 5.65 eV / indirect band gap) [3], $CaGe_2O_5$ (E_g = 4.87 eV / indirect), $Y_2Ge_2O_7$ (E_g = 6.08 eV / direct) and $CaY_2Ge_4O_{12}$ (E_g = 4.95 eV / indirect) belong to the system $CaO–GeO_2–Y_2O_3$ and are characterized by very different crystal structure types. Doping the hosts listed above with Ce^{3+}, Pr^{3+}, Sm^{3+}, Dy^{3+} ions allows constructing phosphors which reveal white persistent luminescence up to 1–5 h. $CaGe_2O_5$ is a self-activated phosphor with white-light afterglow. *Ab initio* calculations in the DFT framework have been performed to study electronic properties of the hosts and to support the findings in optical spectroscopy of the synthesized phosphors.

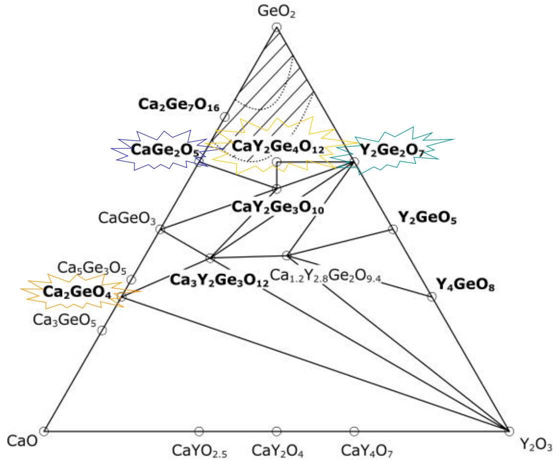

Figure 1: Isothermal section of the system $CaO–GeO_2–Y_2O_3$ at 1200 °C and optical hosts for afterglow phosphors in the present study denoted with frames.

Acknowledgements

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References

[1] J. Xu, S. Tanabe, *J. Lumin.*, **205**, 581–620 (2019).
[2] K. Van den Eeckhout, D. Poelman, P.F. Smet, *Materials*, **6**, 2789–2818 (2013).
[3] L.V. Ermakova, I.I. Leonidov, *Mater. Lett.*, **233**, 39–41 (2018).

Oral

Precursor-directed synthesis of upconverting $LiYF_4$:Yb^{3+}, Tm^{3+} nanoparticles and their composites designed for near infra-red driven photocatalysis

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Titanium dioxide (TiO_2) and graphitic carbon nitride ($g\text{-}C_3N_4$) are among the most promising photocatalysts due to their low cost, non-toxicity and high catalytic activity. However, these photocatalysts also have certain limitations in terms of low efficiency of visible light utilization and high recombination rate of the photo-generated electron-hole pairs. Coupling of these photocatalysts with lanthanide-based upconverting nanoparticles (UCNPs) can lead to utilization of near-infrared part of the solar spectrum and, therefore, enhance the photocatalytic efficiency many folds.[1] In this context, upconverting nanomaterials $LiYF_4$: Tm^{3+}/Yb^{3+} have great potential as they show intense upconverted emissions in the deep-UV region,[2] which would greatly facilitate efficiency of above photocatalysts. However, in comparison to the more thoroughly investigated $NaLnF_4$-based systems, the studies on upconverting nanomaterials based on the $LiYF_4$ host matrix remain in its nascent state.[3]

Here we describe bottom-up synthesis of a series of $LiYF_4$ nanocrystals (NCs) co-doped with varying amount of Yb^{3+} and Tm^{3+} ions using new molecular precursors [Ln(TFA)$_3$(monoglyme)] [Ln = Y, Tm, Yb] and [Li(TFA)(monoglyme)] (where TFA = trifluoroacetate, and monoglyme = dimethoxyethane). These precursors, synthesized in a simple one-pot reaction and characterized by spectroscopy, single crystal X-ray structures and thermogravimetric studies, are advantageous in terms of being anhydrous. The multicolour up-conversion fluorescence studies of the obtained $LiYF_4$:Tm^{3+}/Yb^{3+} NCs established them to be promising UC nanophosphors, which were further used to prepare composites with earlier-mentioned photocatalysts to realize near IR-driven photocatalysis.

[1] a) S. Wu1, J. Lv, F. Wang, N. Duan, Q. Li, Z. Wang, *Sci. Rep.*, ***7***, 14435-14746 (2018); b) Y. Chen, S. Mishra, G. Ledoux, E. Jeanneau, M. Daniel, J. Zhang, S. Daniele, *Chem. Asian J.* **9**, 2415–2421 (2014).
[2] V. Mahalingam, F. Vetrone, R. Naccache, A. Speghini, J. A. Capobianco, *Adv. Mater.*, ***21***, 4025–4028 (2009).
[3] T. Cheng, R. Marin, A. Skripka, F. Vetrone, *J. Am. Chem. Soc.*, ***140***, 12890−12899 (2018).

Oral

Rare earth based nanomaterials; dopant variations and its luminescent properties

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Enriched and unaltered energy levels of rare earth ions provide unique and fingerprint properties to the materials containing these ions. Their luminescence characteristics are well investigated which lead to variety of applications, such sensors, solar cells, catalysis, life sciences, lighting etc. The doping variations provide opportunity to excite these materials from UV to infra-red region, i.e. with high to lower energy radiation, and it also concludes the corresponding emission wavelength: the dopants decide downshifting, downcoverting and upconverting luminescence characteristics of these materials. Though such uniqueness is well investigated in the bulk materials, the macroscopic size of such particles limits their use in application areas like life sciences and solar cells. Where nanoparticles (NPs) play important roles in addressing issues related to surface chemistry, as well nanotechnology enables to develop core@shell nanostructures with active or inactive multilayer having multifunctional properties, which are necessary for cutting edge applications. While considerable efforts have been reported on the synthesis of such NPs, harnessing the properties is still a big challenge to make use these materials in a more efficient way. We have recently demonstrated a fine tuning in the optically inactive shell of upconversion NPs by doping the shell with optically active rare earth ions providing additional excitation wavelengths. The dopants were chosen such that the additional excitation wavelengths lie within the so-called second optical window, making these particles better viable for life science applications. Furthermore, co-doped materials result in multifunctional properties like magnetic and optical in the same nanomaterials. These materials could be used as a bimodal imaging (see the TEM in the figure to the left) probe. Photographs of different downshifting nanomaterials obtained by varying rare earth ions as well as host lattices are also shown below (figure in the middle and to the right).

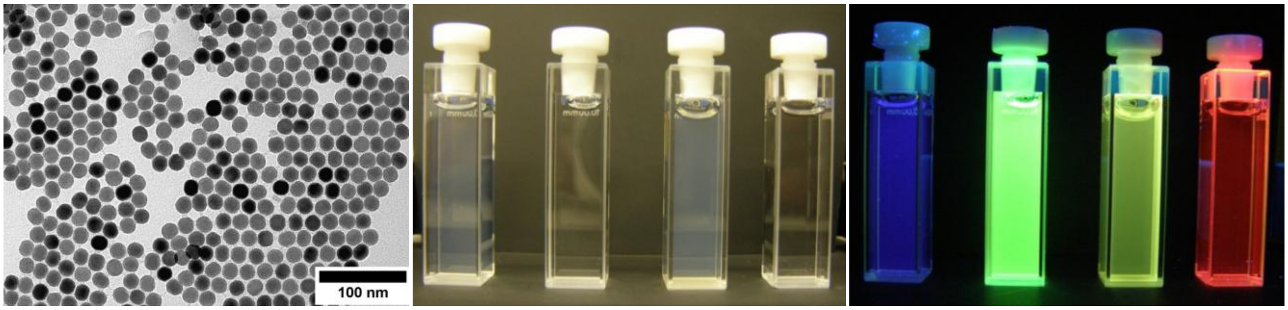

Figure 1: Rare earth ions dopant variation results tuning multifunctional properties. TEM of core@shell upconversion NPs having manetic and optical properties (left); downshifting nanoparticles in water, under daylight (centre) and under UV light (right).

*Fraunhofer CAN is a research division of Fraunhofer Institute for Applied Polymer Research IAP situated in Potsdam-Golm, Germany.

Bi^{3+} influence on physicochemical properties of $Ba_2REV_3O_{11}$ upconverting nanoparticles

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The field of upconversion luminescence (UC) has become of interest to scientists since 1959 [1]. The UC process, based on the sequential absorption of two or more photons with lower energy and resulting emission of photon at shorter wavelength, has already found its possible application in, for example, photovoltaics or bioimaging [2-6]. Research on both upconversion and downconversion luminescence has already demonstrated the influence of other than lanthanides on emission and its intensity, such as Bi^{3+}, which exhibits a broad visible emission under UV excitation and plays an important role in enhancing the luminescence intensity in Yb/Bi/Ln systems [7-8]. The presented research is related to the role of the Bi^{3+} ion introduced to upconverting $Ba_2REV_3O_{11}$: Yb, Ln (RE = La, Gd; Ln = Er, Ho, Tm) nanomaterials synthesized by the hydrothermal method. Sodium citrate (Na_3Cit) in an aqueous environment at pH = 9.3 favored the formation of $[V_3O_{11}]^{7-}$ ions, and prevented from further agglomeration of nanoparticles. Studies have shown improved luminescence properties (extended up-conversion luminescence decay, increased up-conversion luminescence intensity), as well as tuned luminescence color due to increased Bi^{3+} content. Moreover, the structure, morphology and grain size of the discussed materials were confirmed by TEM and XRD methods.

Acknowledgements

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References

[1] N. Bloembergen, *Phys. Rev. Lett.* **2**, 84–85 (1959)
[2] X. Liu, C.H. Yan, J.A. Capobianco, *Chem. Soc. Rev.*, **44**, 1299–1301 (2015)
[3] D. Yang, P. Ma, Z. Hou, Z. Cheng, C. Li, J. Lin, *Chem. Soc. Rev.*, **44**, 1416-1448 (2015)
[4] W. Yin, L. Zhou, Z. Gu, G. Tian, S. Jin, L. Yan, X. Liu, G. Xing, W. Ren, F. Liu, Z. Pan, Y. Zhao, *J.Mater. Chem.*, **22,** 6974 (2012)
[5] W.GJHM van Sark, J. de Wild, J. K. Rath, A. Meijerink, R. EI Schropp, *Nanoscale Res. Lett.*, **8,** 81 (2013)
[6] N. Kaczorowska, A. Szczeszak, S. Lis, *J. Lumin.*, **200**, 59-65 (2018)
[7] M. Zhao, G. Li, J. Zheng, L. Li, L. Yang, *CrystEngComm.*, **14**, 2062 (2012)
[8] K. Lenczewska, M. Stefanski, D. Hreniak, *J. Rare Earths*, **34,** 837–842 (2016)

Oral

Spectroscopic Analysis of Rare-Earth-ion (RE^{3+}) and Mn^{2+} ions in CdS Q-Dot bearing Silicate Glasses

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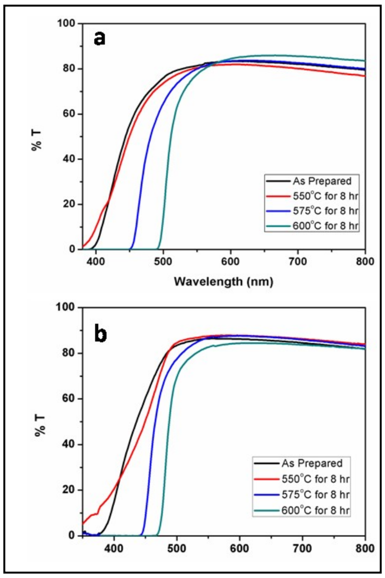
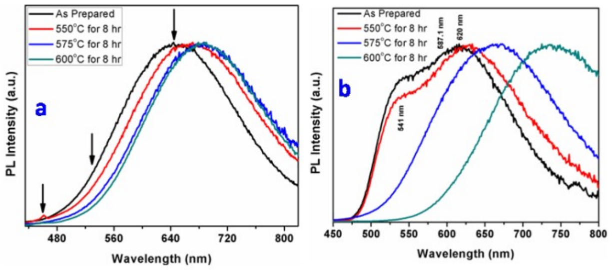
We have studied the effect of incorporation of Mn^{2+} and Tb^{3+} ions on the spectroscopic properties in CdS-QD containing silicate glasses. In this investigation, we have also compared the spectroscopic properties of the standard rare-earth doped glasses without CdS-QDs, for comparing and analysing the influence of local environment in CdS on the rare-earth and Mn^{2+}-ion dopants. The room temperature photoluminescence properties of dopant-CdS Q-dots interactions were investigated using UV-flash-lamp excitation and lifetime analysis. The influence of controlling the QD-structures in (Tb^{3+}:CdS) and (Mn^{2+}:CdS) via glass melting, quenching and annealing after casting is also discussed for controlling the absorption and fluorescence emission properties. The effects of heat treatment on the absorption and emission properties of CdS and Mn^{2+}-doped CdS, for example, are compared in Figures 1 and 2, respectively. The heat treatment induced colour changes correspond to the shift in the resonance bands, as shown in Figure 3.

The absorption and photo-luminescence studies were investigated for both the Mn^{2+} and Tb^{3+}-containing QD CdS and the results demonstrate the energy exchange mechanism amongst the RE^{3+}-ion and Mn^{2+}-ion states with CdS Q-dots. The Q-dot size analysis has also been performed from the X-ray powder diffraction, Bohr radius analysis, and analytical TEM technique.





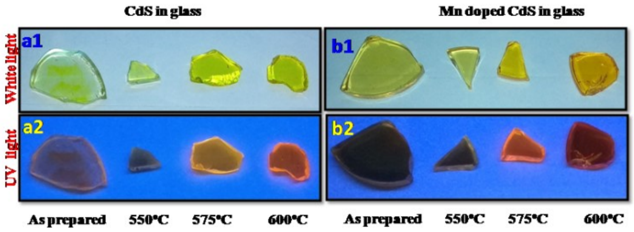


Figure 1: a) and b) compare the room-temperature absorption spectra of CdS and Mn^{2+}-doped CdS glasses. Figure 2: a) and b) are the room temperature photoluminescence spectra of CdS and Mn^{2+}-doped CdS glasses. Figure 3: a) and b) compare the colour changes in the as-cast and annealed glass samples at different temperatures

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New insights into the spectroscopic properties of Yb-doped YAG-derived all-glass optical fibers

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The high powers of light propagating along fiber in a variety of modern applications induces a plethora of parasitic nonlinearities that limit the continued scaling to higher powers. One route to combat these detrimental effects is to employ core glass compositions that exhibit intrinsically low nonlinearities. The molten core method (MCM) has proven particularly effective in realizing fibers from a wide range of materials [1] and has led to numerous insights into the connection between optical nonlinearities and glass structure and composition [2,3]. Of this new palette of optical fiber compositions, glasses derived from crystals are of particular interest. Such “crystal-derived” glasses originate from a precursor crystal, such as sapphire that is sleeved in a silica cladding tube and drawn into fiber. At the draw temperature of the fiber, the core melts and this liquid, which chemically interacts with the cladding composition, quenches into a glass as the fiber cools. The fibers derived from YAG (yttrium aluminum garnet, $Y_3Al_5O_{12}$) are particularly interesting [6] as they exhibit reductions in multiple nonlinearities, including about – 6dB in Brillouin gain coefficient [4] and – 3dB in Raman gain coefficient [5], relative to conventional silica fibers. They have further been shown to have potential as fiber laser and gain media [7] and also exhibit novel athermal Brillouin properties [8]. Perhaps most importantly, these fibers exhibit the lowest attenuation values yet achieved in molten-core fibers; typical values being on the order of 125 dB/km (0.125 dB/m) [6]. In this work, the properties of Yb-doped YAG-derived optical fibers is further studied. In particular, spectroscopic measurements in the UV spectral range are performed and compared with other commonly used Yb-doped silica fibers. Some of the most interesting findings are a relatively large shift of the charge-transfer (CT) band to shorter wavelengths (compared to conventional Yb/Al co-doped silica glass), reduced cooperative luminescence and a very high resistance to photodarkening. A model for the observed results will be presented and discussed.

Acknowledgements

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References

[1] J. Ballato and A. C. Peacock, *APL Photonics* **3**, 120903 (2018).
[2] J. Ballato and P. Dragic, *Journal of the American Ceramic Society* **96**, 2675 (2013).
[3] J. Ballato, M. Cavillon, and P. D. Dragic, *International Journal of Applied Glass Science* **9**, 263 (2018).
[4] P. Dragic, P.-C. Law, J. Ballato, et al, *Optics Express* **18**, 10055 (2010).
[5] P. Dragic and J. Ballato, *Electronics Letters* **49**, 895 (2013).
[6] J. Ballato, T. Hawkins, P. Foy, et al., *Journal of Applied Physics* **105**, 053110 (2009).
[7] P. Dragic, J. Ballato, T. Hawkins, et al. *Optical Materials* **34**, 1294 (2012).
[8] P. Dragic, M. Pamato, V. Iordache, et al., *New Journal of Physics* **18**, 015004 (2016).

Electrons and protons irradiation of Er^{3+}, Yb^{3+} codoped phosphate glasses Oral

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Er^{3+} doped glasses are of great interest due to their potential use in telecommunications, LIDAR, spectroscopy, and bioimaging, just to cite a few examples. However, recently, such materials have been found to be also useful for space applications. Therefore, in the last years, a special attention has been paid on the ionizing radiation induced effects in doped glasses used for fiber amplifiers, targeting their use in space missions. Phosphate glasses are of interest for the engineering of photonic devices, due to the following properties: easy processing, good thermal stability and excellent optical characteristics, such as high transparency in the UV, visible and near-IR region. Besides, phosphate glasses allow high rare earth (RE) ions solubility. Due to these properties, phosphate glasses have recently become appealing for space application.

In this presentation, we will report a study on the electrons and protons irradiation of Er^{3+}, Yb^{3+} codoped phosphate glasses with the composition (100-x) (0.5 P_2O5–0.4 SrO–0.1Na_2O)-xZnO-0.5Er_2O_3-1.5Yb_2O_3 (in mol%). We will explain first how the glasses were prepared and the impact of the progressive addition of ZnO on various glass properties. Then we will discuss the impact of irradiation with electrons and protons on the surface roughness as well as on the optical and the luminescence properties of these glasses. Finally, we will show that the electrons and protons radiation induced change is a reversible process and that these materials can be also considered for posible use in radiation monitoring.

Acknowledgements

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Oral

Drawing of glass containing rare-earth-doped oxide nanoparticles: A study by Molecular Dynamics simulations

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A new family of optical fiber lasers has been developed for few years, consisting in incorporating rare-earth (RE)-doped nanoparticles in silica matrix. Following this approach, D'Acapito *et al.* shown an improvement of the spectroscopic properties when Er^{3+} ions are embedded in Mg-silicate nanoparticles compared to a pure silica matrix [1]. Moreover, nanoparticles less than 50 nm are required to minimize light scattering induced losses. However, it is difficult to maintain the integrity of the small nanoparticles in the preform during the drawing process of such fibers. The idea is to take advantages of the drawing step to obtain small nanoparticles in the fiber starting from "big" nanoparticles in the preform. Using this approach, Blanc *et al.* [2] have observed elongation and break-up of nanoparticles during the drawing process of preforms already containing nanoparticles.

By means of Molecular Dynamics simulations, RE-doped nanoparticles are formed *in situ* through phase separation mechanism within MgO-SiO_2 binary melt using a simple adaptive interatomic potential [3]. Then, we reproduce the drawing process by heating and applying a uniaxial stress to study the influence of the drawing parameters on the size's distribution and on the morphology of the nanoparticles. The modifications of the structural and mechanical properties of the silica matrix under these drawing conditions are also studied.

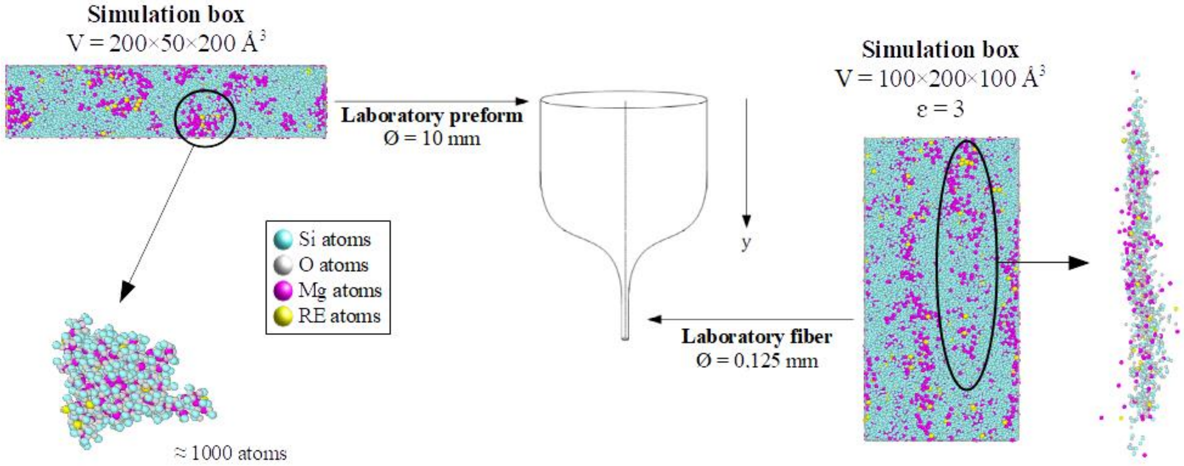

Figure 1: Numerical drawing process of a preform into a fiber. A nanoparticle is shown before and after the drawing step.

Acknowledgements

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References

[1] D'Acapito, F., Blanc, W., and Dussardier, B., *J. Non-Cryst. Solids*, **401**, 50-53 (2014).
[2] Vermillac M., Lupi J.F., Peters F., et al., *J Am Ceram Soc.*, **100**, 1814-1819 (2017).
[3] Bidault, X., Chaussedent, S., and Blanc, W., *J. Chem. Phys.*, **143**, 154501 (2015).

Dye-sensitized blue-to-UVB upconversion nanocrystals for phototherapy

Oral

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Phototherapy using narrowband UVB artificial light sources (λ=311-313 nm) is widely used to effectively treat skin diseases like psoriasis and erythema. [1] However, severe side effects can occur by the UVB exposure of healthy skin surrounding affected areas. [2] Here, we propose a new method based on a blue-to-UVB upconversion material, $NaYF_4:Ho^{3+},Gd^{3+}$ as an alternative and safer treatment in which UVB radiation is applied locally. Following the absorption of two blue photons around 447 nm by Ho^{3+} and cross-relaxation between neighboring Ho^{3+} ions, a highly excited Ho^{3+} ion resonantly transfers its energy to a nearby Gd^{3+} ion, which emits narrow UVB emission at 311 nm. The concentrations of Ho^{3+} and Gd^{3+} were optimized and found to be ~ 1% and 25%, respectively. Energy transfer mechanisms for upconversion were investigated by additionally exciting the green-/red-emitting states of Ho^{3+}, by power-dependent blue-to-UVB upconversion (UC), and by analysing decay curves of UV UC emission of both Ho^{3+} and Gd^{3+} as a function of Ho^{3+} concentration.

Absorption for the parity forbidden intra-$4f^{10}$ Ho^{3+} transitions is weak. To enhance the UV upconversion emission intensity, dye molecules with strong blue absorption were designed and synthesized to serve as antennas after binding with $NaYF_4:Ho^{3+},Gd^{3+}$ nanoparticles (NPs). By employing a direct binding procedure, we succeeded in obtaining various systems of PPA2 dyes bound to $NaYF_4:x\%Ho^{3+},25\%Gd^{3+}$ NPs. NPs with PPA2 dyes excited at ~430 nm show blue-to-UVB UC with a 10-100 times higher UC emission intensity compared to bare $NaYF_4:Ho^{3+},Gd^{3+}$ NPs. Optimization of concentrations showed that NPs with about $10\%Ho^{3+}$ yield the strongest UVB UC intensity. This observation serves as proof for dye binding. Dye-sensitized upconversion involves strong absorption of blue light by the PPA2 dye 'antenna' followed by energy transfer to Ho^{3+}, upconversion by energy transfer between excited Ho^{3+} neighbours and energy transfer from Ho^{3+} to Gd^{3+}. Further proof for dye-Ho^{3+} ET was provided by the reduced lifetime of PPA2 emission after binding, and the similarity of the excitation band monitoring Gd^{3+} UVB UC emission to the absorption spectrum of PPA2 dyes. Blue-to-UVB upconversion is a novel field of research. The encouraging results obtained for the Ho^{3+}-Gd^{3+} couple will be further investigated and optimized to realize safer therapy for skin diseases relying on blue LEDs and suitable for home treatment.

Acknowledgements

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References

[1] M. Berneburn, M. Röcken and F. Benedix, *Acta Derm. Venereol.*, **85,** 98 (2005).

[2] V. Mysore, *Indian J Dermatol Venereol Leprol*, **75,** 119 (2009).

Rare-Earth codoped nanocrystals Cr^{3+},RE^{3+}:$ZnGa_2O_4$ for bioimaging applications

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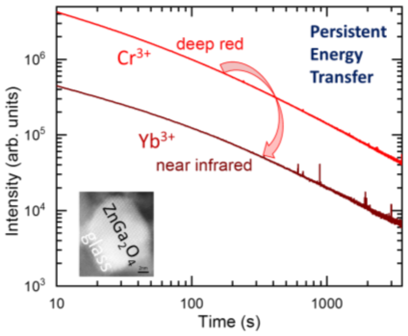
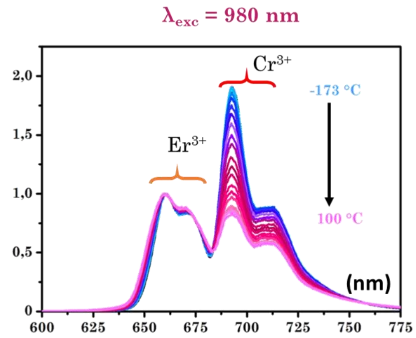
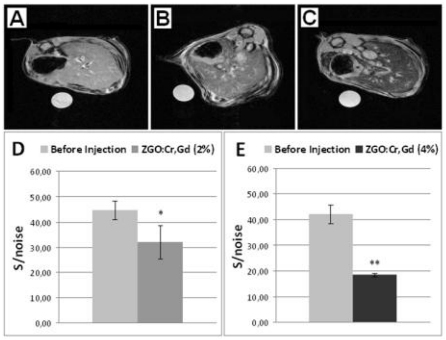
Chromium doped $ZnGa_2O_4$ nanomaterials have been investigated for bio-imaging applications in the recent years [1]. Introduction of rare-earth (*RE*) cations in the spinel host is indeed possible for the smallest *RE* cations. This opens the path to new applications and new energy transfer schemes. Cr^{3+},RE^{3+}:$ZnGa_2O_4$ (ZGO) nanoparticles are synthesized by soft chemistry or could be embedded in glass for the investigation of their optical properties, then further characterized by X-ray diffraction, transmission electron microscopy, EPR and optical spectroscopies. Doped with Yb^{3+} this gives access to persistent luminescence in two biological windows (namely deep red and NIR windows) as seen figure 1-A. Codoped with Yb/Er, upconversion mechanisms allow both excitation and emission in the biological tissues transparency window and nanothermometry measurements (see figure 1-B). The photoluminescence and fluorescence decays versus temperature are studied in a large temperature range in order to investigate the ability of the host to be a temperature sensor. This kind of nanoprobes could allow a local temperature measurement for various applications such as temperature control during hyperthermia treatments. Furthermore, with Gd^{3+}, bimodal ie. optical and magnetic imaging as seen Fig. 1-C can be obtained [3].



1-A : Deep red and NIR persistent luminescence in ZGO:Cr/Yb nanoparticles



1-B: Variation of the emission of ZGO:Cr/Yb/Er nanoparticles with temperature



1-C: Example of MRI images with ZGO:Cr/Gd nanoparticles for bimodal (optical/magnetic) imaging purpose

Acknowledgements

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References

[1] J. Liu, T. Lecuyer, J. Seguin, B. Viana, C. Richard; *Adv. Drug Delivery Reviews*, 138, 193 **(2019)**
[2] E. Glais PhD Thesis Sorbonne University, October (**2018)**
[3] T Maldiney, BT Doan, D Alloyeau, M Bessodes, D. Scherman, C. Richard, *Adv. Functional Materials* 25 (2), 331-338 **(2015)**

Up-conversion luminescence of nanoparticles sensitized by Nd^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+} ions

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Up-conversion (UC) luminescence of nanoparticles (NPs) is a subject of intense studies from the beginning of the XXI century. Receiving luminescence under excitation with near-infrared (NIR) light in the ultraviolet and visible range allowed for numerous applications of materials showing such properties, e.g. in optoelectronics, lightening, security markers or solar cells.[1] However, the most of on-going research in the field of UC is devoted to biomedical applications, as the unique property of achieving luminescence under NIR light can be utilized in bioimaging and therapies, e.g. photodynamic therapy or photo-triggered drug release.[2] Analytical assays and tests, as well as temperature sensors, are other examples of the use of UC.[3–4]
The phenomenon of UC is the most efficient in inorganic materials doped with lanthanide (Ln^{3+}) ions. The most frequently investigated systems are these based on sensitization via Yb^{3+} ions at around 975 nm. The absorbed by Yb^{3+} ions excitation energy can be transferred to other Ln^{3+} ions, such as Ho^{3+}, Er^{3+} or Tm^{3+}, resulting in the emission of visible light. However, excitation by 975 nm light, has some limitations, especially in nanomedicine, where irradiation may lead to heating and damage of tissue. To avoid harmful effects of excitation light the alternative NPs, based on Nd^{3+} absorption have been developed. In such materials, a good match of Nd^{3+} absorption at around 808 nm with biological tissue transparency, allow for better penetration of excitation light and low autofluorescence.
In our studies, we are focused on UC luminescence under excitation at 808, 1208 and 1532 nm. The selected excitation wavelengths, cover with biological transparency windows, i.e. first 700-950 nm (NIR-I), second (NIR-II) 1000-1350 nm and third 1500-1850 nm (NIR-III). To achieve emission under above-mentioned wavelengths, the properties of Nd^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+} ions were utilized. These ions are capable of UC luminescence via ground/excited state absorption (GSA/ESA) or can transfer absorbed energy to another Ln^{3+} ion through energy transfer up-conversion process (ETU).
To obtain UCNPs, showing luminescence under 808, 1208 or 1532 nm, two fluorides were tested as host compounds: SrF_2 and $NaYF_4$, and hydrothermal or precipitation in high-boiling solvents methods for their synthesis. Additionally, core/shell NPs, based on $NaYF_4:Ln(1)^{3+}@NaYF_4:Ln(2)^{3+}$ structure were synthesized, allowing for avoiding cross-relaxation between Ln^{3+} ions a multi-mode excitation. Development of new NPs, excitable under 808, 1208 or 1532 nm wavelengths is important not only because of biological applications but also for the production of efficient converters of energy, useful e.g. in solar cells production.

Acknowledgments

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References

[1] J. Zhou, Q. Liu, W. Feng, Y. Sun and F. Li, *Chem. Rev.*, **115**, 395–465 (2015)
[2] M. R. Hamblin, *Dalt. Trans.*, **47**, 8571–8580 (2018)
[3] H. H. Gorris and U. Resch-Genger, *Anal. Bioanal. Chem.*, **409**, 5875–5890 (2017)
[4] P. Cortelletti, A. Skripka, C. Facciotti, M. Pedroni, et al., *Nanoscale*, **10**, 2568–2576 (2018).

Optimization of Er^{3+} induced intense green emission in calcium aluminozincate phosphor for display devices

Oral

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Rare earth (RE) ions have attained profound attention of researchers owing to their unique characteristics attributed to f-f transitions. RE ions doped in inorganic hosts exhibit utility in display devices such as white light emitting diodes (wLEDs) and lasers [1,2]. Calcium aluminozincate phosphors activated with Er^{3+} ions were prepared using citrate sol-gel method. The X-ray diffraction (XRD) patterns reveal monophasic orthorhombic structure for the as prepared phosphors without any influence of doping on the structure of calcium aluminozincate phosphor. The scanning electron microscope (SEM) was employed to record the micrograph of calcium aluminozincate phosphor. The photoluminescence (PL) analysis delineate the intense emission of the as prepared phosphors in green regime of visible spectrum recorded under 377 nm excitation wavelength at room temperature. The concentration optimization of Er^{3+} ions in the host is achieved by analysing the PL spectra. The PL decay measurements describes lifetime of the order of microsecond which tend to decrease with increase in the concentration of Er^{3+} in the host. The energy transfer mechanism studied, and CIE coordinates were evaluated for the as prepared phosphors using visible emission spectrum. These results dictate the use of as prepared phosphors as green component in display devices.

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References

[1] L. Li, H.Y. Wu, *J. Alloys Compd,.* **702,** 106–119 (2017).

[2] P. Du, J.S. Yu, *J. Lumin.,* **203,** 172–178 (2018).

Spectroscopic investigation of the $YV_xAs_{1-x}O_4$ doped with Tb^{3+} ions

Oral

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Keywords: phosphor, Tb^{3+} ions doping, quenching, yttrium orthooxides

From the beginning of phosphor research history, up to the present time, we still do not know how to efficiently search for novel phosphors with superior spectroscopic properties. Development of phosphor with desirable properties reminds more roaming around instead heading straight to the target. This situation takes place because we still do not know how some factors ie: how crystal structure impact on material spectroscopic properties[1,2].

In the last decade, it has been observed a wide investigation of YVO_4 doped with rare earth ions. In the case of Tb^{3+} ions doped YVO_4, there has not be observed the emission from dopant ions[3,4]. To determine quenching mechanism between the Tb^{3+} and V^{5+} ions, the As^{5+} ion has been doped the YVO_4 matrix leading to obtaining the mixed $YV_xAs_{1-x}O_4$ matrix. The doping with the As^{5+} ions has allowed a determination of maximum concentration of the V^{5+} ions to be involved in quenching process.

In our case the main attention has been paid on Tb^{3+} and V^{5+} ions interactions and a maximum value of the V^{5+} ions quenching the Tb^{3+} ions to be found. An effort has been devoted to synthesize via co-precipitation method a series of nanosized $YV_xAs_{1-x}O_4$ doped with1 mol% Tb^{3+} ions. The spectroscopic properties of the obtained materials have been studied. Additionally, morphology and structural properties have been investigated related to optically active ion in the host lattice.

References

[1] R. J. Wiglusz, A. Bednarkiewicz, and W. Strek *Inorg. Chem*. **51** (2012) 1180.
[2] T. Grzyb, R.J. Wiglusz, A. Gruszeczka and S. Lis, *Dalton Trans.* **43** (2014) 17255.
[3] E.F. Gibbons, R.G. DeLosh, P.J. Zacmanidis, H.L. Stadler, T.Y. Tien, J. Chem. Phys. 53 (2004) 681–685.
[4] L. Yang, S. Peng, M. Zhao, L. Yu, Opt. Mater. Express. 8 (2018) 3805.

Oral

Highly-transparent efficient sol–gel-derived silica–(Gd,Pr)PO_4 glass-ceramic narrow-band UVB phosphors

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Sol−gel method is a wet-chemical process and the low processing temperature would be suitable for preparing glasses with unique nanostructures. However, fracture during drying and sintering interferes the formation of monolithic dried gels and glasses. We have developed a method to form macroporous dried gels suitable as precursors of monolithic silica glasses from a tetraethoxysilane−water binary system without using organic additives including cosolvents (alcohols), organic solvents, and polymers. Macropores in the resultant wet gels facilitate both of drying and sintering, and diminish the processing time of fully densified glasses [1,2]. We found that rare-earth (RE) and phosphorus codoped glasses prepared based on the method [3] are highly-transparent glass-ceramics containing $REPO_4$ nanocrystals as small as ~5–10 nm [4,5]. Because of the small crystal size optical loss due to Rayleigh scattering is negligible, as typically seen from the optical absorption spectra of silica−(Gd,Pr)PO_4 glass-ceramics shown in Figure 1 (left). Figure 1 (right) summarizes the quantum efficiencies of photoluminescence at ~313 nm from the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} ions. Although the glasses contain SiOH groups as much as ~1–3×10^{20} cm^{-3}, the internal quantum efficiency of emission under excitation at 220 nm was close to unity at the fraction of Pr^{3+} ions (z_{Pr}/z_{RE}) less than ~0.1, demonstrating that the silica−(Gd,Pr)PO_4 glass-ceramics are efficient narrow-band UVB phosphors [6].

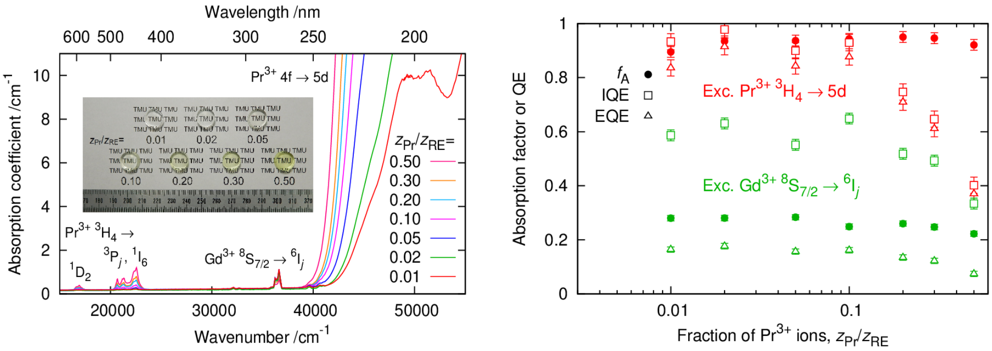

Figure 1: (left) Appearance and optical absorption spectra of silica–(Gd,Pr)PO_4 glass-ceramics prepared at various fractions of Pr^{3+} ions, z_{Pr}/z_{RE}. (right) Absorption factor, f_A, internal quantum efficiency, IQE, and external quantum efficiency, EQE, of photoluminescence at ~313 nm from the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} ions in silica–(Gd,Pr)PO_4 glass-ceramics under excitation via the $^8S_{7/2} \rightarrow {}^6I_j$ transition of Gd^{3+} ions at 275 nm or the $^3H_4 \rightarrow$ 5d transition of Pr^{3+} ions at 220 nm.

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References

[1] K. Kajihara, *J. Asian Ceram. Soc.*, **1**, 121–133 (2013)
[2] K. Kajihara, M. Hirano, H. Hosono, *Chem. Commun.*, 2580–2582 (2009)
[3] K. Kajihara, S. Kuwatani, K. Kanamura, *Appl. Phys. Express*, **5**, 012601 (2012)
[4] K. Kajihara, S. Yamaguchi, K. Kaneko, K. Kanamura, *RSC Adv.*, **4**, 26692–26696 (2014)
[5] S. Yamaguchi, K. Moriyama, K. Kajihara, K. Kanamura, *J. Mater. Chem. C*, **3**, 9894–9901 (2015)
[6] M. Suda, R. Nakagawa, K. Kanamura, K. Kajihara, *Dalton Trans.*, **47**, 12085–12091 (2018)

Optical properties of novel nitridic and oxidic phosphors doped with Eu^{2+}

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Among divalent lanthanides Eu^{2+} is the most frequent investigated ion, due to its relative high stability as well as the variability of the position of the states leading to different emission colors in the UV/Vis range. For some materials very intense 5d-4f emission bands due to the parity-allowed nature of the transitions are observed. By changing the composition of the host lattice and hence the local environment of Eu^{2+} it is possible to modify the emission color. Therefore Eu^{2+} is well investigated in several inorganic hosts as bulk [1, 2] and as nanoscale phosphor [3]. However, there is still a lack of studies for alkaline-earth nitridoborate halides and oxyhalides, although it can be assumed, that the emission and excitation bands are located at low energy, which is important for applications in LEDs.

In this work we present $Ca_2(BN_2)Cl$ doped with Eu^{2+} ions for the first time. The synthesis was performed using Ca_3N_2, BN and $CaCl_2$ and $EuCl_2$ in a tantalum container at 1000°C. The emission band is located in the red range peaking at 643 nm. The low lying excitation spectrum shows that excitation even at 500 nm is possible. Therefore, $Ca_2(BN_2)Cl:Eu^{2+}$ is a promising candidate for future energy saving LEDs.

Moreover, we investigated $Ca_4OCl_6:Eu^{2+}$ prepared from CaO and $CaCl_2$ in tantalum container at 600°C. Again, $EuCl_2$ was used for direct doping. In this case, an emission band in the blue range peaking at 470 nm is located. The excitation spectrum shows a structured band, which can be assigned to $4f^7 \rightarrow 4f^6\ (^7F_J)\ 5d^1$ transitions. The redshifted emission of $Ca_2(BN_2)Cl:Eu^{2+}$ in comparison to $Ca_4OCl_6:Eu^{2+}$ can be attributed mainly by the increasing covalence due to the nephelauxetic effect (Fig. 1).

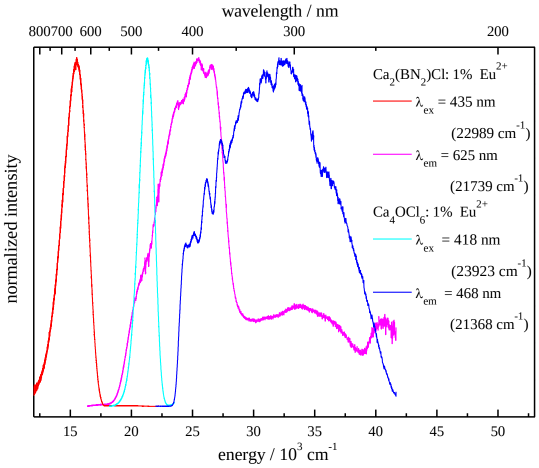

Figure 1: Emission- and excitation spectra of $Ca_2(BN_2)Cl{:}1\%\ Eu^{2+}$ and $Ca_4OCl_6{:}1\%\ Eu^{2+}$ at T = 10 K

References

[1] P. Dorenbos, *J. Lumin.*, **104**, 239-260 (2003)
[2] M. Suta, C. Wickleder, *J. Lumin.*, **210**, 210-238 (2019)
[3] H. Terraschke, C. Wickleder, *Chem. Rev.*, **115**, 11352-11378 (2015)

Oral

Effect of post-preparation annealing on powder and pulsed laser deposited thin film phosphors of oxyorthosilicate doped with rare-earths

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The effect of post-annealing atmospheres (air and Ar-H_2) on the optical properties of $La_{2-x}Y_xSiO_5$ (x = 0, 0.5, 1, 1.5 and 2) co-doped with $_{0.25}Pr^{3+}$ and $_{0.25}Dy^{3+}$ and $La_{2-x}Gd_xSiO_5{:}Dy^{3+}$ powder and pulsed laser deposited thin film phosphors were studied. The X-ray diffraction patterns showed that the as-prepared samples have higher full width at half maximum (FWHM) than the annealed samples. The elemental composition, oxidation states, and chemical and electronic states of the phosphors were determined using the X-ray photoelectron spectroscopy. The band gap values determined from the diffuse reflectance spectra were shown to increase following the post-annealing treatments (with the values increasing in the following manner: Ar-H_2-annealed > air-annealed > as-prepared). The photoluminescence intensities of the phosphors also followed the same trend as the band gap values. Two different cases of the photoluminescence mechanisms were proposed for the $La_{2-x}Y_xSiO_5{:}_{0.25}Pr^{3+},_{0.25}Dy^{3+}$ phosphors. Case 1: The 4f5d energy level of Pr^{3+} lies within the band gap of the host and energy transfer was observed from Pr^{3+} to Dy^{3+} via the overlapping 4f5d emission peak of Pr^{3+} and the $^4I_{15/2}$ excitation peak of Dy^{3+}. Case II: The 4f5d energy level of Pr^{3+} lies close or inside the conduction band of the host and the energy transfer was not observed from Pr^{3+} to Dy^{3+}. The CIE colour coordinates of the phosphors showed tunable emission colours (blue, red and white).

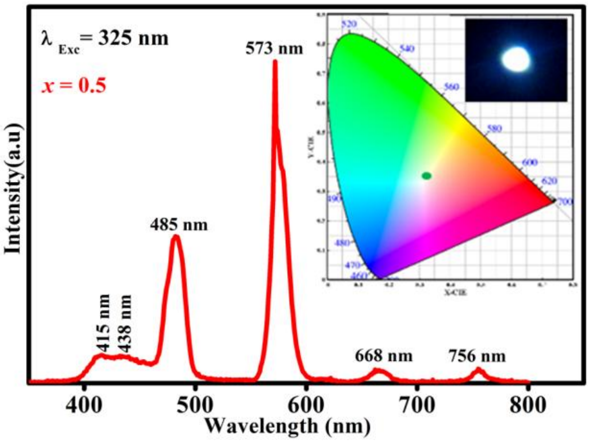

Figure 1: PL emission spectra of the $La_{2-x}Gd_xSiO_5{:}Dy^{3+}$ phosphor. The insets are the CIE colour coordinates and the real-time snapshot of the white light emission from the phosphor

Synthesis of orange emitting Sm^{3+} doped sodium calcium silicate phosphor by sol-gel method for photonic device applications

Oral

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Abstract

Samarium (Sm^{3+}) doped sodium calcium silicate (NCS) phosphors were prepared by employing sol-gel technique with varying Sm^{3+} concentrations. The crystal structure, morphology, dopant concentration dependent excitation and emission spectra were investigated for the as prepared phosphors. The purity in forming single phase NCS phosphor with cubic structure was confirmed by X-ray diffraction (XRD) pattern. The scanning electron microscopic images revealed irregular morphology with an average particle size in micrometre range. The excitation spectra of Sm^{3+} doped NCS phosphors disclose strong absorption in the UV (ultraviolet), n-UV (near UV) and blue spectral region. Based on the excitation spectrum, the emission spectral measurements were carried out at 402 nm excitation wavelength in the visible region for the Sm^{3+} doped NCS phosphors. The emission spectra under 402 nm excitation exhibit characteristic peaks at 565, 602 and 649 nm attributed to 4f-4f transitions of Sm^{3+} ions [1-2]. The Sm^{3+} concentration was optimized for NCS host as 1.0 mol%, and concentration quenching phenomenon was discussed. The chromaticity coordinates for the optimized NCS: Sm^{3+} phosphor were found to exist in the pure orange region. Above mentioned results substantiate the potentiality of Sm^{3+} doped NCS phosphor as an orange emitting component in photonic devices.

References

[1] A. K. Vishwakarma, M. Jayasimhadri, *J. Lumin.*, **176** 112-117 (2016).

[2] X. Shi, Y. Liu, J. Zhang, K. Zhang, P. Li, H. Zuo, J. Li, *Ceram. Int.*, **41** 3162-3168 (2015).

Luminescence performance of Eu^{3+} ions doped Alkaline-Earth Boro Tellurite glasses

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Luminescence performance of Alkaline-Earth Boro Tellurite (AEBT) glasses containing Eu^{3+} ions has been studied. Absorption spectra of Eu^{3+} doped AEBT glasses have been utilized to find out the bonding nature between Eu^{3+} ions and their surrounding ligands by calculating the bonding parameters (δ). Emission spectra of these glasses show characteristic emission of Eu^{3+} ion with an intense and most prominent red emission (613 nm) which is attributed to ${}^5D_0 \rightarrow {}^7F_2$ transition. Judd-Ofelt (Ω_2, Ω_4) parameters have been evaluated from the luminescence intensity ratios of ${}^5D_0 \rightarrow {}^7F_J$ (where J = 2 and 4) to ${}^5D_0 \rightarrow {}^7F_1$ transition as well as absorption spectra under different constraints [1-2] . Using Photoluminescence decay spectra, the experimental lifetimes (τ_{exp}) were evaluated and combined with radiative lifetimes (τ_R) to determine quantum efficiencies (η) of the titled glasses. Emission spectral data of the titled glasses were used to deduce the CIE chromaticity coordinates. The CIE chromaticity coordinates of the titled glasses indicate that the actual emission of the glasses is in red region. The higher values of the stimulated emission cross-sections and quantum efficiencies suggest that the AEBT glass doped with 1.0 mol % of Eu^{3+} ions is quite suitable for designing intense red emitting luminescent devices at 613 nm wavelength corresponding to ${}^5D_0 \rightarrow {}^7F_2$ transition.

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References

1. B.R. Judd, Phys. Rev. ,127, 750-761 (1962)
2. G.S. Ofelt, the Journal of Chemical Physics, 37, 511-520 (1962)

Oral

Up-conversion luminescence of erbium ion in sodium-germanate glasses

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The system of Er^{3+} ions containing germanate glass have steady structure, and the weak ionicity and lower phonon energy lead to higher Er^{3+} emission quantum efficiency and less non-radiative losses in luminescence. Furthermore, significant enhancement of the intensity of up-conversion emission in the visible range can be observed. The thermal stability of glasses is also improved simultaneously. The up-conversion enjoy potentially apply probability in many areas, such as optoelectronics, color display, and medical diagnostics, it is worth to pay attention to the mechanism of up-conversion emission in Er^{3+}-Yb^{3+} co-doped germanate glasses.

Multi-component Er^{3+}-Yb^{3+} co-doped germanate glass $49GeO_2{-}13Na_2O{-}27Yb_2O_3{-}11La_2O_3{-}0.25Er_2O_3$ have been studied to analyze the mechanism of up-conversion emission and thermal sensitivity. In addition, the germanate glass was added with 5 mol% oxide materials, such as BaO, PbO, Al_2O_3, Nb_2O_5, SiO_2, MgO, P_2O_5 and TiO_2, to study the effect of these additives in the germanate glassy matrix. The dominant mechanism for green up-conversion emission transitions is ESA, and red up-conversion emission is mainly due to ETU mechanism. Most intense red emission was observed on initial germanate glass. Additive Nb_2O_5 increase the relative intensity ratio of green and red emission. Compare with original germanate glass, the up-conversion emission spectrum of glass P_2O_5 show redistribution of the relative intensity of red and green up-conversion emissions. Furthermore, the Judd-Ofelt (JO) parameters, line strength and radiative properties of germanate glasses were analyzed by Judd-Ofelt theory. JO analysis gives positive relationship between the JO parameters Ω_t with red and green emissions. Higher parameter Ω_6 implies more green emission and the redder emission, the larger values of parameter Ω_4. The obtained relationship $\Omega_2 > \Omega_4 > \Omega_6$ also give a good explanation about why the red emission of the studied germanate glasses is stronger than green emission. Hypersensitive transitions $^4I_{15/2} \rightarrow {}^4G_{11/2}$ show sensitivity with the change of rare earth ligand field and covalence bond Er-O. Spontaneous radiative probability, the branching ratio and the radiative lifetime were derived from the experimental absorption spectrum and JO analysis. High value of branching ratio for emission transitions $^4F_{9/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ also show good possibility to obtain the efficient red and green emission transition.

Raman spectrum was used to give probable structural reasons behind the different behavior of the studied germanate glasses. The loose structure of germanate glass that found by introduced with P_2O_5 explain the reason that the relative intensity ratio of green and red in up-conversion emission spectrum inverse with initial germanate glass. Interesting found for additive Nb_2O_5 in Raman spectrum show no change of the network forming with single mixed grid with tetrahedrons [GeO_4] when compared with original germanate glass. Multi-center structures were observed for glasses PbO, MgO, Al_2O_3 and TiO_2. The spectra of the green up-conversion luminescence of the erbium ion were measured in the temperature range of 80–700 Kelvin. The maximum value of absolute thermal sensitivity S of 120×10^{-4} K^{-1} was obtained for the initial glass sample. These Er^{3+}-Yb^{3+} co-doped germanate glasses could be used as potential material for optical up-conversion device application

Radiative analysis of orange emitting silica borate glasses for photonic applications

Oral

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Samarium (Sm^{3+}) ions doped silica borate glasses prepared by well-known melt quench method studied for structural and luminescent characteristics. The amorphous nature of the as prepared glasses was confirmed from X-ray Diffraction (XRD) pattern. The Fourier Transform-Infrared (FT-IR) Spectroscopy was used to identify various functional groups present in the as prepared glasses. The absorption, photoluminescence and lifetime spectral measurements were observed at room temperature. The excitation spectra recorded by monitoring 600nm emission wavelength exhibit various excitation bands in UV and blue region with highest excitation at 402nm. The emission spectra under 402nm excitation wavelength exhibits emission at 600 nm attributed to the transition from excited state ($^4G_{5/2}$) to ground state ($^6H_{7/2}$). The optimized concentration of Sm^{3+} ions is identified as 1.0 mol% of Sm^{3+} ions in silica borate glasses. The CIE chromaticity coordinates and correlated color temperature (CCT) were evaluated to understand the utility of the titled glasses in white light generation. The decay curves recorded for the as prepared glasses shows bi-exponential behaviour. All these results indicate the potentiality of Sm^{3+} doped silica borate glasses as red component in white light generation and are useful in designing white light emitting diodes (w-LEDs) and devices [1,2].

Acknowledgement

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References

[1] F. Steudel, S. Loos, B. Ahrens, S. Schweizer, *J. Lumin.*, **170,** 770–777 (2016).

[2] K. Swapna, S. Mahamuda, A. Srinivasa Rao, M. Jayasimhadri, T. Sasikala, L. Rama Moorthy, *Ceram. Int.,* **39**, 8459–8465 (2013).

Er^{3+} / Yb^{3+} doped 1-D Microcavity based on alternating aluminosilicate glass and titania sol-gel layers for visible emission and efficient up-conversion

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Conventional energy sources have severe drawbacks in terms of environmental pollution and limited availability. Therefore, the solar energy market has been growing quickly in the last decades, but one of the challenges is to increase the efficiency of solar photovoltaic technologies. Different paths have been followed, including the matching of the solar spectrum with the solar cell spectral efficiency through down-conversion and up-conversion (UC) processes. In particular, UC is a promising route to solve the transparency losses of sub-bandgap photons [1]. While Ln-doped luminescent layers may be deposited by methods like CVD or PVD, sol-gel (SG) processing is a low-cost technology, which can be a versatile and scalable alternative. This technique has the added advantage that it can easily be coupled with the deposition of multilayered 1-D photonic crystal (PC) structures like Bragg Mirrors (BMs) and microcavities (MCs) in order to integrate the spectral conversion function into a more efficient photonic structure. In the present work, we report the synthesis of a a potential demonstrator in the form of a 1-D photonic crystal (PC) microcavity (MC), with the aim of tailoring the emission of an aluminosilicate glass film co-doped with Er^{3+}/Yb^{3+}, sandwiched between alternating layers of undoped aluminosilicate glass and TiO_2. For the fabrication of the MC, a careful control of their thickness and refractive index were carried out, in order to mimic the MC structure obtained by computer simulation for a pre-defined position of the active pass band defect (547 nm) within the stop band of the cavity. An enhancement of up to 13 times of the Er^{3+} green up-conversion (UC) emission, excited at 975 nm, was observed for a MC when compared with the same doped material without the PC structure.

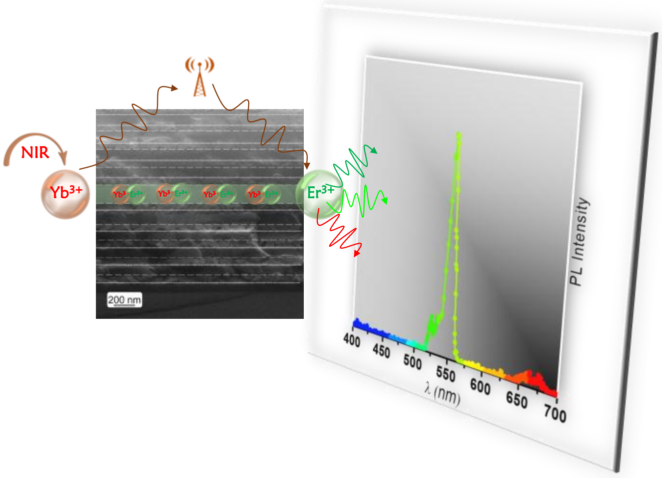

Figure 1: FEG-SEM micrographs of MC structure. The defect layer is highlighted in green. Only the aluminosilicate defect layers are doped with Er/ Yb. The Er /Yb UC PL for the MC structure, pumped with the 975 nm diode laser line, is plotted

References

[1] A. Chiasera, C. Meroni, F. Scotognella, Y.G. Boucher, G. Galzerano, A. Lukowiak, D. Ristic, G. Speranza, S. Valligatla, S. Varas, L. Zur, M. Ivanda, G.C. Righini, S. Taccheo, R. Ramponi, M. Ferrari, *Opt. Mater*. **87**. 107-111, 2019

Tb^{3+} and Sm^{3+} doped $Ga_5Ge_{20}Sb_{10}Se_{65}$ fibers long-wave IR luminescence around 8µm

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Rare earth (RE) doped chalcogenide applications in the mid-IR spectral domain are abundant in the fields of IR laser sources, amplifiers or fluorescence-based detection systems. These low phonon energy materials enable radiative transitions between RE low-lying manifolds like Pr^{3+}, Dy^{3+} or Tb^{3+} for instance. We present here the RE luminescence in the mid and long-wave infrared domains (MWIR and LWIR) of Sm^{3+} and Tb^{3+} ions in a selenide-based glass ($Ga_5Ge_{20}Sb_{10}Se_{65}$). 500 ppm and 1000 ppm Sm^{3+} and Tb^{3+} doped $Ga_5Ge_{20}Sb_{10}Se_{65}$ optical fibers of high purity and optical quality were elaborated from conventional methods. In Fig. 1(a), the Tb^{3+} 8 µm centered emission ($^7F_4 \rightarrow {}^7F_5$) is obtained following a 2 µm optical pumping [2] and will be discussed in details along with the careful removal of all mid-IR parasitic signals, which could be related to thermal noise or higher-order diffracted signals. Other infrared luminescence from the $^7F_4$ and $^7F_5$ manifolds at 3.1 µm ($^7F_4 \rightarrow {}^7F_6$) and 5 µm ($^7F_5 \rightarrow {}^7F_6$) are clearly observed and used to confirm the 8 µm emission from the $^7F_4$ level.
In Fig. 1(b), a LWIR emission band spanning from 6 to 9 µm with an emission peak at 7.3 µm is shown for Sm^{3+} doped $Ga_5Ge_{20}Sb_{10}Se_{65}$ fibers [1]. This emission is attributed to the $^6H_{13/2} \rightarrow {}^6H_{11/2}$ transition. This emission from the $^6H_{13/2}$ level is consistent with other IR emissions from the same level at 1.95 µm and 3.7 µm which will be also presented and discussed. A maximum LWIR intensity is obtained in a 1000 ppm Sm^{3+} doped and 100 mm long fiber, exhibiting a brighter LWIR luminescence than the 8 µm emission observed in Tb^{3+} doped $Ga_5Ge_{20}Sb_{10}Se_{65}$ fibers.

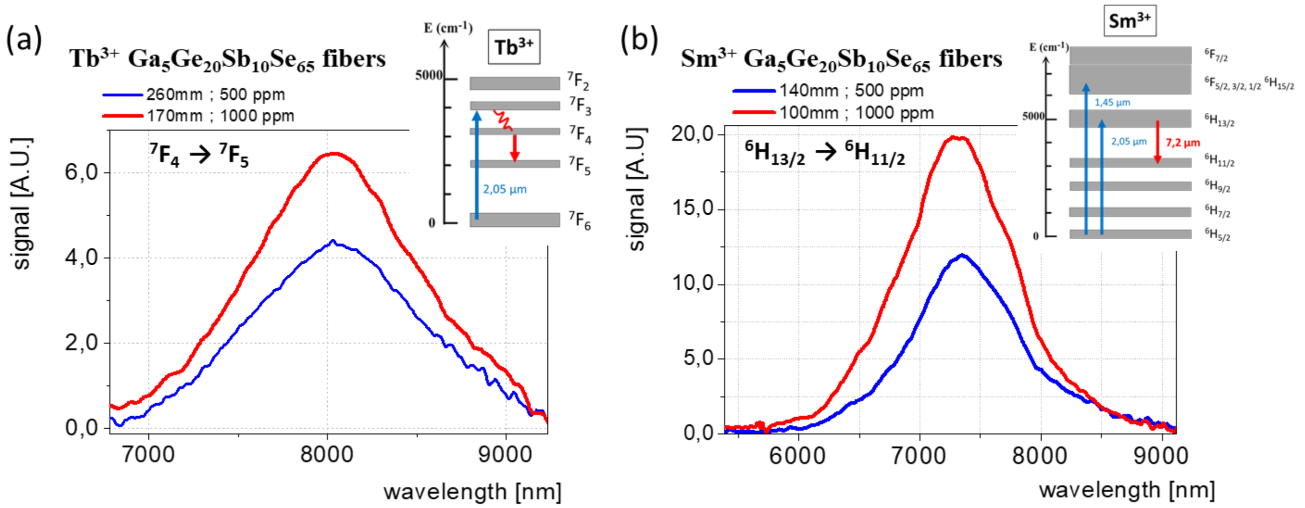

Figure 1: LWIR fiber luminescence of Sm^{3+} and Tb^{3+} doped $Ga_5Ge_{20}Sb_{10}Se_{65}$ fibers, near-IR optical pumping.

References

[1] F. Starecki, N. Abdellaoui, A. Braud, J.-L. Doualan, C. Boussard-Plédel, B. Bureau, P. Camy, and V. Nazabal, "8 µm luminescence from a Tb3+ GaGeSbSe fiber," Opt. Lett. **43**(6), 1211-1214 (2018).
[2] F. Starecki, A. Braud, N. Abdellaoui, J.-L. Doualan, C. Boussard-Plédel, B. Bureau, P. Camy, and V. Nazabal, "7 to 8 µm emission from Sm3+ doped selenide fibers," Opt. Express **26**(20), 26462-26469 (2018).

Fabrication, structural and spectroscopic characterizations of first translucent ceramics from cubic nano-crystalline La_2MoWO_9 activated by Nd^{3+} ions

Oral

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Nd^{3+}-doped mixed molybdato-tungstate powders of chemical formula La_2MoWO_9, which crystallize in the cubic system (space group $P2_13$ (No. 198)), were studied so that in further research they could serve to the fabrication of transparent optical ceramics. Previously, we reported first translucent micro-ceramics activated by Yb^{3+}ions. However, in these ceramics the segregation of the second phase on the grain boundary, containing much higher Yb^{3+} ion concentration than inside the grains was observed [1,2].

With Nd^{3+} ions we obtained much better results. Similar ionic radius of Nd^{3+} ion to La^{3+} one leads to receipt the mono-phase translucent micro-ceramics.

The purpose of these studies was to carry out a detailed structural analysis by XRD technique to confirm that in case of this chemical composition only one, pure cubic phase is observed, regardless of the Nd^{3+} activator concentration, which is a great advantage of this host lattice compared to the simple di-lanthanum di-molybdates. SEM technique confirmed very high homogeneity and phase purity of the obtained materials. The micro-crystalline solid solutions obtained by the high-temperature solid-state reaction characterized by an intense luminescence are useful for both detailed fundamental analysis and for application as efficient phosphors and ultra-short pulses (pico, femto) laser materials.

Both in nano/micro-crystalline molibdato-tungstates, and in first translucent ceramics a big structural disorder was observed. High-resolution techniques, such as absorption spectra at 4.2K, as well as low-temperature site selective laser spectroscopy confirmed a multisite character of Nd^{3+} ions in this host lattice.

Acknowledgements

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References:

[1] M. Bieza, M. Guzik, E. Tomaszewicz, Y. Guyot, K. Lebbou, E. Zych, and G.Boulon, *J. Phys. Chem. C,* 121, 3290−13302 (**2017**).
[2] M. Bieza, M. Guzik, E. Tomaszewicz, Y. Guyot, K. Lebbou, and G.Boulon, J. *Phys. Chem. C,* 121, 13303−13313 (2017).

Transparent oxyfluoride glass-ceramics prepared by Spark Plasma Sintering (SPS) for optical applications

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Oxyfluoride glass-ceramics (GCs) containing $KLaF_4$ nanocrystals doped with different concentrations of Nd^{3+} ions (0.1 and 0.5 mol%) were synthesized by combining melt quenching and spark plasma sintering. The base glass compositions of the system SiO_2-Al_2O_3-K_2O-Na_2O-LaF_3-NdF_3 (mol%.) were melted and the obtained glasses were milled and sieved with different particle sizes (40-100 µm) and <60 µm. Glass powder pellets were sintered by SPS under vacuum atmosphere optimizing temperature, pressure and holding time. A systematic study has been carried out to achieve final full densification and maximum transparency. Carbon contamination that comes from the employed dies in the SPS experiments was highly reduced by covering the die with platinum foil. The prepared oxyfluoride GCs exhibit excellent stability and are transparent in visible region. The $KLaF_4$ crystalline phase was identified by XRD and its nanometric size was confirmed by transmission electron microscopy. Optical properties of the glass and GCs have been investigated by measuring absorption, photoluminescence spectra and fluorescence lifetimes. Enhanced intensity and spectral change of GCs compared with the precursor glass confirmed the incorporation of Nd^{3+} ions in the crystalline phase. The photoluminescence results are comparable with those of transparent GCs obtained by a conventional route which requires comparably much longer treatment times. Selective excitation measurements allowed the luminescence response of the RE ions incorporated in the fluoride crystalline phase to be isolated.

Keywords: Transparent glass-ceramics; Spark plasma sintering; Optical materials

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References

[1] A. A. Cabral, R. Balda, J. Fernández, G. Gorni, J. J. Velázquez, L. Pascual, A. Durán, M. J. Pascual, *CrystEngComm*, **20**, 5760-5771 (2018).

[2] P. Riello, S. Bucella, L. Zamengo, U. Anselmi-Tamburini, R. Francini, S. Pietrantoni, Z.A. Munir. *Journal of the European Ceramic Society,* **26** 3301–3306 (2006).

[3] A. de Pablos-Martín, F. Muñoz, G. C. Mather, C. Patzig, S. Bhattacharyya, J. R. Jinschek, Th. Höche, A. Durán and M. J. Pascual. *CrystEngComm*, **15**, 10323-10332 (2013).

Chemical Characterization of LaF_3:Tm^{3+} Doped Phase-Separated Dielectric Nano-Particles (DNPs) via Secondary Ion Mass Spectrometry (SIMS) Imaging

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Rare-earth (RE) doped optical fibers are extensively used in lasers and optical amplifier devices. Among all the luminescent ions, thulium (Tm^{3+}) has demonstrated emissions in a 0.45 to 3.9 µm range in low phonon fluoride glasses. However, the high fabrication cost, poor reliability, difficulty to connect to silica-based fibers, and low resistance to heating are major impediments that limit utilization of fluoride glasses. Silica glasses, on the other hand, are one of the rare materials which can sustain operation at high optical power in fiber devices. Yet, silica glass propensity for favoring RE element clustering is detrimental to the development of devices with new wavelengths and high-power laser fibers. To overcome this limitation, one recent strategy consists of developing a fabrication method which triggers RE encapsulation in Phase-Separated Dielectric Nanoparticles (DNPs) [1]. However, the development of this approach depends on our ability to measure the composition at the nm-scale.

Here, we used the ZEISS ORION NanoFab, configured with a Secondary Ion Mass Spectrometer (SIMS) to characterize LaF_3:Tm^{3+}doped phase-separated DNPs in optical fiber cores. The ORION NanoFab is an ion microscope [2] that allows for high resolution secondary electron (SE) imaging with a He^+ ion beam that can be focused to a 0.5 nm probe size. The same instrument offers a Ne^+ ion beam with a focused probe size of 2 nm. Importantly, SIMS with neon provides elemental imaging with an unprecedented 15 nm spatial resolution [3,4]. The Si^+ and La^+ ion images obtained with this instrument clearly reveal a change in composition with the NPs size: the larger ones have elevated Lanthanum and low Silicon contents while the reverse is observed for the very small.

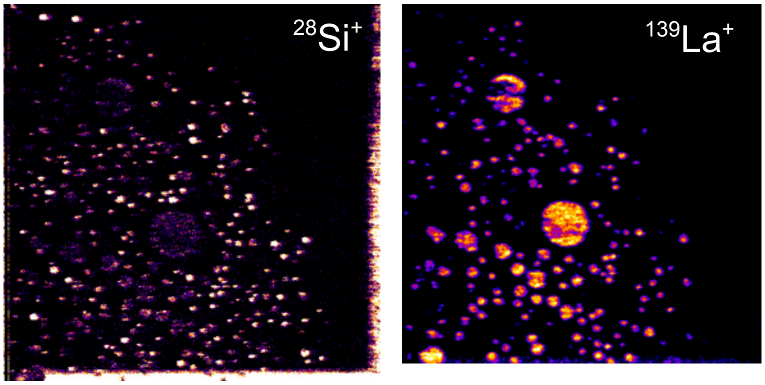

Figure 1: Si^+ and La^+ secondary ions images of an optical fiber's core doped with LaF_3:Tm^{3+} NPs. 6 µm field of view

References

[1] M. Vermillac *et al.*, *Optical Materials*, **68**, 24-28 (2017).
[2] B. W. Ward, J. A. Notte, N. P. Economou, *Journal of Vacuum Science & Technology,* **B24,** 287 (2006).
[3] D. Dowsett, T. Wirtz, *Analytical Chemistry,* **89,** 8957 (2017).
[4] S. Sijbrandij *et al.*, *Microscopy Today* **27.3**, 22-27 (2019).

Oral

Crystallization study of Er^{3+} doped glasses in $NaPO_3$-CaF_2-TiO_2/MgO/ZnO system

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Fluorophosphate glasses are known to have low phonon energies and wide optical transmission window from Ultraviolet (UV) to mid-IR regions which make them good glass candidates for Er^{3+} doping [1]. Transparent oxyfluoride glass–ceramics (GCs) possess lower phonon energy than oxide glasses and higher mechanical and chemical stability than fluoride glasses [2]. The precipitation of fluoride crystals can significantly improve the luminescence efficiency of the rare-earth ions due to the low phonon energy and the structure of the fluoride crystals if the crystals are doped with the rare-earth (RE) ions. Therefore, oxyfluoride GCs have been of great interest as fiber lasers and optical amplifiers [3].

In our previous study [4], we showed that the glass composition in the system (75 $NaPO_3$-(25-x) CaO-5CaF_2) (in mol%) had an impact on the diffusion mechanism of Er^{3+} ions during heat treatment. The heat treatment of the glass with x=25 led to transparent glass-ceramic with the precipitation of CaF_2 crystals doped with Er^{3+} ions. However, this glass had a poor glass stability preventing us to drawn it into fibers.

In our current study, new glasses with the composition (100-x-0.25) (75 $NaPO_3$-25 CaF_2) - x (TiO_2/ZnO/MgO), doped with 0.25mol% Er_2O_3, with x=0 and x=1.5 were prepared in order to increase the thermal stability of the glass without modifying the nucleation and growth properties of the glass. In this presentation, the effect of the glass composition and crystallization on the spectroscopic properties of the newly developed glasses will be presented. We will explain how to prepare the glass-ceramics from the as-prepared glasses using controlled heat-treatment. A complete study of the nucleation and growth will be reported such as the activation energy associated with the crystallization peak, the Johnson–Mehl–Avrami (JMA) exponent of the glasses which was calculated using the equation proposed by Augis and Bennet and later verified by the method proposed by Ozawa to determine the dimensionality of the crystallization. We will also present the crystal growth rate for these glasses which is used in order to control the growth of the crystals in the glass. We will confirm that the changes in the glass composition has no impact on the crystallization: crystallization in the new glasses still occurs in the bulk with the precipitation of CaF_2 crystals doped with Er^{3+}. We will show that the addition of TiO_2, ZnO and MgO increases slightly the thermal stability of the glasses while increasing the crystallization tendency of the glasses.

Acknowledgements

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References

[1] S.E. Stokowski, W.E. Martin, S.M. Yarema, J. Non-Cryst. Solids 40 (1980) 481–487
[2] B. Karmakar, P. Kundu, R.N. Dwivedi,, Mater. Lett. 57 (2002) 953–958
[3] M.C Goncalves, L.F Santos, R.M Almeida, C.R. Chim. 5 (2002) 845-854
[4] A. Nommeots-Nomm, .N.G. Boetti, T. Salminen, J. Massera, M. Hokka,, L. Petit, J. Alloys and Comp 751 (2018) 224-230

Characterization of Ce^{3+} or Pr^{3+}- single doped type III $KGd(PO_3)_4$ bulk crystals as scintillator materials

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Scintillator materials are widely used for a variety of applications such as high energy physics, astrophysics and medical imaging. Novel research is focused on finding new scintillator materials with alternative properties that suit the different needs of each application. Here, Ce^{3+} or Pr^{3+}- single doped $KGd(PO_3)_4$ bulk crystals with $P2_1$ monoclinic structure are grown from high temperature solutions and their optical properties are studied as a new candidates for scintillation material. These polyphosphate crystals are interesting due to their wide optical transparency window, the large Ln^{3+}-Ln^{3+} distance allowing high doping levels, and the possibility of being prepared in both bulk single crystal, micro and nanopowder [1,2]. The luminescence of $KGd_{0.996}Ce_{0.004}(PO_3)_4$ crystal by exciting with VUV-UV synchrotron radiation shows strong emissions at 322 and 342 nm from the $5d_1$ to $^2F_{5/2}$ and $^2F_{7/2}$ levels with a decay time of ~16 ns. The absorption bands from the ground state of Pr^{3+} to the $5d_3$, $5d_2$ and $5d_1$ levels are at 166, 196 and 218 nm, respectively. The luminescence of $KGd_{0.989}Pr_{0.011}(PO_3)_4$ by exciting the $5d$ levels shows intense emissions centered at 256 and 265 nm from with a short decay time of 6 ns. Due to the presence of the gadolinium in the host, energy transfer processes between this ion and the active Ce^{3+} and Pr^{3+} ions have been observed. Radioluminescence studies of these crystals under X-ray synchrotron excitation have been carried out showing down-conversion processes. In the radioluminescence spectra of Ce:KGdP, after excitation with different X-ray energies, an intense band between 300 and 385 nm, is observed, with the absence of the emission from the $^6P_J \rightarrow {}^8S_{7/2}$ transitions of Gd^{3+} (~312 nm). On the contrary, in Pr:KGdP crystals, this Gd^{3+} emission band is present, being the most intense one, together with the bands for scintillator applications, centred at 236 and 259 nm corresponding to the $5d_1 \rightarrow {}^3H_J$ and $5d_1 \rightarrow {}^3F_{3,4,}{}^1G_4$ electronic transitions of Pr^{3+}.

Acknowledgements

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References

[1] I. Adell, R.M.Solé, M.C. Pujol, M. Lancry, N.Ollier, M.Aguiló, F. Díaz**,** *Sci. Rep.***,** **8**, 11002 (2018)
[2] I. Adell, R.M.Solé, M.C. Pujol, M. Aguiló, F. Díaz, *ACS Omega*, **3**, 11307-11316 (2018)

Melt growth and luminescence properties Lu_2O_3 based high dense single crystals grown by indirect heating method using arc plasma

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Inorganic scintillators have been playing a major role in many fields of radiation detection, including medical imaging, security, astrophysics, and well logging. In these applications, heavy scintillator composed of high effective atomic number ions are strongly needed, For example, Lu_2O_3 have 9.42 g/cm^3 of density and containing high effective atomic ion of (Lu:71). HfO_2 has also attracted attention due to its high density of 9.7 g/cm^3, a high effective atomic number (Hf:72) and negligible intrinsic background. These materials itself and their compounds can be promising host materials as acintilllators. However Lu_2O_3 and HfO_2 have generally high melting temperatures of more than 2490 and 2700 °C, respectively. Solid solution of $(Lu,Hf)O_x$ have extremely high melting point of >2900℃ at 44 at.% of Lu. Conventional growth technique using Ir crucible such Chochralski, Bridgman-Stockbarger and micro-pulling down method. Especially, quick materials survey using single crystals is important to discover novel scintillators. Crucible free growth technique such skull melting and floating zone (FZ) method can be adapted to high melting temperature materials, but these technique are unsuitable for quick materials survey due to their difficulty coming from massive raw material and power supply capacity, frequent replacement of power supply equipment, time-consuming sintering and preparing of raw materials, difficulty of crystal growth and heating difficulty for high transmittance crystal against to FZ beams.

In this study, we propose a novel indirect heating growth method using arc plasma and Ir metal melt for materials survey. Arc plasma preferentially head for metal due to the difference of electrical conductivity. Oxide material melts on the molten Ir metal were melted by the heated molten metal. After the gradual cooling by decreasing arc plasma power, single crystal of synthesized oxide can be obtained. The presence of metal enables control of heating and cooling, and promotes directional solidification. In this study Nd, Tb, Ru doped Lu_2O_3 and $(Lu_{0.44}Hf_{0.56})O_{1.78}$ single crystals were grown by indirect heating growth method using arc plasma. Figure 1 shows an example photograph of the grown undope and Tb doped Lu_2O_3 crystals. These crystals shows enough transparency and size for luminescence and radiation response measurements. The Tb doped sample shows green Tb^{3+} emission under UV light. Details of growth procedure, crystal phase, XRC, optical and scintillation properties will be presented.

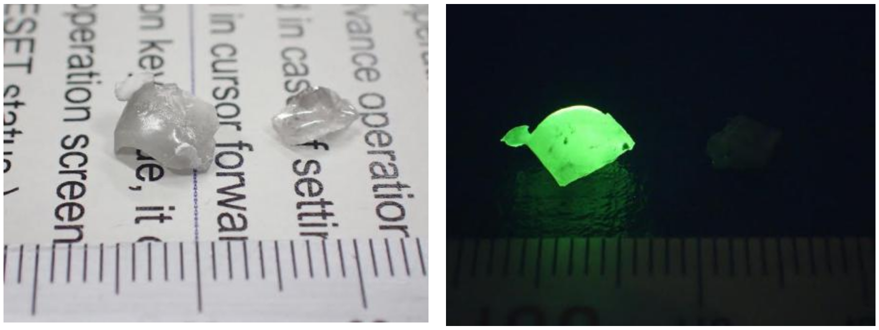

Figure 1: (left) Grown undope and Tb doped Lu_2O_3 crystals and (right) photograph under UV eradiation.

Oral

Comparison of Mo ion co-doping effects in Ce:$Y_3Al_5O_{12}$ and Ce:$YAlO_3$ single crystal scintillators

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Inorganic scintillators with high light yield and high energy resolution are of major interest for application in high energy physics and medical imaging detectors, etc[1]. Ce:$Y_3Al_5O_{12}$(YAG) and Ce:$YAlO_3$(YAP) are common scintillator materials and used for detectors in X-ray spectroscopy, mamma camera and Compton camera, etc. Most recently, Ce:YAG is a promising scintillator for new generation detectors in high energy physics. CERN Intelum project are planning to use pixelized Ce:YAG scintillator array as the detector (https://intelum.web.cern.ch/). Up to now, it was reported that co-doping of a small amount of divalent ions increaseed the light yield and accelerate decay time. Radioluminescence (RL) spectra shown anti-site defects (Y(Al) or Al(Y)) related emission band at 310 nm was decreased with increasing co-dopant concentration[2]. In opposite, divalent ions co-doping in Ce:YAP increase Ce^{4+} absorption at around 350 nm and decrease its light yield[3].
In this study, the effects of co-doping Mo^{6+} ions are reported by comparing Ce:YAG and Ce:YAP. The Mo codoped Ce:YAG and Ce:YAP single crystals have been grown by micro pulling down (μ-PD) method with various Mo concentration of 200, 500, 1000 and 3000 ppm. As a result, Mo 1000 ppm co-doped Ce:YAG showed the largest increase of 121% light yield comparing to non co-doped one. The first decay time was accelerated from 92 ns to 85 ns by Mo cooping. On the other hand, Ce:YAP showed the decrease of light yield of 52% light yield comparing to non co-doped on. The first decay time was accelerated from 26 ns to 22 ns. From RL spectra, intensity of anti-site defects (Y(Al) or Al(Y)) related emission at 310 nm was decreased by Mo codoping in Ce:YAG (fig,1 left). In the case of Ce:YAP only Ce^{3+} 4f5d emission was observed (fig.1 right). The emission intensity was decreased by Mo co-doping. Ce^{4+} absorption was not observed in both Mo co-doped Ce:YAG and Ce:YAP, although confirmed in divalent ions co-doping. In my presentation, details of crystal growth, chemical composition analysis, optical, luminescence and radiation response properties will be reported.

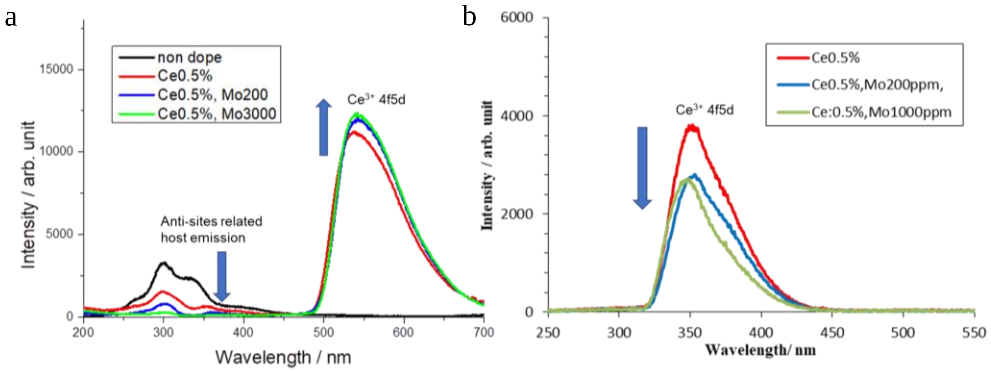

Figure 1: (a) RL spectra of Ce:YAG single crystal and comparison of (b) Ce:YAP single crystal

References

[1] M. Nikl et al., Meas. Sci. Technol, **17** R37, (2006)
[2] N.Aya et al., Japanese Journal of Appl. Phys., **54**, 45, (2015)
[3] F. Moretti et al., Chem. Phys. Chem., **18**, 493-499, (2017)

Optical Study on Garnet-Type Scintillator with Longer-Wave-Emitting

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Alpha-ray particle imager is strongly required for decommissioning of Fukushima Daiichi Nuclear Power Station and other station before workers enter the inside, because we must check some dusts emitting alpha rays. The diameter of the dust size is predicted to be around 10 μm, and the dusts have risk of the body-exposure for the workers. Alpha rays are visualized with scintillation materials, and Si-based photo-imagers with fine position resolution of less to 10 μm, such as CMOS or CCD cameras, have high sensitivity wavelength region of around 550 - 800 nm. Since conventional scintillators have ultra-violet to green emission band (350 - 500 nm), we have developed novel scintillation materials with longer emission wavelength. Ce-doped garnet scintillators, like $Ce:Y_3Al_5O_{12}$ (Ce:YAG), have green emission wavelengths of around 550 nm, and some researcher reported optical properties of $Ce:Y_3(Mg, Al, Si)_5O_{12}$ powders or ceramics as phosphors with loner emission wavelengths than the emission of Ce:YAG [1,2]. In this paper, we fabricated the single crystal samples of $Ce:Y_3(Mg, Al, Si)_5O_{12}$ to obtain high transparency and evaluated its optical and scintillation properties.

We succeeded in growing $Ce:Y_3(Mg_x\ Al_{5-2x}\ Si_x)O_{12}$ (x=0.0, 0.5, 2.0) crystals grown by the micro-pulling-down method. After cutting and polishing the samples, even Mg and Si-admixed samples with thicknesses of 1 mm reached transmittances of over 70% at 550 nm. Figure 1 shows the red-shift of emission bands were observed for Mg and Si-admixed samples due to changing lattice constants and crystal fields. Moreover, scintillation photons were also observed at the same emission bands as photo-luminescence band for each sample.

In this paper, we show the above properties, band gap structure and scintillation light yields, decay time and band structures. Especially, our purpose is to detect alpha-ray particles, and discrimination among gamma-ray (photon) excitation and charged-particle excitation by decay profile.

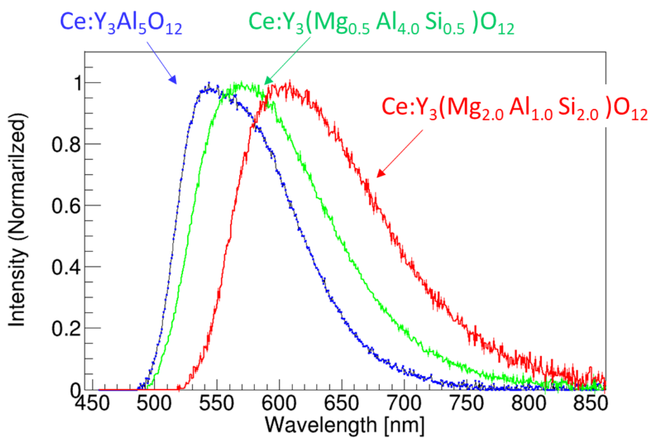

Figure 1: Emission wavelength for $Ce:Y_3(Mg_x\ Al_{5-2x}\ Si_x)O_{12}$ (x=0.0, 0.5 and 2.0) samples excited by 450, 460 and 470-nm photons, respectively.

Acknowledgements

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References

[1] A. Katelnikovas, *et al.*, *Opt. Mater.*, **32**, 126 (2010)
[2] Q. Du, *et al.*, *J. Mater. Chem. C*, **6**, 12200 (2018)

Poster presentations

The pathway to an optimum luminescent thermometer – Bending the Boltzmann distribution

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Luminescence (nano)thermometry has evolved to a valuable technique for remote temperature sensing with appreciable spatial resolution below 10 µm [1]. Its applicability has already been successfully proven in, e.g. *in situ* monitoring of the temperature changes in catalytic reactions [2] or *in vivo* thermal imaging [3]. In most cases, ratiometric thermometry is used that is based on a calibration of a temperature signal by detection of an intensity ratio of the emitted light stemming from two thermally coupled excited states that obey a Boltzmann equilibrium. Trivalent lanthanides with their rich $4f^n$-based electronic level structure and narrow line-like emissions are especially suited for that purpose.

In some cases, however, the Boltzmann distribution as a model for the temperature-dependent intensity ratio is doomed to fail for certain temperature ranges [4,5]. Moreover, the often-attempted trial-and-error principle for a lanthanide ion and its choice based on a desired emission color may actually lead to a substantial loss in otherwise potentially gainable thermal sensitivity. On the presented poster, the optimum conditions to gain the maximum thermal sensitivity out of such a thermometer will be demonstrated in connection to some real-case examples based on these predictions. Moreover, the influencing factors by the lanthanide and host to be in the validity regime of the Boltzmann distribution will be discussed in a quantitative manner. Finally, more general models for the case of a failure of the Boltzmann distribution as well as possible approximations frequently encountered in the applied field of *in vivo* imaging are shortly presented. In total, these considerations aim at offering clear guidelines towards the choice of an optimum Boltzmann-type luminescent thermometer [5].

Acknowledgements

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References

[1] a) D. Jaque, F. Vetrone, *Nanoscale* **2012**, *4*, 4301-4326; b) C. D. S. Brites *et al.*, *Nanoscale* **2012**, *4*, 4799-4829; c) C. D. S. Brites, A. Millán, L. D. Carlos, *Lanthanides in Luminescent Thermometry*, in: *Handbook on the Physics and Chemistry of Rare Earths* (eds.: J.-C. Bünzli, V. K. Pecharsky), Vol. 49, Ch. 281, **2016**, pp. 339-427, Elsevier, Amsterdam.
[2] a) R. G. Geitenbeek *et al.*, *ACS Catal.* **2018**, *8*, 2397-2401; b) R. G. Geitenbeek *et al.*, *Chem. Eng. Sci.* **2019**, *198*, 235-240; c) R. G. Geitenbeek, *Lab Chip* **2019**, *19*, 1236-1246.
[3] a) U. Rocha *et al.*, *ACS Nano* **2013**, *7*, 1188-1199; b) A. Benayas *et al.*, *Adv. Opt. Mater.* **2015**, *3*, 687-694; c) E. C. Ximendes *et al.*, *Nano Lett.* **2016**, *16*, 1695-1703.
[4] R. G. Geitenbeek, H. W. de Wijn, A. Meijerink, *Phys. Rev. Appl.* **2018**, *10*, 064006.
[5] M. Suta, A. Meijerink, *submitted* **2019**.

Poster

Luminescence investigation of Ln^{3+}-doped inorganic materials in high-pressure

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Materials doped with lanthanide Ln^{3+} ions exhibit visible luminescence after excitation by ultraviolet (UV), and co-doped with Yb^{3+}/Er^{3+} ions shows up-convertion luminescence after near-infrared (NIR) radiation. Upconversion (UC) is a phenomenon when two or more low-energy photons are converted into one photon with higher-energy (Vis) [1]. Ln^{3+}-doped materials can be applied as light-emitting diodes, bioimaging materials, photovoltaics, forensic, security markers and sensors.

The properties of materials are highly-dependent on their composition, structure, and morphology. The synthesis of a high-quality materials with good luminescent properties is not a trivial task. However, in this work, well-defined luminescent inorganic nanoparticles (YVO_4, SrB_2O_4, etc.) were successfully synthesized by the different method. The structure, morphology and luminescence properties of the obtained products were investigated [2].

Measurements of luminescence and up-conversion luminescence were carried out under high-pressure in a Diamond Anvil Cell (DAC) to investigate the influence of pressure on the materials properties. The obtained materials exhibit the red-shift of the emitted light as the pressure increases due to increasing interactions between the ions and the decreasing differences between their ground and excited energy states. Structural changes (plastic and elastic deformations) induced by pressure have a large impact on the luminescence properties of Ln^{3+}-doped materials. This phenomenon in Ln^{3+}-doped materials can be applied as novel pressure sensors [3].

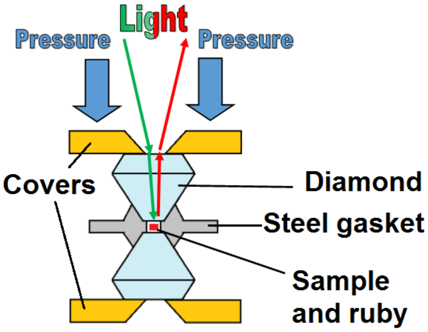

Figure 1: Scheme of high-pressure luminescence investigation.

Acknowledgements

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References

[1] P. Woźny, M. Runowski, S. Lis, *J. Lumin.* **209,** 321-327 (2019)
[2] P. Woźny, A. Szczeszak, S. Lis, *Opt. Mater.*, **76,** 400-406 (2018)
[3] M. Runowski, P. Woźny, V. Lavín, S. Lis, *Sensors Actuators B Chem.* **273,** 585-591 (2018)

Up-conversion luminescence and energy transfer mechanism of $ZnTiO_3$: Er^{3+},Yb^{3+} phosphor

Poster

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Er^{3+} and Er^{3+}/Yb^{3+} doped zinc titanate ($ZnTiO_3$) were successfully synthesized using conventional solid-state reaction method. The spectroscopic characterization of these samples was carried out using X-ray diffraction, scanning electron microscopy, absorption and luminescence spectroscopy. Microscopy analysis showed the formation of agglomerated uniform particle shapes formed during the process of calcination. The results from the optical properties showed an interesting band gap engineering of the $ZnTiO_3$ due to doping. The UC luminescence properties of the phosphors $ZnTiO_3$:Er^{3+},Yb^{3+} phosphor was carried out under near infra-red excitation at 980 nm. The prominent green and red visible emission peaks were observed at 527, 545 and 665 nm for Er^{3+} doped systems. The co-doping with Yb^{3+} intensifies the Er^{3+} up-converted visible emission region through energy transfer. The energy transfer mechanisms involved between Er^{3+}- Yb^{3+} co-doped systems were illustrated and discussed in detail.

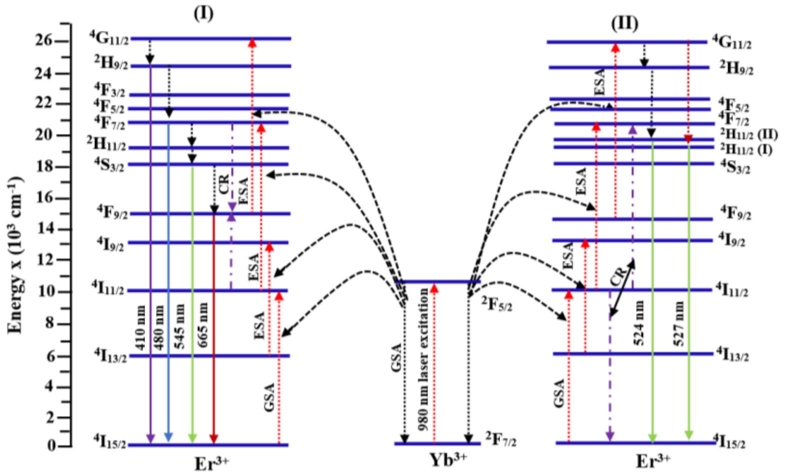

Figure 1: Schematic energy level diagram of Er^{3+}/Yb^{3+} showing the possible energy transfer mechanism involved in UC process under an excitation of 980 nm.

Acknowledgements

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References

[1] B.P. Kore, A. Kumar, L. Erasmus, R.E. Kroon, J.J. Terblans, S.J. Dhoble and H.C. Swart, Inorganic chemistry, **57,** 288−299 (2018).

Influence of the synthesis route on the structural and spectroscopic properties of Nd^{3+}-doped YPO_4 nano and micro-powders

Poster

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Nowadays, the usage of materials with luminescent properties is increasing in modern technologies. The requirements for luminescent material include not only chemical, mechanical or spectroscopic properties, but also concern grain size or morphology of the material being designed [1,2]. By using different synthesis routes it is possible to obtain compounds with specific purity, grain size, morphology and other physico-chemical properties. Previous studies showed that the size of lanthanide(Eu^{3+} or Tb^{3+}) -doped YPO_4 nanoparticles can modify the intensity of luminescence [3].

In this work we would like to show how the synthesis method could change the structural and spectroscopic properties of Nd^{3+}-doped yttrium orthophosphate. Nano and micro-materials with different concentrations of active ion were prepared by both, combustion method (nano-powders) and solid-state reaction method (micro-powders). The phase purity of obtained samples were controlled by X-ray diffraction method (XRD). The morphology of particles were analyzed by using electron microscopy techniques (SEM and TEM). The compound crystallizes in the tetragonal system conforming to space group model $I4_1$/amd (D^{19}_{4h}, No. 141), Z = 4 and is isostructural with Nd^{3+}-$LuPO_4$. The spectroscopic properties were analyzed by using low-temperature high-resolution techniques like absorption spectroscopy at 4.2K and tuneable laser site selective spectroscopy at 77K. Detailed structural and spectroscopic studies of Nd^{3+}-doped YPO_4 micro- and nano-powders were performed, taking account the role of Nd^{3+} dopant ion as a structural probe. We will show that the different methods of synthesis has a strong influence on the luminescence properties of samples under investigation.

Acknowledgements

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References

[1] J. Cybinska, M. Guzik, C. Lorbeer, E. Zych, Y. Guyot, G. Boulon, A.-V. Mudring, *Optical Materials*, 63, 76-87 (2017).

[2] J. Cybinska, C. Lorbeer, E. Zych, A.-V. Mudring, *Journal of Luminescence*, 189, 99-112 (2017).

[3] Z. Way, M. K. Wallace, A.L. Diaz, *ECS Journal of Solid State Science and Technology*, 7, R3163-R3170 (2018).

Site selective spectroscopy as an efficient tool for structural and spectroscopic studies of Nd^{3+}-doped $LuPO_4$ nano/micro-powders

Poster

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Recent studies show that Nd^{3+}-doped orthophosphates could be potential good materials for both bio-imaging and also laser sources due to their high-thermal stability, high insolubility and relatively cheap synthesis. Surprisingly, despite many studies conducted, for well-known luminescent material RE^{3+}-doped $LuPO_4$, the basic structural research is still missing. It is very important to fulfill this gap in order to properly understand potential applications.

That is why, nano- and micro-powders of Nd^{3+}-doped $LuPO_4$ were synthesized by two common methods: hydrothermal based on ionic liquid (IL) and solid-state reaction. Both synthetic routes allow to obtain pure phase of Nd^{3+}-doped $LuPO_4$. The hydrothermal method with IL leads to forming nano-powders ranging a few nanometers. This synthesis route possesses many advantages as it is a fast and facile preparation method of the desired phosphate nanomaterials without the necessity to obtain a pure phosphate phase for post-reaction heat treatment.

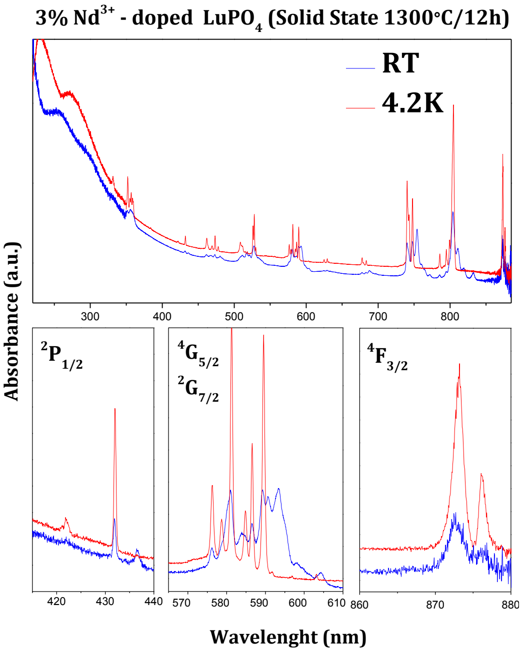

Fig. 1 Absorption spectra at RT and 4.2K of 3% Nd^{3+}-doped $LuPO_4$ obtained by solid state reaction.

The compound crystallizes in the tetragonal system conforming to space group model $I4_1$/amd (D^{19}_{4h}, No. 141), Z = 4. Solid-state reaction however, leads to creationof bigger grains with better crystallinity. Nd^{3+} ion, an usual laser ion, can be used as structural probe by applying the low-temperature high-resolution technique of absorption spectroscopy at 4.2K (Fig.1) and site selective tuneable laser spectroscopy at 77K. Detailed structural and spectroscopic studies of nano- and micro-powders show only one crystallographic site for the Nd^{3+} dopant.

In addition, we have focused on the possible application of this material as a thermometer by analysing the thermal dependence of the intensity of $^4F_{5/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission lines under λ_{ex}=532 nm excitation of a YAG:Nd^{3+} laser, in the temperature range between 293 and 613 K.

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Tb2(BDC)3 high-quality luminescent metal-organic framework films

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The luminescent characteristics of Tb2(BDC)3 (Tb=terbium) (BDC=1,4-benzenedicarboxylate) MOF films using ultrasonic spray deposition on top of several types of substrates including glass slides, metal oxides films, filter paper, and polyimide sheets are presented. The glass supported films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), profilometry, infrared (IR), and luminescence spectroscopies. As expected, the luminescence emission spectra present high intensity characteristic emission bands of the sensitized terbium ion for all the films. Nevertheless, the temperature of the substrate, during deposition, plays a crucial role in the final structural and morphological characteristics of the MOFs, which in turn, dramatically modifies the excitation features.

Acknowledgements

References

[1] J.U. Balderas, et al., *Journal of Luminescence 212 (2019) 322–327*

Poster

Dy^{3+} ions as optical probes for structural study of $K_4SrGe_3O_9$

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$K_4SrGe_3O_9$ belongs to the $M^I_4M^{II}X_3O_9$ (M^I = Na, K; M^{II} = Ca, Sr; X = Si, Ge) family of silicates and germanates whose unit cells adopt cubic symmetry (the space group $Pa\bar{3}$) and contain highly distorted twelve-membered $[X_{12}O_{36}]$-rings (X = Si, Ge) centered on the 3-fold inverse axis [1]. Whereas its basic features are well established in crystalline and amorphous optical hosts, Dy^{3+} ion is used as a spectroscopic probe to study the crystal structure and local symmetry of $K_4SrGe_3O_9$. Furthermore, a new series of promising phosphors based on $K_4Sr_{1-3x}Dy_{2x}Ge_3O_9$ ($x = 0.005$–0.05) have been synthesized using a solid-state method. Structural analysis shows that the solid solution $K_4Sr_{1-3x}Dy_{2x}Ge_3O_9$ ($x = 0.005$–0.05) crystallizes at 298 K in the space group $Pa\bar{3}$, Z = 16. The trivalent Dy^{3+} ions occupy two crystallographically different Sr^{2+} sites (both 8*c*) with the C_3 symmetry. Raman spectroscopy corroborates the X-ray diffraction results and confirms the crystal structure features of $K_4SrGe_3O_9$ with the maximum phonon energy of ~820 cm^{-1}. *Ab initio* calculations within the DFT framework employing B3PW, WC1LYP and B3LYP hybrid functionals have been performed to describe the crystal structure, electronic properties and vibrational spectra of $K_4SrGe_3O_9$ ($E_g = 5.29$ eV; direct allowed transition). The comparison between calculated and experimental frequencies shows a general good agreement for the spectral region below 700 cm^{-1}. The relationship between selected infrared bands and Raman lines, the vibrations of O–Ge–O and Ge–O–Ge bonds in the $[Ge_{12}O_{36}]$ ring unit and metal-oxygen bonds has been analyzed to distinguish the isostructural compounds in the family of $M^I_4M^{II}X_3O_9$ (M^I = Na, K; M^{II} = Ca, Sr; X = Si, Ge). The $K_4SrGe_3O_9$:Dy^{3+} phosphors exhibit yellow emission under excitation at 350 nm. Calculation of the Ω_2 and Ω_4 Judd–Ofelt intensity parameters and quantum efficiencies from the recorded emission spectra allows a more extensive study of the luminescence properties of Dy^{3+}-doped $K_4SrGe_3O_9$ and related compounds. The maximum light emission is revealed at the activator content of $x = 0.015$ in $K_4Sr_{1-3x}Dy_{2x}Ge_3O_9$. CIE chromaticity coordinates of $x = 0.473$ and $y = 0.471$ are calculated for $K_4Sr_{0.955}Dy_{0.03}Ge_3O_9$ which is characterized by internal quantum yield of 47%.

Acknowledgements

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References

[1] E. Arroyabe, R. Kaindl, V. Kahlenberg, *Z. Anorg. Allg. Chem.*, **635**, 337–345 (2009).

Poster

Core-Shell architecture to enhance RE doped UC NanoCrystals Luminescence Emissions for Photocatalytic Applications

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The low-usage of sunlight has been restraining the photocatalytic efficiency of pure TiO_2 in the environmental remediation. Different strategies have been adopted to take advantage of visible light to modify TiO_2, such as to enhance the range and capacity of photocatalysts to absorb the incident radiation and generate electron-hole pairs, extending the activation ranges to more convenient wavelengths in order to optimize the harnessing of the available solar radiation.[1] On the other hand, spectral conversion of light is an emerging route for enhancing the efficiency of various solar energy harvesting schemes by means of wavelength shifting luminescence processes (quantum cutting, down-shifting, up-conversion…), as a very promising, and not yet fully explored, route.[2] In this work we present intense UV-blue UC emissions coming from solvothermal synthetized $Sr_2YbF_7:Tm^{3+}@Sr_2YF_7$ UC agent under low-power commercial 980 nm laser diode radiation for photocatalytic degradation of an organic dye (MB) using a commercial TiO_2 photocatalyst, to show clearly evidence that UC emission of itself can activate photocatalytic processes. Besides Core-shell nanoparticles luminescent improve by a factor 10 due to the presence of an outer inert shell is discussed.

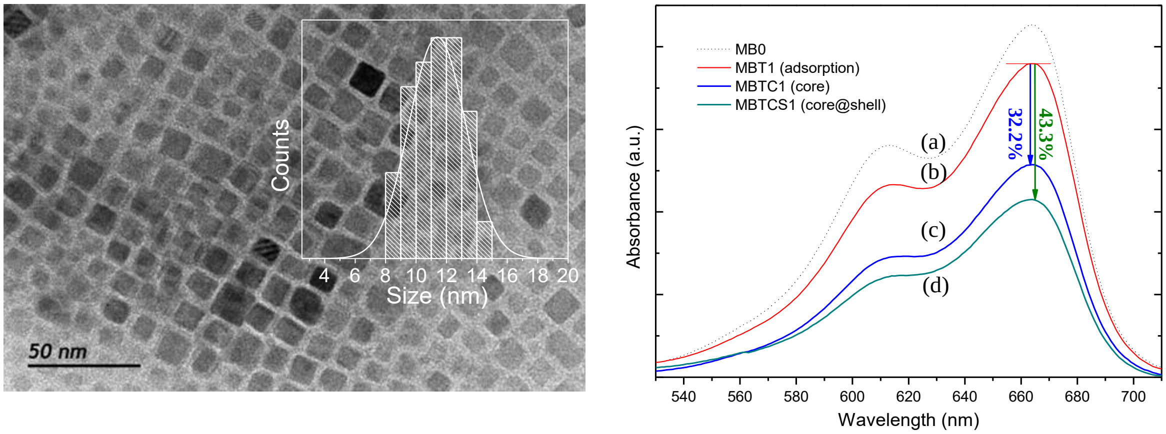

Figure 1: (Left) TEM image of Sr2YbF7@Sr2YF7 core-shell NCs including size histogram. (Right) Absorbance spectra of methylene blue solutions for peak maxima at 664 nm. (a) Starting solution. (b) After 1.5h in the dark due to the adsorption effect of the TiO_2 particles. Finally, after 1.5h under illumination with two 300 mW 980 nm laser diodes focused onto the up-conversion of the Sr_2YbF_7 NCs (c) and of the $Sr_2YbF_7@Sr_2YF_7$ core-shell NCs (d).

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References

[1] P. Acosta-Mora, K. Domen, T. Hisatomi, H. Lyu, J. Méndez-Ramos, J. C. Ruiz-Morales and N. M. Khaidukov, Chem. Commun., **54**, 1905, (2018)

[2] P. Acosta-Mora, K. Domen, T. Hisatomi, H. Lyu, J. Méndez-Ramos, J.C. Ruiz-Morales and N.M. Khaidukov, Optical Materials, **83**, 315-320, (2018)

Poster

Structural and optical characterization of Tm^{3+}-doped apatite related $NaLa_9(GeO_4)_6O_2$ phosphors

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Thulium-doped materials are drawing a great deal of interest for numerous laser applications in the near and mid-infrared regions of the spectrum, since they provide broad emission bands in the 1400–2700 nm region not covered by neodymium and erbium activated systems [1]. In addition, strong water absorption observed at these wavelengths makes thulium-doped compounds very attractive for biomedical applications [2].

In this work, new $NaLa_{9-x}Tm_x(GeO_4)_6O_2$ ($x = 0.025\text{-}0.2$) germanates with the apatite structure type (space group $P6_3/m$, $Z = 1$) have been prepared using the solid state method. The samples were characterized by powder X-ray diffraction, scanning electron microscopy and diffuse reflectance spectroscopy. Photoluminescence measurements of $NaLa_{9-x}Tm_x(GeO_4)_6O_2$ compounds were carried out both in the 425–850 nm range under 356 nm excitation and in the infrared region under 808 nm excitation. The typical luminescence spectrum of the samples measured under 356 nm excitation is presented in Fig. 1a. The most intensive line at 478 nm is associated with the $^1G_4 \rightarrow {}^3H_6$ radiative transition, the peak at a shorter wavelength (453 nm) is assigned to the $^1D_2 \rightarrow {}^3F_4$ transition, the additional lines located at 625–850 nm are caused by the $^1G_4 \rightarrow {}^3F_4$, $^3F_2 \rightarrow {}^3H_6$ and $^3H_4 \rightarrow {}^3H_6$ transitions in Tm^{3+}. The spectra measured in the infrared spectral range (Fig. 1b) consist of two broad emission bands centered at 1450 nm and 1810 nm, which correspond to the series of cascade transitions: $^3H_4{}^\circ\rightarrow{}^{\circ 3}F_4$ and $^3F_4{}^\circ\rightarrow{}^{\circ 3}H_6$, respectively. The composition with dopant concentration $x = 0.1$ possesses the most intensive emission in this wavelength range.

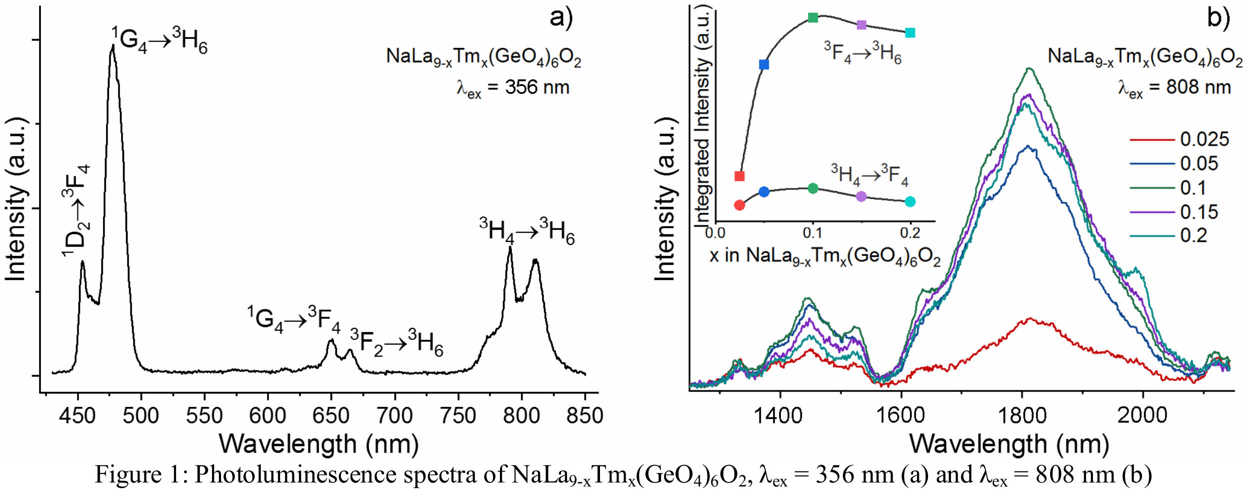

Figure 1: Photoluminescence spectra of $NaLa_{9-x}Tm_x(GeO_4)_6O_2$, λ_{ex} = 356 nm (a) and λ_{ex} = 808 nm (b)

Acknowledgements

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References

[1] J. Wu, Z. Yao, J. Zong, S. Jiang, *Opt. Lett.*, **32**, 638–640 (2007).

[2] T. Bilici, H.O. Tabakoglu, N. Topaloglu, H. Kalaycioglu, A. Kurt, A. Sennaroglu, M. Gulsoy, *J. Biomed. Opt.*, **15**, 038001 (2010).

Synthesis and spectroscopic properties of red-emitting lithium tantalate garnet phosphors for solid state lighting

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Luminescent materials based on garnet-type compounds are among the most widely used components for white light-emitting diodes (wLEDs). Conventional commercial w-LED consists of a yellow cubic garnet phosphor YAG:Ce^{3+} with a blue In-doped GaN chip or the combination of an RGB phosphor with a near-UV chip. Along with excellent advantages, such as high quantum efficiency and excellent thermal stability, YAG based phosphors possess a poor color rendering index (~ 76) and excessively high CCT value (above 4000 K) due to the lack of the red spectral component[1]. In recent years cubic garnets $Li_3Ln_3Te_2O_{12}$:Eu^{3+}, Sm^{3+} (Ln = Y, Gd) have been considered as efficient phosphors for near-UV chip-based wLEDs and for display devices[2,3]. Compared with commercial red-emitting phosphors lithium garnets has some benefits, e.g., good excitation profile, stable luminescence properties at high temperature and red color purity[2,3]. Such promising characteristics allow us to predict the high luminescence performance for the related class of compounds. The present report is an overview on spectroscopic properties of new potential red lithium garnet $Li_{5+x}Ca_xLa_{3-x}Ta_2O_{12}$:$Sm^{3+}$ phosphors.

The garnet-type $Li_{5+x}Ca_xLa_{3-x-y}Sm_yTa_2O_{12}$ ($x = 0$, 1, $y = 0.0$–0.3) compounds synthesized using a conventional solid state and citrate methods crystallize in the cubic space group Ia-$3d$ ($Z = 8$). The phosphors exhibit good thermal stability over a wide temperature range and an intense luminescence in the orange-red spectral range upon UV excitation. The wide band located at ~ 230 nm in the excitation spectra is associated with the O^{2-}–Ta^{5+} charge transfer process. The lines below 300 nm originate from the $4f$–$4f$ transitions in Sm^{3+}. The excitation band at 407 nm caused by the $^6H_{5/2} \rightarrow {}^4K_{7/2}, {}^6P_{3/2}$ transitions is sufficiently intense, which indicates that the Sm^{3+}-doped $Li_{5+x}Ca_xLa_{3-x}Ta_2O_{12}$ garnet phosphors can be suitable for excitation by near-UV based LEDs. The photoluminescence spectra contain the well-known emission lines in a spectral range of 550–750 nm assigned to the characteristic transitions from the excited $^4G_{5/2}$ level to the ^6H_J ($J = 5/2$, 7/2, 9/2 and 11/2) states in samarium ions. The energy transfer among the dipole–dipole interaction plays a major role in the mechanism of concentration quenching in $Li_6CaLa_2Ta_2O_{12}$:Sm^{3+} phosphors. The maximum light emission is revealed for $Li_{5+x}Ca_xLa_{3-x-y}Sm_yTa_2O_{12}$ compounds with 3–4 mol% samarium concentration. CIE chromaticity coordinates of $Li_{5+x}Ca_xLa_{3-x}Ta_2O_{12}$:$Sm^{3+}$ (0.60, 0.39) are close to those of the commercially available red Y_2O_3:Eu^{3+} phosphor (0.62, 0.37). The $Li_6CaLa_2Ta_2O_{12}$:Sm^{3+} phosphors have good thermal properties and can retain up to 65% of their luminescence at 420 K, which significantly exceeds the values obtained for $Li_3Gd_3Te_2O_{12}$:Sm^{3+} compounds[3].

Acknowledgements

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References

[1] J. Li, J. Yan, D. Wen, W. Khan, J. Shi, M. Wu, Q. Sua, P. Tanner, *J. Mater. Chem. C*, **4**, 8611–8623 (2016).
[2] W.S. Zhang, H.J. Seo, *J. Alloys Compd.*, **553**, 183–187 (2013).
[3] Z. Gao, N. Xue, J.H. Jeong, R. Yu, *J. Mater. Sci.: Mater. Electron.*, **28**, 12640–12645 (2017).

Rare earth-doped phosphate and germanate glasses for near-infrared power amplifiers and laser sources

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In recent decades, multicomponent oxide glasses have demonstrated the capability to outperform silica glass as host material for emitters in the near-infrared (NIR) wavelength region. In particular, phosphate and germanate glass compositions can be doped with high amounts of rare earth ions (up to ten times more ions per unit volume with respect to silica) and thus allow the possibility of realizing compact optical amplifiers and fiber lasers able to minimize non-linear effects [1].

We report on the recent advances regarding Yb-Er co-doped phosphate glasses for power amplifiers and Tm-doped germanate glasses for NIR laser sources. Phosphate glasses offer an interesting platform for the realization of optical power amplifiers for ns pulsed sources at 1.5 µm wavelength, by using Er^{3+} ions as activators and Yb^{3+} ions as sensitizers. They have been properly engineered to be suitable for crystal-free fiber drawing and subsequently shaped into rods and optical fibers for testing as coherent sources for LIDAR systems.

Table 1: Yb-Er co-doped phosphate glass compositions for optical amplifiers. 2:1, 4:1 and 6:1 refer to the Yb^{3+}/Er^{3+} molar ratio.

Glass name	**Er^{3+} [10^{20} ions/cm^3]**	**Yb^{3+} [10^{20} ions/cm^3]**
YE 2:1	1.93	3.86
YE 4:1	1.92	7.69
YE 6:1	1.92	11.50

With the aim to develop new compact amplifiers operating in the 2um wavelength region, novel germanate glass compositions have been developed. Thermal analysis and preliminary fiber drawing test reveal suitable glass thermal stability against crystallization and good glass homogeneity towards the manufacture of performing fiber amplifier.

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References

[1] D. Milanese, J. Lousteau, X. Zhu, A. Chavez-Pirson, D. Pugliese, N. G. Boetti and N. Peyghambarian. Nonsilica Oxide Glass Fiber Laser Sources: Part I, Advances in Glass Science and Technology, Vincenzo M. Sglavo, IntechOpen (2018).

Insight into the effect of Li^+ concentration on the structure and photoluminescence properties of $Ca_{10}(PO_4)_6(OH)_2$: Sm^{3+} intended for theranostic application

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Hydroxyapatite is an attractive biomaterial for bone regeneration due to its high biocompatibility and osteoconductive properties as well as relatively low genotoxicity. Lithium ion as dopant possess an excellent bioactivity and it's one of the most well-studied element in bone-tissue engineering. The rare-earth ion doped nanoapatite with detectable and stable fluorescent signal can be a promising candidate for bio-imaging in order to understand a biological interaction of such biomaterial with tissues and cells at the molecular level.

Nanocrystalline hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, nHAp) co-doped with Sm^{3+} and Li^+ ions was synthesized using a co-precipitation method at relatively low temperature. The influence of Li^+ ion concentration on the structure and luminescence properties of the nHAp doped with Sm^{3+} was analyzed in details. The lithium ion was used as a charge compensator to improve luminescence properties of the nHAP and as an ion directly affecting the acceleration of the regeneration process. The structural and morphological properties of the obtained materials were determined by using XRPD (X-ray powder diffraction) and SEM (Scanning electron microscopy) techniques, as well as infrared (FT-IR) spectroscopy. The charge compensation mechanism has been proposed based on Kröger–Vink-notation [1]. The spectroscopic properties of obtained materials have been investigated in detail using emission kinetics and emission spectra measured at different temperatures.

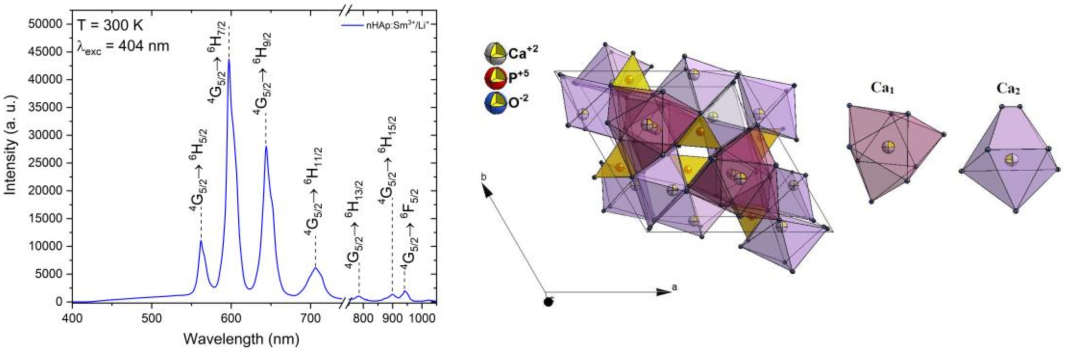

Figure: The emission spectrum of the nHAp:Sm^{3+}/Li^+ measured at room temperature (left) and the projection of the nHAp unit cell with the indication of the Ca_1 and Ca_2 crystallographic position (right).

Acknowledgements

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References

[1] F.A. Kröger, H.J. Vink, *Solid State Phys*. **3**, 30–435 (1956).

Study of luminescence properties of Eu^{2+} ion depending on changes of Eu^{3+} ion concentration in the silicate-substituted apatite

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Apatite doped with divalent europium ion is the well-known as a blue phosphor in high efficiency fluorescent lamps [1]. The broad emission band with maximum around 440 nm is assigned to $4f^6 5d \rightarrow 4f^7$ ($^8S_{7/2}$) transition. The luminescence properties of Eu^{2+} centers depend on the chemical environment into the matrix. In apatite lattice the Ca^{2+} ion could be replaced by Eu^{3+} ions as result of creation of negative vacancy in the calcium site. To compensation of a total charge a significant amount of Ca^{2+} site could be occupied by Eu^{2+} ions. In our case, it has been observed the luminescence properties of both europium(III) and europium(II) ions in the obtained silicate-substituted apatites [2,3].

The Eu^{3+}/Eu^{2+} ions-doped nanostructured silicon-substituted apatite was obtained using a microwave assisted hydrothermal method. The concentration of europium ions was established to be at 1.0 mol% in a ratio to entire calcium ions molar content.

The structural and morphological properties of the obtained materials were determined by using XRD (X-ray powder diffraction), SEM (Scanning Electron Microscopy) technique as well as infrared (IR) spectroscopy. The particle size was verified and calculated by the Rietveld method. The luminescence properties (the emission, excitation spectra and emission kinetics) of the Eu^{2+} and Eu^{3+} ions were recorded and analyzed as a function of dopant concentration and heat-treatment temperature. There has been paid attention to structural and spectroscopic properties as a function of an amount silicate group in the obtained materials.

Acknowledgements

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References

[1] A. Madadi, K.C. Glass, B.C. Williams, O.A. Graeve, R. Kanakala, *Biomaterials*, **31**, 4259-4267 (2010)

[2] R. Jagannathan, T.R.N. Kutty, *Journal of Luminescence*, **71**, 115–121 (1997)

[3] S. Targonska, R.J. Wiglusz, K. Szyszka, J. Rewak-Soroczynska, *Dalton Transactions*, (2019)

The effects of local symmetry on the upconversion emission intensity, color and dynamics under ns pulsed excitation

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The increase of the radiative transition rates by lowering the local symmetry around lanthanide activators represents an effective way for the enhancement of quantum yield and colour selectivity of cw excited upconversion (UPC) emission [1]. Here, we present our latest results regarding the effects of local symmetry on the upconversion emission intensity, colour and mechanisms of Er doped ZrO_2 using ns excitation around 980 and 1530 nm [2]. The tetragonal and monoclinic zirconia polymorphs ensure distinct local symmetry around Er activator (higher D_{2d} and lower $\sim C_1$ symmetry, respectively) while these display close structural and vibrational properties. The samples investigated and experiments were carefully designed in order to get an accurate comparison between the UPC properties. The local symmetry defines not only the intensity and shape of UPC emission but also the "composition" of UPC mechanisms (ground state absorption followed by excited state absorption or energy transfer) with the energy transfer being obviously more active in the higher local symmetry, as a result of the longer lived intermediary levels. This issue is overlooked in the well-investigated Er/Tm, Yb based UPC, since the activators emission is inherently due to energy transfer *via* Yb sensitizer. The upconversion emission is comparable and up to 110 more intense in the higher symmetry of the tetragonal polymorph than in the lower local symmetry of the monoclinic one, a result that contrasts with the general trend observed for cw excited UPC.

Acknowledgements

The authors acknowledge Romanian National Authority for Scientific Research and Innovation (CNCS-UEFISCDI) through project PN-III-P4-ID-PCE-2016-0305, contract PCE 67/2017 for the financial support.

References

[1] B. Zhou, B. Shi, D. Jin, X. Liu, *Nature nanotechnology*, **10**(11), 924 (2015); S. Han, R. Deng, X. Xie, X. Liu, *Angew. Chem. Int. Ed.*, **53**(44), 11702-11715 (2014).
[2] D. Avram, C. Colbea, M. Florea, C. Tiseanu, *paper submitted for publication.*

Spectral, luminescent, laser and holographic properties of photo-thermo-refractive glass doped with rare earth ions

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Today active photo-thermo-refractive (PTR) glass is a very promising medium for monolithic integration of laser and holographic elements on one chip. Spectral, luminescent, laser and holographic properties of PTR glass doped with neodymium, ytterbium and erbium ions has been studied in present work. The spectroscopic analysis of Nd^{3+}, Yb^{3+} and Er^{3+} in PTR glass has been reported and discussed. Spectroscopic intensity parameters Ω_t have been calculated using Judd-Ofelt theory. Radiative lifetimes, branching ratio and emission cross section have also been calculated for each transition of each glass. Fluorescence decay has been analyzed. The dependence of fluorescence lifetime on temperature has been detected. For example, it was found that, for the sample doped with 1 mol% of Nd_2O_3, the fluorescence lifetime at 1063 nm increases from 211 μs to 249 μs with a change in temperature from 290 K to 90 K, this happens due to the multiphonon relaxation, that disappears in very low temperatures. It was demonstrated that the induced emission cross section of the enhanced transition $^4F_{3/2}\rightarrow {}^4I_{11/2}$ increases from 1.743×10^{-20} cm^2 to 2.041×10^{-20} cm^2, but the quantum efficiency deceases from 90.3% to 26.2% as the Nd_2O_3 concentration changes from 2.5×10^{20} cm^{-3} to 10.2×10^{20} cm^{-3}. It was also found that, for the sample doped with 0.5 mol% of Nd_2O_3, the saturation intensity is about 26 kW/cm^2, which is lower than that in some commercially produced glasses of same Nd^{3+} concentration.

We demonstrated laser action of neodymium and ytterbium-erbium doped PTR glasses. A laser oscillator with 0.5 mol% Nd_2O_3 doped PTR glass active element was built, and it was shown that the round-trip losses are 0.34%, this value is low, and is comparable to that in some commercially fabricated Nd-YAG crystals. Also, we have got the laser oscillation for PTR glass active element doped with ytterbium-erbium. Efficiency of the Yb-Er laser was comparable for that obtained in a bulk Yb-Er-doped silicate glasses. Round-trip losses for Yb-Er doped system was as low as for the Nd-doped system, which may attribute to a good quality of the glass.

In addition, it was shown that thermal treatment of undoped and doped PTR glass results in increase of scattering in UV and VIS spectral range caused by growth of NaF nanocrystals. In near IR range (at wavelengths of Nd-, Yb- and Er-lasers) the scattering effect is small. Volume Bragg grating are recorded in laser PTR glasses. We measured the refractive index modulation amplitude of the gratings as a function of heat treatment duration time. This experiment allowed us to investigate crystallization kinetics of laser PTR glasses during photo-thermo-induced crystallization process. It was shown that doping RE ions and increasing their concentration resulted in a slowdown of crystallization kinetics. Thus, in order to achieve the same refractive index modulation amplitude the highly concentrated PTR glasses require more long time heat treatment than the lowly concentrated glasses. We made a conclusion that the rare earth ions hold fluorine and prevent it from participation in crystal growth. Thus, we can conclude that addition of the rare-earth ions in the glass composition lowers the photo-refractive properties of the material. To compensate this negative effect, we had to increase fluorine concentration in the glass composition to ensure that there is enough fluorine for the crystallization.

Praseodymium-doped Type III $KGd(PO_3)_4$ nanocrystals: synthesis and characterization

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Potassium gadolinium phosphate, $KGd(PO_3)_4$, hereafter KGdP, is a monoclinic crystal that belongs to the wide family of condensed phosphates of double phosphates of alkali and lanthanide ions. KGdP can crystallize in three different monoclinic crystalline structures: type III phase ($P2_1$), type IV ($P2_1/n$), and type B phase ($C2/c$) [1]. KGdP can be easily doped with lanthanide ions, such as praseodymium (Pr^{3+}), because gadolinium (Gd^{3+}) is a constitutive ion of the host. Besides, the optical transparency window of KGdP extends from 160 nm to 4 μm. This large transparency allows the observation of the d−f electronic transitions of Pr^{3+}.

In this work, non-centrosymmetric monoclinic $Pr:KGd(PO_3)_4$ nanocrystals have been obtained by the modified Pechini method. The experimental parameters have been optimized to obtain a single crystalline phase product [2]. The unit cell parameters of the obtained products have been refined. By the excitation of the material by X-ray radiation, the emission bands corresponding to the $5d_1 \rightarrow {}^3H_4$, ${}^3H_5$, ${}^3H_6$ and $5d_1 \rightarrow {}^3F_3, {}^3F_4, {}^1G_4$ transitions of Pr^{3+} and the ${}^6P_{3/2}$, ${}^6P_{5/2}$, ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transitions of Gd^{3+} were observed.

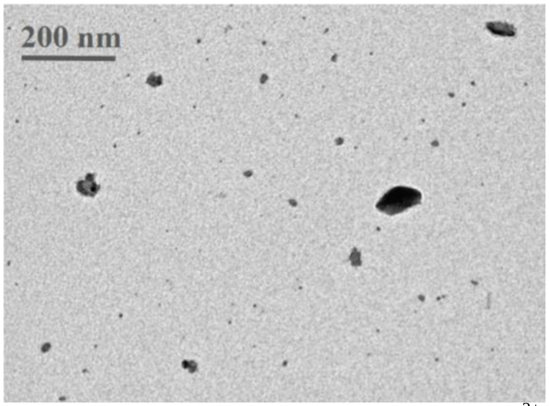

Figure 1: Representative Transmission electron microscope image of the Pr^{3+} doped KGdP nanocrystals.

Acknowledgements

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References

[1] I. Parreu, J.J. Carvajal, X. Solans, F. Díaz, M. Aguiló, *Chem. Mater.* **18**, 221−228 (2006)
[2] I. Adell, R.M.Solé, M.C. Pujol, M. Aguiló, F. Díaz, *ACS Omega*, **3**, 11307-11316 (2018)

The changes of the photoluminescence properties caused by ion implantation of erbium into single-crystalline and nano-crystalline ZnO

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Zinc oxide (ZnO, hexagonal wurtzite structure type) is a II-VI type wide-bandgap semiconductor ($E_g \approx 3.3$ eV) with low phonon energy and very good physical and chemical stability [1]. ZnO crystal materials are studied in photonics for many applications – e.g. nanostructures such as 1D nanowires for nanophotonics. For advanced device applications, however, a doping of the semiconducting nanostructures with various ions is often required. The structure changes induced by ion doping are used for the modification of the optical, electric and magnetic properties of ZnO. Erbium (+III) ions belong to the lanthanide rare-earth ions with the main emission transitions at the wavelength of around 1.5 μm. Ion doping of nanostructured ZnO with erbium ions enables to utilize both special properties of ZnO as well as light emission of erbium ions.
In this contribution we report on the results of Er^+ ion implantation into various ZnO structures – single-crystal ZnO, ZnO nanocrystalline thin films and ZnO nanorods. Er^+ ions were implanted using 400 keV energy and implantation fluences in the range from 5×10^{14} to 5×10^{15} ions/cm^2. The nanostructured thin films were deposited using reactive magnetron sputtering technique. ZnO nanorods were grown on fused silica glass substrates by hydrothermal process. Images of nanostructured ZnO were done by Scanning Electron Microscopy (SEM). Er concentration depth profiles and a degree of crystal damage were measured using Rutherford Backscattering Spectrometry (RBS) and RBS/Channeling. Additionally, Raman spectroscopy was used to analyse structural modifications of the prepared samples. Luminescence properties of the prepared thin films were investigated by photoluminescence spectroscopy in the ultraviolet-visible (UV-VIS) and near-infrared (NIR) spectral regions. Particular attention was given to the detailed analysis of the changes in complex UV-VIS luminescence of ZnO structures which originates from exciton-related and defect-related luminescence [2]. Substantial differences in luminescence found between different structure types of ZnO for both non-implanted and Er-implanted as well as annealed samples were studied and discussed.

Acknowledgements

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References

[1] Ü. Özgür, Ya. I. Alivov, C. Liu, et al., *Journal of Applied Physics*, **98**, 041301 (2005)
[2] P. A. Rodnyi, I. V. Khodyuk, *Optics and Spectroscopy*, **111**, 776–785 (201)

Poster

Experimental and theoretical study of erbium incorporation in various crystal materials – ZnO, $LiNbO_3$ and Al_2O_3

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The presented work deals with the study of luminescence properties of erbium ions incorporated in different crystal materials for the use in photonics and optoelectronics. Nowadays, various laser-active ion-doped crystalline materials are studied in the field of photonics. Zinc oxide (ZnO, wurtzite structure type) is a II-VI type wide-bandgap semiconductor ($E_g \approx 3.3$ eV) hexagonal crystal with low phonon energy and very good physical and chemical stability. Lithium niobate ($LiNbO_3$), on the other hand, is a trigonal crystal with unique combination of special properties – especially acoustooptic and electrooptic effect. Aluminium oxide in alpha-modification (also called sapphire) is a trigonal crystal with very similar structure type as $LiNbO_3$, exhibiting high optical transparency, very good physical and chemical stability and various special optical properties utilised for the modulation of optical radiation. Selected crystals are nowadays in photonics broadly studied and represent different crystal surroundings for the incorporated erbium. Erbium (+III) ions belong to the rare-earth lanthanide ions with the main emission transition at around the wavelength of 1.5 μm. Ion doping of crystals with laser-active ions is enabling to utilize both the emission of rare-earth ions and the properties (and special effects) of the crystals.

In this contribution we present a theoretical and experimental study of Er^+ ion implantation doping into the crystals of ZnO, $LiNbO_3$ and Al_2O_3. A study of subsequent annealing at the temperatures of 400–1000 °C in oxygen was done, as well. Samples were characterized by means of Er concentration depth profiles, disorder of the structures, positions of erbium as well as luminescence properties.

For the better understanding of Er-doped crystal structures, several theoretical models containing Er-ions in the most probable site locations were studied. Using density functional theory (DFT) ab-initio approach various properties were calculated including total energies of the structures, cohesive energies, Er defect-formation energies, etc. The theoretical results were compared with the experimental ones and the detailed study of the positions of Er atoms in the crystal structures was discussed.

It was found that in order to achieve good luminescence properties, erbium ions must occupy substitutional positions connecting with oxygen atoms, ideally with octahedral geometry. If erbium ions are incorporated in the tight structures, such as ZnO, they occupy unstable tetrahedral positions and the resulting intensity of erbium luminescence and the cohesive energy are low.

Acknowledgements

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Poster

β-$NaYF_4$ nanoparticles with core@shell morphology doped with Er^{3+}, Tm^{3+} and Yb^{3+} ions: their synthesis, characterisation and photoluminescence study

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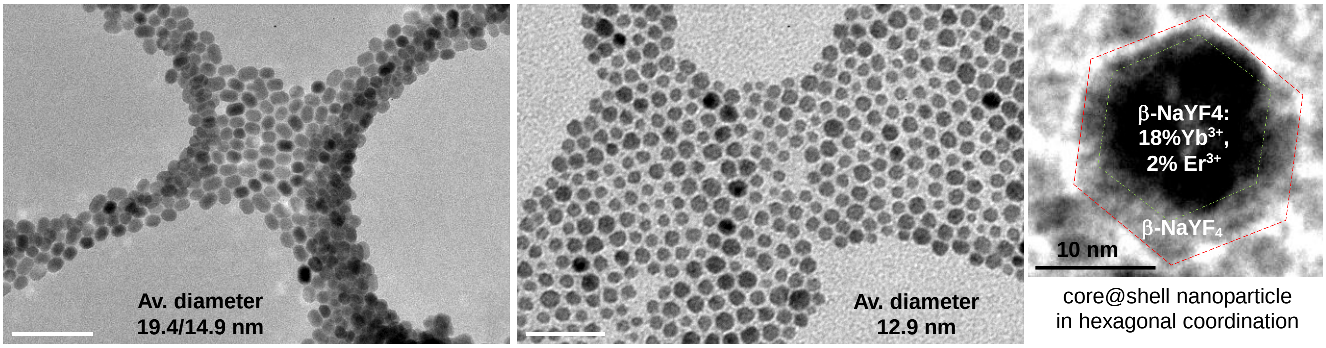
Rare earth fluorides ($NaREF_4$) can be applied as a matrix for various optical active lanthanide ions (Ln^{3+}), and these systems can be able to the photon upconversion process. They possess high refractive index and low phonon energy, which lead to the low probability of nonradiative decay, which consequently make the luminescent quantum yields are higher than in many inorganic matrixes [1]. These unique properties made that this group of materials could be applied in light-emitting devices, optical amplifiers, displays as well as biomedical fields including bioimaging, therapy and drug delivery, which make them significantly important in modern chemistry and material science [2].

In our work, the sodium-yttrium fluorides doped with lanthanide ions in the form of core@shell structure were prepared by a co-precipitation in high boiling solvents, because this method guarantees to obtain nanoparticles with hexagonal crystal phase and their diameter should be below 50 nm [2].

Rare earth fluorides were prepared in several steps, the first led to obtain $NaYF_4$ nanoparticles with α-phase morphology. Then the nanoparticles were transformed to β-phase morphology with larger diameter (around 15-20 nm). The final materials were achieved by the co-precipitation in high boiling solvents in which α-$NaYF_4$ shell nanoparticles were mixed with β-$NaYF_4$ core nanoparticles in selected molar ratio (phases were doped with Yb^{3+}, Tm^{3+} and/or Er^{3+} ions). The novelty of this work was the verification of influence of lanthanides precursors on the size and shape of nanoparticles (Fig. 1) and their photoluminescence properties. The materials were characterised using selected techniques, e.g. XRD and TEM were applied in the order to estimate the morphology and size of nanoparticles, photoluminescence spectroscopy was applied to understand the mechanism of photon up-conversion.



core@shell nanoparticle
in hexagonal coordination

Figure 1: TEM images of β-$NaYF_4$: 18% Yb, 2% Er@β-$NaYF_4$ (as source of Ln^{3+} ions were used acetates or chlorides).

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References

[1] Ch. Li, J. Lin , *J. Mater. Chem.* **20** 6831-6847 (2010)
[2] S. Dühnen, T. Rinkel, M. Haase, *Chem. Mater.* **27** 4033-4039 **(**2015)

Detailed analysis of Nd^{3+},X^{3+} (X=Gd,Y,Sc,Lu,Ce,La) codoped CaF_2 laser crystals for broadband laser operation

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Research on neodymium-doped fluoride crystals for laser applications has greatly advanced over the past few years, leading to very promising results [1] for broadband laser emission around 1.05µm. This near-infrared emission, previously known as completely quenched because of cross-relaxation energy transfers in singly Nd^{3+} doped materials increases spectacularly when co-doping the crystals with non-optically active “buffer” ions like Y^{3+} or Lu^{3+}. Broadband laser emission and ultra-short laser operation have been demonstrated and large scale high peak power diode-pumped amplifiers, because of a well mastered crystal growth, can be already anticipated. However, a detailed analysis of the spectroscopic and thermo-mechanical properties of these materials is yet to be done. In this work, we detail the main properties of different Nd^{3+} incorporation sites, which enable the optimisation of these materials as oscillators and laser amplifiers. Absorption and excitation spectroscopy measurements on CaF_2 samples with 0.5% Nd and various buffer ions show that the absorption band shape substantially changes when changing the buffer ion indicating the existence of different centres comprising Nd-Nd and Nd-X (X=Gd,Y,Sc,Lu,Ce,La) clusters. Furthermore, fluorescence spectra recorded around 1.05µm change significantly when pumping at different wavelengths further confirming the presence of different emitting Nd^{3+}-X^{3+} centres. Time-resolved excitation and emission spectroscopy has been used to distinguish these different emitting centres by carefully choosing the buffer co-dopant, the recording time window and the emission or excitation wavelength for the excitation and emission spectra respectively.

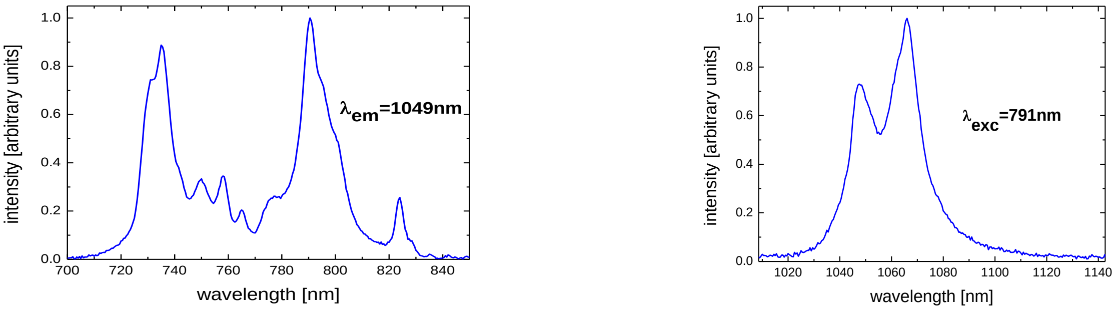

Figure 1: Left, excitation spectra of CaF_2:0.5%Nd,5%Gd detected at 1049nm. Right, emission spectra of CaF_2:0.5%Nd,5%Gd excited at 791nm.

Acknowledgements

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References

[1] J. L. Doulan, L. B. Su, G. Brasse, A. Benayad, V. Mènard, Y. Y. Zhan, A. Braud, P. Camy, J. Xu and R. Moncorge, *J. Opt. Soc. Am. B*, **30**, 3018-3021 (2013)

Concentration dependence of spectroscopic properties and energy transfer analysis of the fluorophosphate glasses with small phosphates additives doped with Er^{3+}/Yb^{3+} ions

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Fluorophosphate glasses (FPG) have been the subject of numerous studies [1]. Among various glasses, fluorophosphate glasses have been regarded as important host due to their, physical properties: low phonon energy, high concentration of doped rare earth (RE) ions, high transparency, negative variation of the refractive index with the temperature and low nonlinear refractive index (n_2).

In the work the new fluorophosphate glasses co-doped with Er^{3+}/Yb^{3+}ions with composition $5Ba(PO_3)_2$–(85-x)(AlF3 –CaF2 –MgF2 –BaF2–SrF2)–5 YbF3-xErF3, x=0, 0.1, 0.5, 1.0, 2.0, 3.0,4.0, 5.0 have been developed. Influence of the concentration of the rare earth ions on the luminescent properties and the crystallization ability has been studied. Using the Judd-Ofelt theory the phenomenological intensity parameters Ωt (t= 2; 4; 6) were obtained for all glasses studied. The stimulated emission cross-sections of $^4I_{13/2} \rightarrow ^4I_{15/2}$ transitions have been determined by the Fuchtbauer-Landenburg equation (FL) and the modified reciprocity method (MR) for glasses and ceramics. Emission decay behavior at 1.5 μm have been examined with respect to energy transfer between ytterbium and erbium. The analysis of the luminescence quenching depending on the glass composition has been carried out. The gain cross-section spectra have been calculated for the glasses.

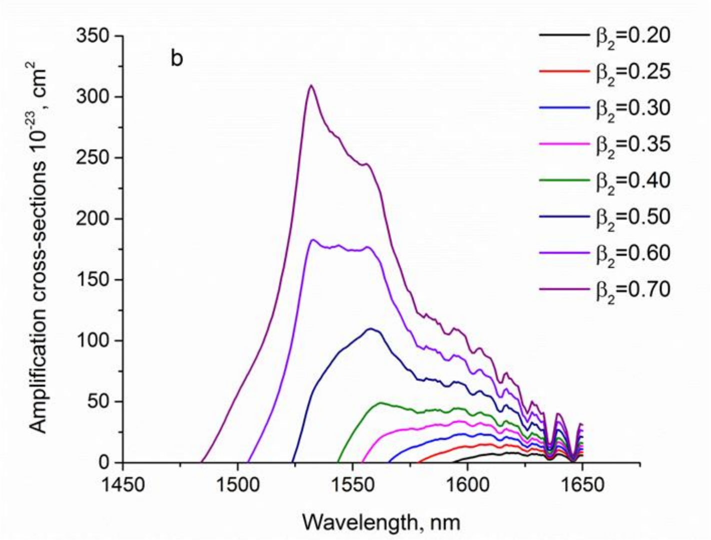

Figure 1: Spectra of gain cross-sections glasses at different values of β_2

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Acknowledgements

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References

[1] J.F. Philipps, T. Töpfer, H. Ebendorff-Heidepriem, D. Ehrt, R. Sauerbrey, *Appl. Phys. B Lasers Opt*. 72, 399–405(2001).

Poster

Study of persistent luminescence in $SrSi_2N_2O_2:Eu^{2+}$, M (M=Ce, Cr, Er, Dy, Nd)

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Persistent luminescent (PersL) materials are capable of emitting light for several minutes to hours after the source of the excitation light has been removed. The most popular applications of the PersL materials are safety signage, displays, decorations and toys. [1, 2] However, persistent luminescent phosphors are recently in interest of the application like bioimaging and information storage materials [3,4] due to their storage ability of excitation light. In this work the extensive spectroscopic study of novel persistent luminescence materials $SrSi_2N_2O_2:Eu^{2+}$, M (SSON:Eu, M, M = Ce^{3+}, Cr^{3+}, Er^{3+}, Dy^{3+}, Nd^{3+}) are presented. Steady state luminescence and luminescence excitation spectra, as well as the time resolved spectra, temperature dependent luminescence kinetics and thermoluminescence investigations were performed. The luminescence of SSON:Eu and SSON:Eu, M consists of broad band peaked at 550 nm related to transitions from the lowest $4f^6 5d^1$ state to the ground state $4f^7$ ($^8S_{7/2}$) of Eu^{2+} ions.

To investigate the PersL phenomena in SSON:Eu, M the thermoluminescence (TL) and temperature influence on the time evolution of luminescence were analyzed. The TL glow curve of SSON:Eu shows a broad band with maximum around 335 K. The samples codoped with Er, Cr and Ce show similar TL glow curves like SSON:Eu. The TL glow curves of samples codoped with Nd and Dy are significantly different and shifted towards higher temperature compared to SSON:Eu. The codoping with Nd and Dy enhances the population of deeper traps producing TL band peak around 370 K and two overlapping bands at 350 and 370 K for Dy and Nd, respectively. Samples SSON:Eu, M (M=Ce, Cr, Er) exhibit persistent luminescence which is visible a few minutes after switching off UV light, while for M=Dy, Nd which do not exhibit PersL at RT, the PersL appear at higher temperature which confirms that the deeper traps are responsible for PersL in this samples.

Acknowledgements

References

[1] Matsuzawa, T.; Aoki, Y.; Takeuchi, N.; Murayama, Y., J. Electrochem. Soc., 143, 2670– 2673 (1996)

[2] Trojan-Piegza, J.; Niittykoski, J.; Hölsä, J.; Zych, E., Chem. Mater., 20, 2252– 2261 (2008)

[3] Pan, Z.; Lu, Y. Y.; Liu, F. ,Nat. Mater., 11, 58– 63 (2012)

[4] Abdukayum, A.; Chen, J. T.; Zhao, Q.; Yan, X. P., J. Am. Chem. Soc., 135, 14125– 14133 (2013)

Tm^{3+} photoluminescence in $Si_{0.75x}Al_{1-x}N$ libraries grown by combinatorial magnetron sputtering

Poster

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Divalent thulium (Tm^{2+}), as a dopant in industry standard materials (e.g. SiAlONs), has a good potential to establish higher efficiency luminescence solar concentrators (LSC) for electricity generating glass applications. Tm^{2+} has been reported to provide 65% absorption of the solar spectral range with no losses due to self-absorption, while remaining relatively colourless [1]. However, understanding the valence stability of Tm in SiAlONs is still a big challenge. Mostly because direct experimental information of luminescent RE-doped SiAlONs thin films is still scarce. This work contributes to this challenge by adding new excitation and emission photoluminescence information of Tm^{3+} doped $Si_{0.75x}Al_{1-x}N$ alloys grown by combinatorial magnetron co-sputtering deposition. The resulting libraries have gradient composition with a wide range of Al/Si to N ratios. They were characterized with automated xy-characterisation (transmission, reflection, photoluminescence) methods combined with position dependent EDX elemental composition [2,3]. Phase diagrams were constructed from this data correlating properties versus composition. There is a linear relationship between the lowest d → f excitation energy transition of Tm^{3+} and the relative content of Al to Si, according to the polarization model and the ligands average electronegativity [4,5].

References

[1] O.M. ten Kate, K.W. Krämer, and E. van der Kolk, *Sol. Energy Mater. Sol. Cells*, **140**, 115 (2015).
[2] E.P.J. Merkx, S. van Overbeek, and E. van der Kolk, *J. Lumin.*, **208**, 51 (2019).
[3] E.P.J. Merkx and E. van der Kolk, *ACS Comb. Sci.*, **20**, 595 (2018).
[4] C.A. Morrison, *J. Chem. Phys.*, **72**, 1001 (1980).
[5] P. Dorenbos, *Phys. Rev. B*, **65**, 235110 (2002).

Up-conversion emission in strontium fluoride doped with erbium ions upon 1532 nm excitation

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Lanthanide ions (Ln^{3+}) are characterized by unique photo-chemical properties [1]. Nanoparticles based on pairs of Ln^{3+} e. g. Yb^{3+}/Er^{3+}, reveals energy transfer up-conversion (ETU) and their up-conversion properties are the most often investigated [2,3]. Nanoparticles doped with one type of Ln^{3+} ion can also present up-conversion luminescence, usually resulting from ground and excited state absorption processes, what can be utilized in optoelectronics, photovoltaics or phosphors production [4,5].
In our work nanocrystals of strontium fluoride doped with 2.5% to 20% of erbium ions (SrF_2:x%Er^{3+}) were obtained by hydrothermal synthesis, in the form of powders and aqueous colloids. The proper reagents ratio and synthesis conditions were established and applied.
The structural and morphological characteristic of synthesized nanoparticles was carried out by using X-ray powder diffraction, transmission electron microscopy, inductive coupled plasma and dynamic light scattering methods.
Spectroscopic properties of obtained nanocrystals were investigated by measurements of excitation and emission under excitation in near-infrared range at 978 nm and 1532 nm (second and third biological window), luminescence lifetimes and emission power dependencies. The mechanisms responsible for the observed up-conversion behavior was proposed.
The structural, morphological and spectroscopics properties of obtained nanocrystals were compared, showing dependence on the amount of Er^{3+} ions in products.

Acknowledgements

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References

[1] J.-C. G. Bunzli, *Accounts of Chemical Research.*, **39**, 53-61 (2006)
[2] M. Runowski, J. Marciniak, T. Grzyb, D. Przybylska, A. Shyichuk, B. Barszcz, A. Katrusiak, S. Lis, *Nanoscale*, **9**, 16030-16037 (2017)
[3] C. Zhang, P. an Ma, C. Li, G. Li, S. Huang, D. Yang, M. Shang, X. Kang, J. Lin, *Journal of Materials Chemistry*, **21**, 717-723 (2011)
[4] K. V. Ivanovskikh, V. A. Pustovarov, A. Smirnov, B. V. Shulgin, *Journal of Alloys and Compounds*, **451**, 65-67 (2008)
[5] K. Zheng, W. Song, G. He, Z. Yuan, W. Qin, *Optics Express*, **23**, 7653-7658 (2015)

Radioluminescence of $Lu_3Al_5O_{12}$:Ce single crystal and transparent polycrystalline ceramic at high temperatures

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Scintillators are luminescent materials used for the detection and measurement of ionizing radiation that find application in many fields, including medical imaging, oil exploration, security, and high energy physics experiments. Among the many possible forms, polycrystalline ceramic scintillators have received increasing attention due to advantages over single crystals, including faster and lower cost fabrication methods, higher homogeneity of the dopant, greater shape control, and easier fabrication of high melting temperature materials. Presently, it is important to establish a benchmark between the performance of single crystal and polycrystalline ceramic scintillators. Also, the luminescence response of garnets at high temperatures is of current technological relevance [1,2]. Within this context, the radioluminescence (RL) performance of a $Lu_3Al_5O_{12}$:Ce (LuAG:Ce) single crystal and a transparent polycrystalline ceramic was comparatively evaluated under X-ray excitation at high temperatures, from room temperature (RT) up to 600 °C. Two emission bands were observed, one within 1.8-2.8 eV ascribed to Ce^{3+}, and another within 2.8-4.5 eV ascribed to the collective behavior of different types of defects. The RL intensity of the Ce^{3+} band increased by a factor of 1.4x from RT up to 450 °C for the single crystal, and by a factor of 2x up to 300 °C for the polycrystalline ceramic. Beyond these respective temperatures, it decreased linearly with a rate ~1.3x faster for the single crystal. At about 530 °C, RL intensity was the same as at RT for both materials. These results demonstrated that LuAG:Ce scintillators can be effectively used over a broad range of temperatures.

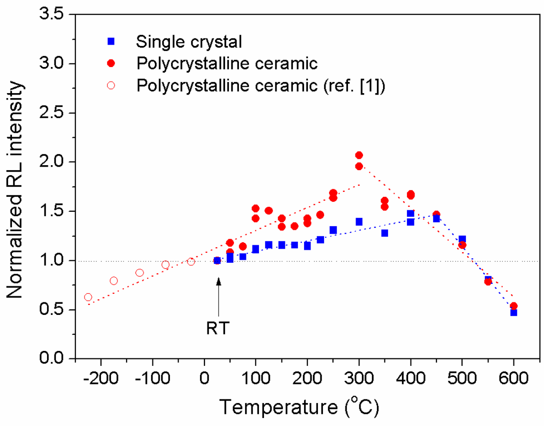

Figure 1: RL intensity normalized for the room temperature intensity as a function of the temperature for the single crystal (solid squares), polycrystalline ceramic (this work = solid circles; data from ref. [1] = open circles).

Acknowledgements

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References

[1] J. Xu, L. Fan, Y. Shi, J. Li, J. Xie, F. Lei, *IEEE Trans. Nucl. Sci.*, **61**, 373-379 (2014)
[2] A.A. Trofimov, C. Li, K.S. Brinkman, and L.G. Jacobsohn, *Opt. Mater.*, **68**, 7-10 (2017)

Poster

Up-conversion phenomenon of core@shell nanoparticles based on SrF_2, doped with Yb^{3+}, Er^{3+} and Nd^{3+} ions excited at 808 nm and 975 nm wavelength

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A significant part of the present study relates to nanoparticles showing luminescence, especially up -conversion phenomenon. This process is a conversion of energy from the infrared to visible or ultraviolet light. In contrast to the classical luminescence, up-conversion is an anti–Stokes phenomenon. By sequential absorption of two or more photons (or simultaneously in some cases), the emission of light occurs, with a shorter wavelength than the excitation, which is the emission of radiation of higher energy [1]. The use of fluoride nanomaterials doped with lanthanide ions Ln^{3+} (Ln = Yb, Er, Nd) have reasonable grounds - they have low phonon energy, high chemical stability, are good electron acceptors and phosphors based on them could have a high quantum yield of emission [2,3]. Due to their properties, fluorides can be used in the production of efficient phosphors, new light sources, semiconductor lasers, televisions or computers. Also important are their potential biomedical applications [4]. Nanomaterials presented in this research contain Nd^{3+} ions in the active shell structure. Thanks to this they can be excited by two different wavelengths from near infrared radiation (NIR)- 808 nm and 975 nm. The use of NIR light allows the penetration of tissue localized deep below the skin. This is a result of the existence of "optical window" for biological tissues, thanks to which the harmful effect of radiation to healthy cells can be reduced. Furthermore, excitation under 808 nm enables to avoid heating of cells, due to smaller absorbance of mentioned radiation by tissue components [5]. To obtain efficient luminescence from the products, structures with active core and active shell have been synthesized [6]. The above-mentioned luminophores were prepared by the hydrothermal method. Morphology and structure of obtained materials were described using X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier- Transmission Infrared Spectroscopy (FT-IR), dynamic light scattering (DLS) and zeta potentials. Obtained nanoparticles were characterized by small size not exceeding 60 nm and spherical shape. Spectroscopic properties of obtained nanopowders were analyzed on the basis of emission and excitation spectra, luminescence decays and dependencies of luminescence intensity on laser powers measured for all observed transitions.

Acknowledgments

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References

[1] F. Auzel, *Chem. Rev.,* **104**, 139–73, (2004)
[2] G. De, W. Qin, W. Wang, and B. Gui, *Opt. Commun.,* **282**, 2950–2953 (2009)
[3] T. Grzyb, S. Balabhadra, D. Przybylska, M. Węcławiak, *J. Alloys Compd.,* **649**,606-616,(2015)
[4] M. V. DaCosta, S. Doughan, Y. Han, U.J. Krull, *Anal. Chim. Acta,* **832,** 1–33(2014)
[5] B. Liu, C. Li, P. Yang, Z. Hou, J. Lin, *Adv. Mater.* **29,** 1605434 (2017).
[6] Y. Chen, B. Liu, X. Deng, S. Huang, Z. Hou, C. Li, J. Lin, *Nanoscale,* **7,** 8574–8583 (2015)

Scintillation properties of Tm-doped $GdAlO_3$ crystals doped with different Tm concentrations

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Scintillators which convert high energy ionizing radiation to thousands of low-energy photons, have been playing a major role in many fields of radiation detection, including medical imaging, security, environmental monitoring, and high-energy physics. Recently, scintillators emitting near infrared (NIR) photons have attracted much attention because NIR photons have unique characteristics such as a high penetration power without a fatal damage to a human body [1]. Since an optical window is from 700-1200 mm in the human body, the scintillator materials emitting NIR photons can be applied for radiation-based bio imaging applications [2]. However, in spite of such usefulness as above, there have been few reports on NIR-emitting scintillators, and there remains much room for studying on this topic. In order to expand the research on scintillators emitting NIR photons, in this study, we synthesized $GdAlO_3$ (GAP) single crystals doped with different concentrations of Tm by the Floating Zone method and then evaluated the photoluminescence (PL), and scintillation properties. Since Rare earth doped GAP exhibit high density, chemical and thermal stability, and unique electronic and spectroscopic properties, their photoluminescence properties have been already studied. However, Scintillation properties of Tm-doped GAP have not been studied yet.

Figure 1 shows PL emission map of 1% Tm-doped GAP. The sample showed two emission and these can be identified as the electronic transitions of Tm^{3+} as: $^1G_4 \rightarrow {}^3H_6$ (440 nm) and $^3H_4 \rightarrow {}^3H_6$ (800 nm) [3]. **Figure 2** represents X-ray induced scintillation spectra of 1% Tm-doped GAP in NIR wavelength. The sample showed emission due to electronic transitions of $^3H_4 \rightarrow {}^3H_6$ (800 nm) and $^3H_4 \rightarrow {}^3F_4$ (1460 nm). Throughout the present work, we confirm that Tm-doped GAP single crystals work as a scintillator.

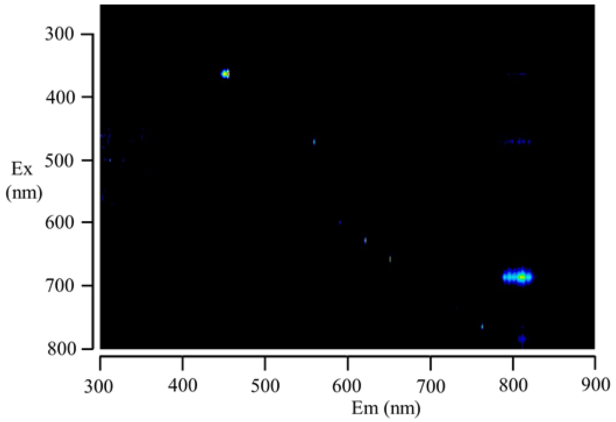

Figure 1. PL maps of 1% Tm-doped GAP samples. The horizontal and vertical axes show emission and excitation wavelength, respectively.

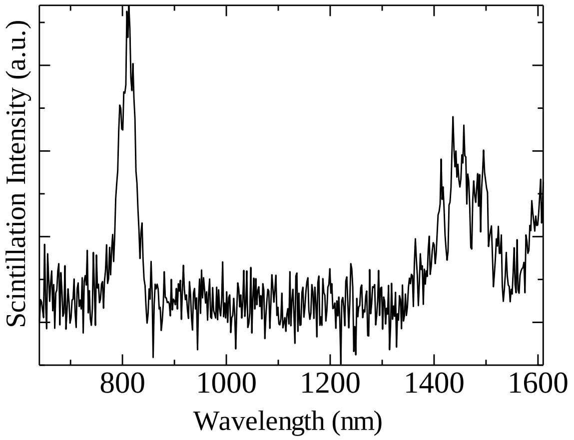

Figure 2. X-ray induced scintillation spectra of 1% Tm-doped GAP in NIR wavelength.

References

[1] J.-L. Boulnois, *Lasers Med. Sci.*, **1**, 47 (1986).
[2] L. Sudheendra, *et al.*, *Chem. Mater.*, **26**, 1881 (2014).
[3] H. Zhang, *et al.*, *Solid State Commun.*, **132**, 527 (2004)

A NIR emitting scintillator material $YAlO_3$: Re^{3+} (Re= Er, Ho, Pr, Tm)

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Inorganic scintillators are a kind of the fluorescent materials, and they have a function to convert the absorbed energy of ionizing radiation with typically keV-GeV orders of energy to thousands of photons with a few eV immediately [1]. They are used in various different fields; for example, medical imaging, security, oil-logging, environmental monitoring and high energy physics. Among scintillator materials, perovskite materials have, in particular, superior fluorescence properties, and many studies were performed to investigate their scintillation properties [2]. In recent years, the scintillators emitting near-infrared (NIR) photons have attracted much attention because NIR photons are more suitable for biomedical imaging and probe than ultraviolet or visible emitting ones due to the high transparency to the human body [3]. However, there have been few reports on NIR emitting scintillators, and there remains a large room for study about this topic. In this study, we synthesized Rare-earth (Er, Ho, Pr, Tm) doped $YAlO_3$ perovskite single crystals by the Floating Zone (FZ) method. After the crystal growth, we evaluated their photoluminescence (PL), and scintillation properties.

Figure 1 illustrates all the samples used in this study. We consider that color of these samples is influenced by Rare-earth. **Figure 2** represents X-ray induced scintillation spectra of all samples in the NIR range. The Er doped sample emitted around 1000 and 1550 nm. The Ho doped sample showed emission around 1000 and 1200 nm. The emission peak of Pr doped sample appeared 900 and 1250 nm. At last, the Tm doped sample emitted around 800 and 1500 nm. Throughout the present work, we report PL and scintillation properties of Rare-earth doped $YAlO_3$ single crystals.

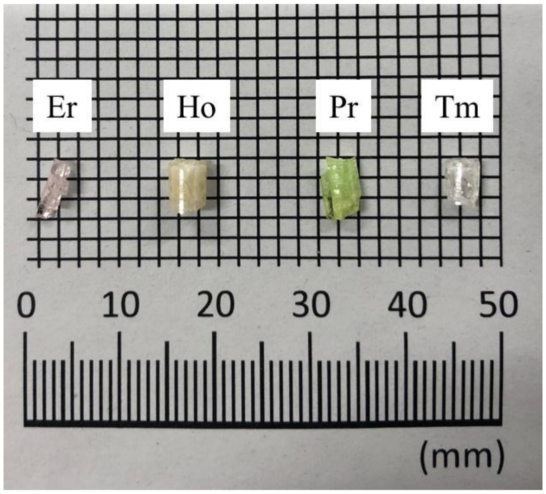

Figure 1. Photograph of Rare-earth doped YAlO3 samples.

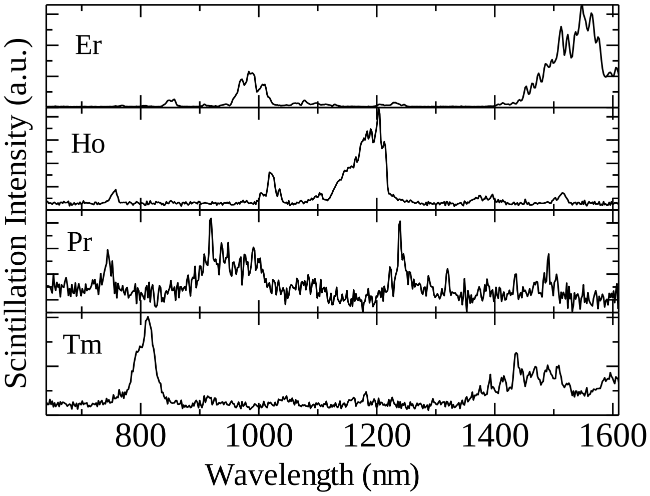

Figure 2. X-ray induced scintillation spectra of Rare-earth doped $YAlO_3$ in the NIR range

References

[1] T. Yanagida, *Opt. Mater.*, **35**, 1987 (2013).
[2] T. Kuro, D. Nakauchi, G. Okada, N. Kawaguchi, T. Yanagida, *Opt. Mater.*, **64**, 282 (2017)
[3] R. Weissleder, *Nat. Biotechnol.*, **19**, 316 (2001).

Rare-earth doped optical fiber employing in-situ metal oxidation

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This paper will highlight a new twist on the molten core method [1]; namely, a reactive molten core (rMC) whereby metallic core precursors are employed, which undergo oxidation during fiber fabrication. More specifically, two cases will be discussed: (1) an erbium doped yttrium-aluminosilicate optical fiber, and resultant optical amplifier [2], originating from Er:YAG wrapped in an aluminum foil, drawn in a silica cladding and (2) a ytterbium metal wire encapsulated in a sapphire tube, sleeved in silica and drawn into fiber. In the former example, the sesquioxide dopants promote an intrinsically low Brillouin gain coefficient (~ 11 dB below conventional optical fiber), with losses of about 0.25 dB/m, and a slope efficiency of 38.2% (limited by background losses). In the latter, the high Yb_2O_3 content (~ 15 mole %) completely quenches the Yb^{3+} emission such that pump light is entirely converted to heat. This then was used as a flexible fiber micro-heater that had very fast on/off rates that followed closely the pump power (Figure 1). An all-fiber modulator based on this same fiber also will be discussed.

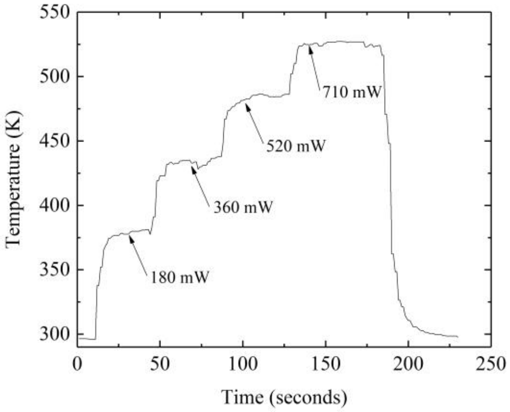

Figure 1: Temperature at an optical fiber micro-heater obtained through the *in-situ* oxidation of a rare-earth metal during molten core fiber fabrication.

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References

[1] J. Ballato and A. C. Peacock, *APL Photonics* **3**, 120903 (2018).
[2] M. Tuggle, C. Kucera, T. Hawkins, M. Cavillon, G. Pan, N. Yu, P. D. Dragic, and J. Ballato, *Optical Materials X* **1**, 100009 (2019).
[3] N. Yu, M. Tuggle, C. Kucera, T. Hawkins, A. Mironov, J. Ballato, and P. Dragic, Conference on Lasers and Electro-Optics, OSA Technical Digest (online) (Optical Society of America, 2019); in press.

Photoluminescence and photoluminescence excitation spectra of Eu and Si co-doped AlN films for visible light-emitting devices

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1. Introduction

GaN/InGaN multi quantum wells (MQWs) have been widely used as active region for blue LEDs, but the use of rare elements (Ga, In) and harmful elements (As, P) should be avoided to build a sustainable future. AlN is an environmentally friendly material and it has attracted the attention as an optoelectronic material in the ultraviolet spectral range due to its wide direct band-gap of 6.2 eV. Furthermore, visible EL and CL have been observed from p-Si/AlN/Au heterostructured films [1] and Eu, Si co-doped AlN powders [2], respectively. Thus, AlN can be one of alternative materials to replace existing visible LED materials. It has been reported that singly Eu doped AlN exhibits a sharp red emission due to the Eu^{3+} 4f shell transition, while the Si and Eu co-doped AlN shows a broad blue emission from Eu^{2+} [2]. In this work, Eu and Si co-doped AlN films were formed by reactive co-sputtering to optimize blue PL from Eu^{2+} in AlN by changing Eu precursors and annealing temperature.

2. Experimental

Eu and Si co-doped AlN films were deposited on c-axis oriented sapphire substrates by reactive RF magnetron co-sputtering using an Al target with Eu_2O_3 or EuS chips and Si chips in Ar/N_2 flow. After the deposition, the samples were subjected to thermal annealing at T_a=1000-1200°C for 60 min in N_2 atmosphere to promote crystallization of AlN and optical activation of Eu^{2+}. They were characterized by XRD, TEM, CL, PL (λ_{ex} = 325 nm) and PLE measurements.

3. Results and Discussion

XRD measurements showed that the AlN (0002) peak is dominant for Eu_2O_3 and Si co-doped AlN films (Eu_2O_3-films), while the AlN (10-12) peak is dominant for EuS and Si co-doped AlN films (EuS-films). A surface decomposition was observed from Eu_2O_3-films after the thermal annealing at 1100°C, but it was hardly seen from EuS-films. Figures 1 and 2 show PL and PLE spectra for Eu_2O_3-films annealed at 1100°C and EuS-films annealed at 1200°C, respectively. PL from Eu^{2+} is efficiently excited above the band-gap of AlN in both cases. PLE intensity at 275 nm (4.51 eV) strongly increases for Eu_2O_3-films, while it remarkably decreased for EuS-films, which suggests that the density of N_i (interstitial N atom)-related defect levels (4.51 eV) [3] was reduced by using EuS as a doping precursor.

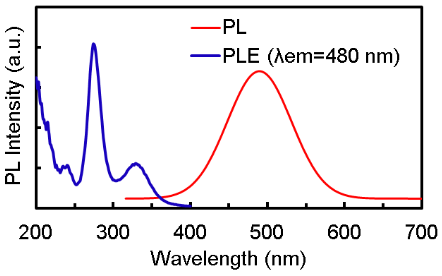

Figure 1 PL and PLE spectra for Eu_2O_3-films

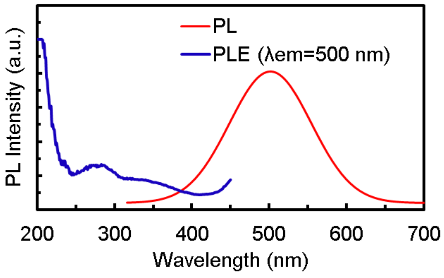

Figure 2 PL and PLE spectra for EuS-films

References

[1] J. L. Zhao et al., *Appl. Phys. Lett.*, **94**, 093506 (2009). [2] Benjamin Dierre et al., *J. Am. Ceram. Soc.*, **92**, 1272-1275 (2009). [3] I. Gorczyca et al., *Solid State Communications*, **101**, 747 (1997).

Poster

Luminescent properties of Titania doped with nanoparticles of Gadolinium oxide and Europium

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In this work were synthetized four samples of Titania doped with nanoparticles of gadolinium oxide which, previously, were doped with Europium at 2 mol %. The doped samples of Titania were synthetized using the sol gel method and the nanoparticles of gadolinium oxide were synthetized by the precipitation reaction of precursors of gadolinium nitrate hexahydrate and europium nitrate pentahydrate [1]. All the samples were submitted to a thermal treatment to obtain the Anatase as crystalline structure. The optical properties as the absorption, emission and emission decay times, besides the X-ray diffraction patterns and the Raman spectra were recorded and analysed. The band gap was calculated from the extrapolation of the linear fit in the absorption edge range in the Tauc plot, the electronic transitions of the Europium were identified, and the behaviour of the ion was explained. Finally, due that the high luminescent intensity of the nanoparticles of gadolinium oxide doped with europium, the possible incorporation of these into the matrix of Titania, the possibility for exciting these using lower energy (393 nm) and consequently the shift in the band gap; made it possible to propose the material be used for photonic applications, for example, LED´s or sensors for 393 nm and for photocatalytic applications.

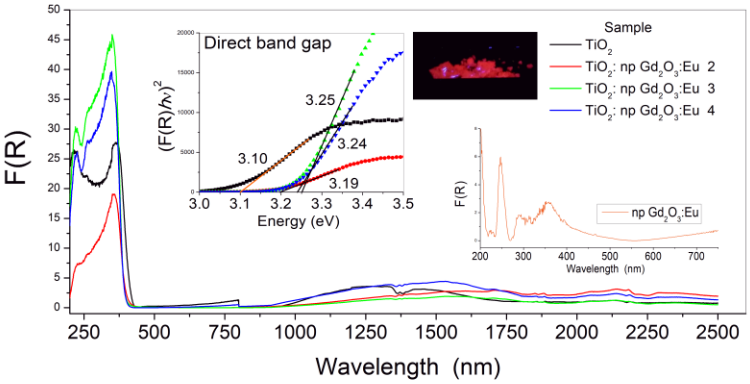

Figure 1: Absorption spectra of the four TiO_2 samples and of the nanoparticles of Gadolinium oxide. The absorption spectra for the undoped and doped samples are shown in the range between 240 and 2500 nm, while for the nanoparticles is shown between 240 and 750 nm. In the inset $(F(R)h\nu)^2$ vs photon energy is presented in the absorption edge range. The image shows the emission of the nanoparticles using a source of 365 nm.

Acknowledgements

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References

[1] Ranu K Dutta, Avinash C. Pandey, *Nanoscience & Technology*, **2(2)**, 1-6 (2015)

Synthesis and characterization of an hybrid SiO_2-PMMA material doped with luminescent Eu doped Gd_2O_3 nanoparticles

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Luminescent gadolinium oxide nanoparticles doped with europium were synthesized by precipitation reaction using gadolinium and europium nitrates as precursors. This particles were used because their magnetic and luminescent properties that make them useful for optoelectronic and imaging applications. [1]

The Eu^{3+} doped Gd_2O_3 nanoparticles were introduced in a hybrid SiO_2-PMMA matrix synthesized using the sol-gel method by the simultaneous hydrolysis of tetraethyl orthosilicate (TEOS) and the polymerization of methyl methacrylate (MMA) using ethanol as solvent. Trimethoxysilyl propyl methacrylate (TMSPM) was used as bonding agent between the polymer and the SiO_2 molecules. The hybrid matrix was chosen because its high transparency and improved mechanical properties over a simple SiO2 matrix. Also the sol-gel method allows for a easy doping the material and the fabrication of thin films and monoliths. [2]

The material was characterized by UV-vis and luminescence spectroscopy, the Eu^{3+} doped Gd_2O_3 nanoparticles preserved their luminescent properties inside the matrix as shown in figure 1. Also a phase separation was observed between the nanoparticles and the matrix forming a two layer material. The nanoparticles formed a thin luminescent layer and the SiO_2-PMMA matrix functioned as substrate. This could be useful in sensors development by the functionalization of the nanoparticles layer.

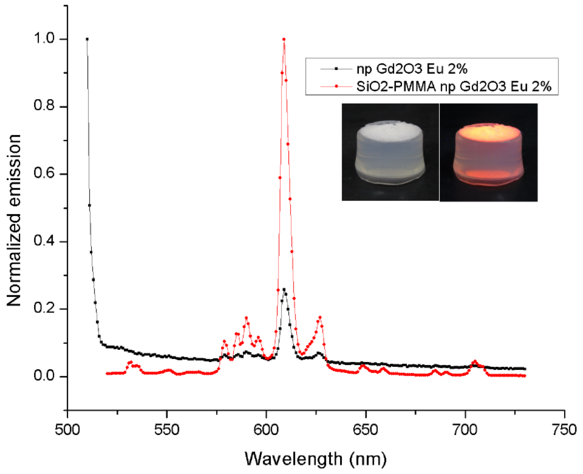

Figure 1: Emission spectra of the Eu^{3+} doped Gd_2O_3 nanoparticles inside and outside the matrix.

References

[1] Chaudhary, Savita & Kumar, Suraj & Umar, Ahmad & Singh, Jasmeet & Rawat, Mohit & Mehta, Surinder, *Sensors and Actuators B Chemical*, **243**, 579-588 (2017)

[2] J. De la Cruz, R. Palomino Merino, P. Trejo-García, J. E. Espinosa, R. Aceves Torres, E. Moreno-Barbosa, J. J. Gervacio-Arciniega, E. Soto, *Optical Materials*, **87**, 42-47 (2019)

The effect of Zn, Al and Ge on the phonon energy and Er^{3+} photoluminescence in silicate glasses

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Glasses doped with rare-earth (RE) ions have been extensively studied in past decades due to their vast potential in photonics and optoelectronics. One of the most studied ions for the use in visible and infrared spectral regions is erbium ion. Er^{3+} ions are very perspective in photonics due to their photoluminescence around 1.5 μm, which corresponds to second telecommunication window. Silicate glasses are amongst the most widely used materials as matrices for RE ions because of their low cost, easy manufacturing and good compatibility with existing optical networks. However, photoluminescence of RE ions in silicate glasses is severely limited due to their high phonon energy and low solubility of RE ions. The exact relationship between glass composition and photoluminescence of RE ions is not yet fully understood due to a hardly defined amorphous structure of glass and bonds between RE ions and glass network. In the past, our group has confirmed positive influence of zinc on photoluminescence of Er^{3+} ions in silicate glasses [1]. In this work, we aim to expand on this research by preparing silicate glasses with different intermediate oxides and study the relationship between glass structure, phonon energy and Er^{3+} photoluminescence.

In this work, we have prepared a group of zinc(Zn^{2+})-silicate, aluminium(Al^{3+})-silicate and germanium(Ge^{4+})-silicate glasses doped with erbium and studied the impact of aforementioned elements on glass structure, phonon energy of the glasses and photoluminescence of erbium. The glasses were prepared by standard melt-quenching technique. Basic optical and physical properties of the glasses were measured, such as refractive index by m-line spectroscopy, density by pycnometer and glass transition temperature by differential scanning calorimetry. Transmission of glasses was measured by absorption spectroscopy, phonon energy was measured by Raman spectroscopy. The influence of zinc, aluminium and germanium on the photoluminescence of glasses was measured by photoluminescence spectroscopy in the infrared region and the relationship between glass composition, structure, phonon energy and Er^{3+} photoluminescence was evaluated.

Acknowledgements

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References

[1] Vytykacova, S. et al., *Ceramics-Silikáty*, **62**, 188-193 (2018)

Poster

Surface modification of $NaYF_4$: Yb^{3+}, Er^{3+}@$NaYF_4$ up-conversion nanoparticles for biological applications

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Nanoparticles (NPs) have at least one dimension in less than 100 nm range. Core/shell type nanostructures are composed of at least two different compounds and matrices: core surrounded by the external layers of the shells. These structures have both the properties of the core and the shells, which is a reason of their unique multifunctionality. Intense and multicolored luminescence is a result of 4f-4f electronic transitions in lanthanide ions. Inorganic materials doped with some of the lanthanide ions are known as nanoluminophores. They can emit light under irradiation by wavelengths from ultraviolet to the near infrared range (NIR) [1]. Particularly interesting is the up-conversion phenomenon (UC). Up-conversion is the process in which the sequential absorption of two or more photons leads to the emission of light at a shorter wavelength than the excitation wavelength, e.g. conversion from infrared to visible light [2].

The $NaYF_4$:Yb^{3+}, Er^{3+}@$NaYF_4$ nanoparticles were obtained using precipitation in high-boiling solvents. Because of hydrophobic ligand (oleic acid) coordinating NPs after synthesis, their surface is hydrophobic. Further functionalization is necessary to perform biocompatibility. NPs were transferred to aqueous solutions by ligand-free modification. The NPs were treated with HCl, which protonates the oleate ligand resulting in the release of oleic acid from the surface. The biocompatibility of NPs means that e.g. they are non-toxic for the organism, and the immune system. Modification of nanoparticle's surface should not significantly increase the size of nanoparticles. Appropriately functionalized NPs can be applied in biosensing and biomedical imaging [3].

Moreover, biocompatible NPs were obtained by modification and functionalization of their surface with e.g. silica and polyacrylic acid. In the described study, the stability of colloids, size of nanoparticles and emission spectra upon continuous-wave excitation at 980 nm were presented (confirmed by zeta potential measurement, dynamic light scattering and spectrometer with CCD camera, respectively) and measured directly after surface modification and additionally after 24, 48 hours and one month. Furthermore, the TEM images showed changes in size of the NPs coated with an appropriate ligand and ligand-free NPs.

Acknowledgements

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References

[1] Sun, L.; Li, L.; Gao, R.; Tang, K.; Fu, L.; Ai, X.; Zhang, J.; *Physical Chemistry Chemical Physics*, **20**, 17141-17147 (2018)
[2] Grzyb, T.; Przybylska, D.; *Inorganic Chemistry*, **57**, 6410-6420 (2018)
[3] Chen, X.; Tang, Y.; Liu, A.; Zhu, Y.; Gao, D.; Yang, Y.; Sun, J.; Fan, H.; Zhang, X.; *ACS Applied Materials & Interfaces*, **10**, 14378-14388 (2018)

How to tune the UC luminescence in YPO_4 nanoparticles doped with lanthanide ions?

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Trivalent lanthanide ions (Ln^{3+}) are widely used for luminescence purposes due to abundant energy levels and unique **spectroscopic properties**, like high luminescence efficiency, sharp emission bands (being the result of the infra f-f transitions), long lifetimes and ability of showing down - (DC) and up-conversion (UC) [1]. The latter is a particularly interesting process, especially when occurs in **inorganic phosphate matrices**, like YPO_4 [2]. However, obtaining the typical UC emission in $Yb^{3+}/Er^{3+}/Tm^{3+}$ doped nanomaterials is not a challenge. The really interesting thing is **to tune** the UC luminescence to obtain a multicolor and intense emission. It can be achieved by changing the type of the ions and its' concentrations or using **different equipment** (excitation source, laser beam frequency, etc.) [3]. For us, it was important to synthesize samples with fixed amount of Ln^{3+} ions, **without using multiple complex syntheses**. Tetragonal YPO_4:20%Yb^{3+}/x%Tm^{3+}/x%Er^{3+} ions (x = 1 and 0.75) nanomaterials were synthesized using the co-precipitation method.

To answer the title question, we have used different laser sources (Ti:sapphire, Optical Parametric Oscillator), switched the excitation wavelengths – 975 and 800 nm (to avoid sample overheating), performed the **time-resolved spectroscopy** and changed the laser pump power. Then, there was a **SUCCESS**! As a result, we have observed a very high **color shift** (from green, through white and finally to blue – confirmed by the CIE chromaticity calculations), being the result of intensity changes of the emission bands of Er^{3+} (**green** and **red**) and Tm^{3+} (**blue** and **red**). We have also measured the luminescence lifetimes, temporal evolution and the pump power dependences in order to propose the UC mechanisms between the emitting ions.

This kind of materials may draw worldwide attention and potentially may be used in light emitting diodes, solid state multicolor displays, bioimaging or in solar cells (utilizing different excitation wavelength). Especially interesting may be functionalized **anti-counterfeiting materials** (documents or clothes) [4-5] composed of several UC emitting ions within one particle that could be excited only in specific conditions, dependent on the excitation source. Then, these kind of tunable materials may be very difficult to falsify.

Acknowledgements

The Chairs and the Committees greatly acknowledge all the contributors for submitting their abstracts to PRE'19.

References

[1] G. Chen, H. Qiu, P.N. Prasad, X. Chen, *Chem. Rev.*, **114** [10] 5161–214 (2014)
[2] A. Tymiński, T.Grzyb, *J. Lumin*, **181** 411–420 (2017)
[3] S. Tabanli, G. Bilir, G. Eryurek, *J. Lumin.*, **182** 146–153 (2017)
[4] A. Zhou, F. Song, Y. Han, F. Song, D. Ju, K. Adnan, L. Liu, *J. Lumin.*, **194** 225–230 (2018)
[5] V.A.G. Rivera, Y. Ledemi, M. El-Amraoui et al. *J. Non. Cryst. Solids*, **392–393** 45–50 (2014)

Poster

Photoluminescence and scintillation properties of Cs_3PrCl_6 crystal

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Scintillation materials plays a central role in the detection and measurement of ionizing radiations such as X-rays and gamma-rays as they provide an efficient means of converting high-energy electromagnetic radiation into UV-visible photons of light that can be detected with photosensitive sensors. For the development of a scintillation detector with good coincidence timing and high count-rate capability, a scintillator with a combination of high light yield and short decay time is strongly required. Some researchers currently focus on CsCl-$CeCl_3$ based self-activated chloride scintillators such as Cs_3CeCl_6 and $CsCe_2Cl_7$ [1] crystals, because of the large atomic number of Ce (Z = 58), as well as their high light yields and short decay times due to the 5d-4f allowed transitions of Ce^{3+}. Thus, in this study, we investigated a newly Cs_3PrCl_6 crystalline scintillator because the decay time of Pr^{3+} 5d-4f luminescence is usually shorter than that of Ce^{3+}. To the best of our knowledge, no other study on the photoluminescence and scintillation properties of crystalline Cs_3PrCl_6 has been reported so far.

A sample of Cs_3PrCl_6 crystal was grown under vacuum using the vertical Bridgman–Stockbarger method. The excitation and emission spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer equipped with a xenon lamp as the excitation source. The obtained excitation and emission spectra are shown in Fig. 1. The excitation spectrum, monitored at an emission wavelength of 310 nm, showed at least three excitation bands in the wavelength range from 200 to 275 nm. These excitation bands corresponded to the transitions from 4f ground states to 5d excited states of Pr^{3+} split by the ligand-field interaction and the spin-orbit coupling. Upon UV excitation at 260 nm, the characteristic Pr^{3+} 5d–4f (^3H_J and ^3F_J) emission band was observed at 280 and 310 nm. A shoulder band at around 360 nm is due to allowed transitions from 5d excited state to 4f ($^1G_4$) state. Similar emission bands were reported previously for crystalline Cs_2LiYCl_6:Pr^{3+} [2]. The scintillation spectrum obtained under X-ray excitation is provided in Fig. 2. The spectrum shows two emission bands in the UV region peaked at 280 and 310 nm, which is consistent with the photoluminescence, and can thus be assigned to the transitions from the 5d excited state to the 4f (^3H_J and ^3F_J) ground states owing to Pr^{3+}.

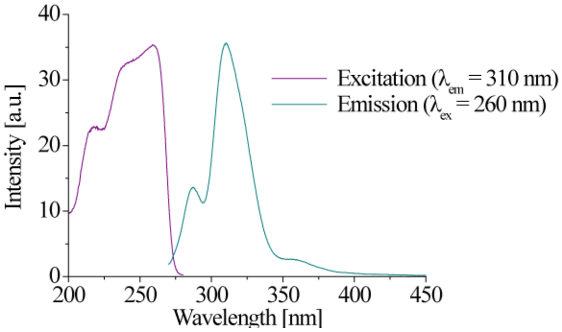

Figure 1: Excitation and emission spectra of the Cs_3PrCl_6 crystal.

Acknowledgements

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References

[1] M. Zhuravleva, K. Yang, and C. L. Melcher, J. Cryst. Growth, **318**, (2011) 809–812.
[2] E.V.D. van Loef et al., IEEE Trans. Nucl. Sci., **52**(5), (2005) 1819–1822.

Luminescence characteristics of Cs_3ScCl_6:Ce crystals

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[Introduction] Scintillators doped with Ce as a luminescence center are known to have the desirable property of a fast decay constant of approximately 40 ns, which is attributed to Ce^{3+} 5d–4f luminescence and the high light yield. For instance, Gd_2SiO_5:Ce (GSO) exhibits a decay time of 60 ns [1] and a light yield of 10000 photons/MeV [2]. The properties of a Ce-doped scintillator depend on the host components. In this study, we fabricated Cs_3ScCl_6:Ce crystals. Owing to the similar ionic radii of Ce and Sc, Ce^{3+} ions can be expected to enter Sc^{3+} sites. Further, we investigated the luminescence characteristics of Cs_3ScCl_6:Ce crystals with various concentrations of Ce.

[Experimental procedure] Crystal samples of Cs_3ScCl_6:Ce were fabricated using the solidification method. CsCl, $ScCl_3{\cdot}6H_2O$, and $CeCl_3{\cdot}7H_2O$ powders were mixed in the desired stoichiometric ratios. The concentrations of Ce were 0.5, 1.0, and 2.0 mol%. For the samples, the photoluminescence (PL), X-ray excited radioluminescence (XRL), and γ-ray excited pulse-height spectra were measured.

[Results and discussion] Fig.1 shows the emission and excitation spectra of Cs_3ScCl_6:Ce. The emission band at 390 nm and shoulder at 420 nm were observed. Excitation bands at 240 and 355 nm were observed. These excitation wavelengths are typical for the Ce^{3+} 5d–4f transition. Therefore, the emission band at 390 nm can be ascribed to the Ce^{3+} 5d–4f transition. Fig. 2 shows the XRL spectra of Cs_3ScCl_6:Ce. The Cs_3ScCl_6:Ce peaks were observed at approximately 390 and 410 nm. These bands correspond to the bands in PL emission spectra and can be ascribed to Ce^{3+} emission. Fig. 3 shows the pulse-height spectra of GSO and Cs_3ScCl_6:Ce. Broad bands were observed at approximately 500 ch for Cs_3ScCl_6:Ce and at 550 ch for GSO. Assuming the light yield of GSO was 10000 photons/MeV and considering the wavelength-dependent sensitivity of the photomultiplier tubes the light yields of Cs_3ScCl_6:Ce samples were estimated to be approximately 9100 photons/MeV. For Cs_3ScCl_6:Ce at 2 mol%, the channel of the peak was slightly lower than that of the other samples. This can be ascribed to concentration quenching.

[1] C. L. Melcher et al., IEEE Trans. Nucl. Sci., 37, 2, 161–164 (1990).

[2]C. W. E. Van Eijk et al., Nucl. Instrum. Methods, A, 348, 546–550, (1994).

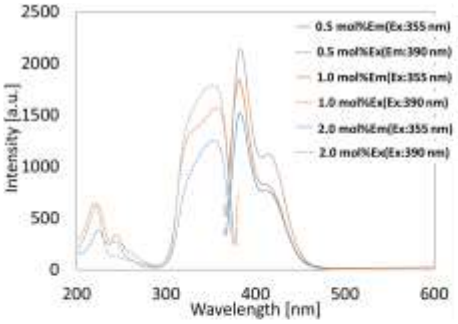

Fig. 1 Emission and excitation spectra of Cs_3ScCl_6:Ce.

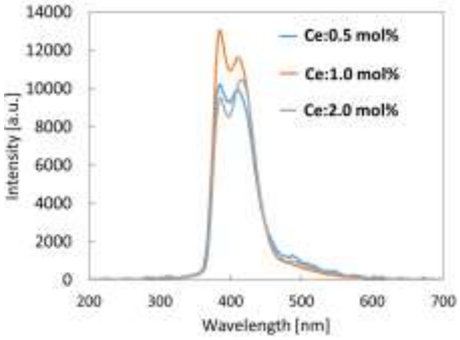

Fig. 2 XRL spectra of Cs_3ScCl_6:Ce.

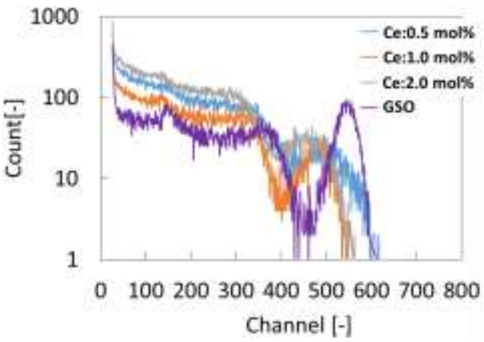

Fig. 3 Pulse-height spectra of GSO and Cs_3ScCl_6:Ce.

Poster

Tb^{3+}- and Dy^{3+}-doped $CaO–Al_2O_3–B_2O_3$-based glasses for neutron detection

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Introduction Borate-based glass with ^{10}B is used for the window glass in nuclear reactor facilities. ^{10}B has a large reaction cross section to thermal neutrons and has an excellent neutron capture ability. When ^{10}B absorbs neutrons, α particles, ^{7}Li, and γ-ray are emitted (^{10}B (n, α)^{7}Li reaction). We intend to develop a new neutron dosimeter material using this property. We previously investigated the thermoluminescence (TL) properties of Tb^{3+}-doped $CaO–Al_2O_3–B_2O_3$-based glass irradiated with X-ray and reported that this glass exhibits a good response to X-rays[1]. In this study, we fabricated Tb^{3+}- and Dy^{3+}-doped glasses using ^{10}B and ^{11}B, and investigated the TL properties after irradiation with X-rays, α-rays, or neutrons.

Materials and Methods Glasses were prepared according to a conventional melt quenching method using an alumina crucible at atmospheric pressure in air. High-purity $CaCO_3$ (4N), $H_3{}^{10}BO_3$ or $H_3{}^{11}BO_3$, Al_2O_3 (4N), Tb_4O_7 (3N), and Dy_2O_3 (3N) powders were used as starting materials. The concentrations of Tb^{3+} and Dy^{3+} were 0.5–5.0 mol% each. The mixture in the alumina cubicle was melted at 1100°C for 20 min and quenched to room temperature, and ^{10}B glass and ^{11}B glass were fabricated. These glasses were irradiated with X-rays (in our laboratory), α-rays (at HIMAC) or neutrons (at NASBEE) and we measured the TL photons (at a range of 300–700 K with a heating rate of 0.5 or 1.0 K/s).

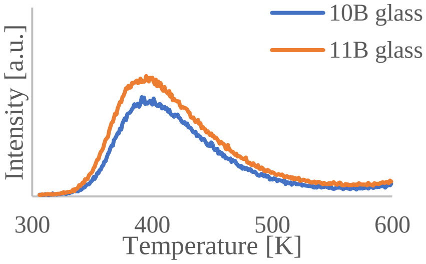

Figure 1: TL glow curves of Dy^{3+}-doped glasses irradiated with α-rays (150 MeV/n).

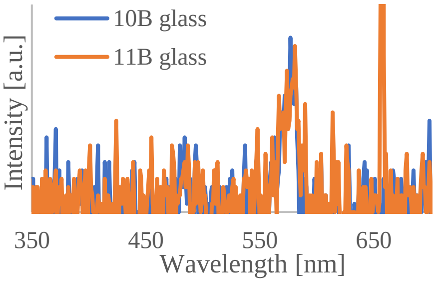

Figure 2: TL spectra at 390 K of Dy^{3+}-doped glasses irradiated with α-rays (150 MeV/n).

Results and discussion Figure 1 shows the TL glow curves of the Dy^{3+}-doped glasses irradiated with α-rays (150 MeV/n). A TL peak was observed at 390 K. Figure 2 shows the TL spectra at 390 K of these glasses irradiated with α-rays (150 MeV/n). TL emission bands were observed at 485 and 580 nm, which are attributed to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ electronic transitions of Dy^{3+}. These results suggest that these glasses have a high sensitivity to α-rays.

Figure 3 shows the TL glow curves of the Tb^{3+}-doped glasses irradiated with neutrons (10^{11} n/cm^2). The TL intensity of the ^{10}B glass is much larger than that of ^{11}B glass. This result suggests that the α-rays and γ-rays from ^{10}B (n, α) efficiently induced TL. This glass can be used in a new neutron dosimeter.

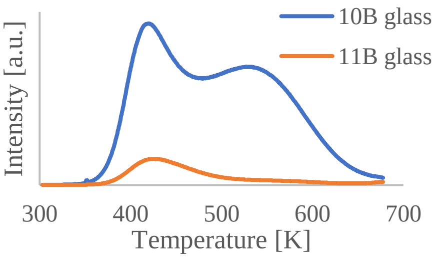

Figure 3: TL glow curves of Tb^{3+}-doped glasses irradiated with neutrons (10^{11} n/cm^2).

References

[1] H. Ohno et al., *Opt. Mater.*, **87**, 24–28 (2019).

Poster

Photoluminescence and scintillation properties of $Al(PO_3)_3$–$CeCl_3$–CsCl–$CsPO_3$–based glass scintillators

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[Introduction] Scintillators are phosphor that can convert the energy of absorbed ionizing radiation, such as X-rays, gamma rays, or charged particles, to UV or visible light photons. These scintillators play critical roles in the detection and measurement of radiation. Halide-based single crystals having high light yelds, such as NaI:Tl, are conventionally used for gamma ray detection. However, the main disadvantages of those crystal scintillators include deliquescency and long decay time (longer than 100 ns).

Glasses are alternatives to scintillators because of their high transparency, low cost, feasibility of large-scale production, and their thermal, mechanical, and chemical stabilities. In this study, we aimed to develop an oxide–halide hybrid glass scintillator that exhibits chemical stability and excellent scintillation properties. We used $CsPO_3$–$Al(PO_3)_3$ as a host glass because phosphate glasses can easily dissolve halide compounds. We investigated the photoluminescence and scintillation properties of $Al(PO_3)_3$–$CsPO_3$–$CeCl_3$ and $Al(PO_3)_3$–$CsPO_3$–CsCl–$CeCl_3$ glasses.

[Experimental Approach] The $Al(PO_3)_3$–$0.5CeCl_3$–$1.5CsPO_3$ and $Al(PO_3)_3$–$0.5CeCl_3$–0.5CsCl–$CsPO_3$ glasses (reported in molar ratio) were prepared according to the melt quenching method under vacuum conditions. The powders of $Al(PO_3)_3$, $CeCl_3 \cdot 7H_2O$, CsCl, and CsH_2PO_4 were used as starting materials for the production of the glass samples. The mixtures were placed in quartz tubes and melted at 1100°C in an electric furnace for 30 min. After completely melting all compounds, the samples were quenched at room temperature. The X-ray diffraction (XRD) patterns, photoluminescence emission and excitation spectra, and ^{137}Cs gamma ray-irradiated pulse height spectra of the samples were measured.

[Results] The XRD patterns of the glasses are shown in Fig. 1. All the XRD patterns showed a broad peak without any specific diffraction peaks, which indicate the amorphous nature of the samples. Fig. 2 shows the photoluminescence emission and excitation spectra. The glasses showed an emission peak at 350 nm and two excitation bands peaking between 240–260 and 300–330 nm, which are attributed to the transition between the Ce^{3+} 5d excited state and the 4f ground state. The pulse height spectra of the glasses and a commercialized glass scintillator, GS20, used as reference are shown in Fig.3. A clear photoabsorption peak of 662 keV gamma rays can be observed in all the glasses. The light yields of the glasses were estimated using the light yield of GS20 (4000 photons/MeV). The light yield of the $Al(PO_3)_3$–$0.5CeCl_3$–0.5CsCl–$CsPO_3$ glass is estimated to be 2000 photons/MeV, which is 1.2 times higher than that of the $Al(PO_3)_3$–$CsPO_3$–$CeCl_3$ glass.

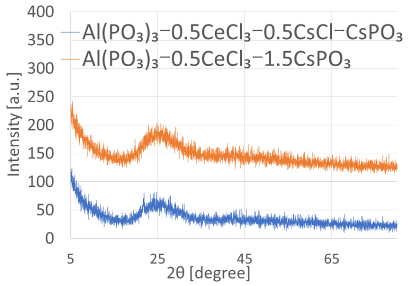

Fig. 1 X-ray diffraction patterns of the glass samples.

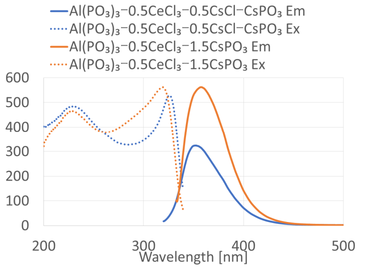

Fig. 2 Photoluminescence emission and excitation spectra.

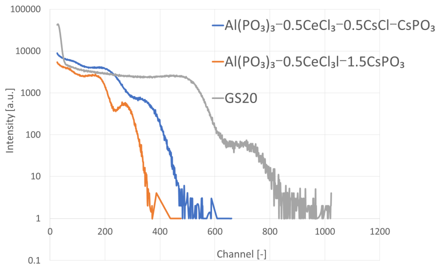

Fig. 3 ^{137}Cs-gamma-ray-irradiated pulse height spectra

Optical, Scintillation and Dosimetric Properties of $Ca_3(PO_4)_2$ Transparent Ceramics Doped with Rare Earth Ions

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Radiation monitoring with high precision are important from the viewpoint of medical, security and personal dosimetry. In these applications, dosimeter materials for personal dosimetry are required several performances; however, dosimeter materials developed up to now do not full all required performances. Hence, our research group focused a form of dosimeter material and undertook developments on new dosimeter materials. In particular, we have reported that transparent ceramics recently attracted as new optical materials have great dosimetric properties [1].

In this study, we prepared $Ca_3(PO_4)_2$ transparent ceramics doped with rare earth ions (Ce, Eu and Tb) and investigated optical, scintillation and dosimetric properties of them. There is only study reported by Kawagoe et al. about $Ca_3(PO_4)_2$ transparent ceramics so far [2]. On the other hand, the number of study about the emission properties such as photoluminescence (PL), scintillation and thermally stimulated luminescence (TSL) of $Ca_3(PO_4)_2$ is less. An effective atomic number of $Ca_3(PO_4)_2$ is close to that of human soft tissue, which is potentially applicable as dosimeter materials. Rare earth ions doped $Ca_3(PO_4)_2$ transparent ceramics were prepared by the spark plasm sintering method, and their in-line transmittance spectra, PL spectra, PL decay time constants, scintillation spectra and TSL glow curves were measured. Moreover, pure $Ca_3(PO_4)_2$ transparent ceramics was also prepared to compare.

Figure 1 shows appearances of the obtained samples. It can be confirmed by naked eyes that the horizontal lines on the back of samples are clearly seen. Scintillation spectra are shown in Figure 2. The Eu- and Tb-doped samples showed sharp emission peaks due to 4f-4f transitions. On the other hand, the pure sample showed broad emission peak centering around 450 nm. This spectral shape is same to one of the Ce-doped sample; therefore, it is assumed that an emission from 5d-4f transitions of Ce^{3+} ions dose not detected.

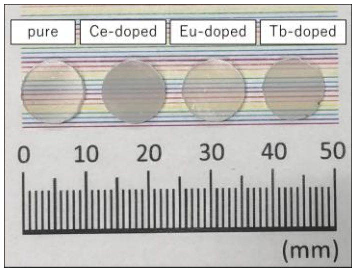

Figure 1 Appearances of the obtained samples.

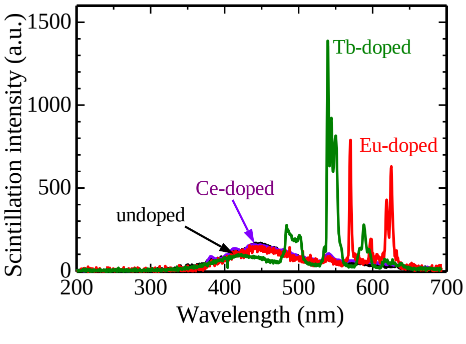

Figure 2 Scintillation spectra.

References

[1] T. Kato et al., *Ceram. Inter.*, **42**, 5617-5622 (2016)
[2] D.Kawagoe et al., *J. Ceram. Soci. Jpn.*, **112**, 462-463 (2004)

Emission Properties of Dy-doped $MgAl_2O_4$ Transparent Ceramics

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Dosimeter materials are one of phosphors used for personal dosimetry. When such materials are irradiated a radiation, they store a radiation energy temporarily. Then, they show a luminescence by a stimulation of heat or light. Since the luminescence intensity in this case is proportional to the radiation dose, we can use the materials as personal dosimetry. Several properties are required in dosimeter materials, which are dose linearity, suitable sensitivity, low fading and energy response. In addition to these properties, it is important that an effective atomic number (Z_{eff}) of the dosimeter material is close to that of human soft tissue from the viewpoint of bioequivalence.

Dosimetric properties of undoped, Tb-doped and Dy-doped $MgAl_2O_4$ in form of a single crystal and opaque ceramic have been investigated because Z_{eff} of $MgAl_2O_4$ is relatively close to that of human soft tissue. On the other hand, C. Wang et al. reported how to prepare $MgAl_2O_4$ transparent ceramics in recent years. However, there is no report on dosimetric properties of $MgAl_2O_4$ transparent ceramics so far.

In this study, we prepared Dy-doped $MgAl_2O_4$ transparent ceramics by using the spark plasma sintering method, and then investigated emission properties such as photoluminescence (PL), scintillation and thermally stimulated luminescence (TSL) properties.

Figure 1 shows PL excitation and emission spectra. In the excitation spectra, peaks at 300, 360 and 390 nm were observed. On the other hand, under 360 nm excitation, peaks at 480 and 570 nm were detected in the emission spectra, which were due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{3+} ions. Figure 2 indicates TSL glow curves of an irradiated dose of 100 mGy. All the samples showed three glow peaks which is located at 60, 200 and 460 °C. A TSL intensity of the 1.0% Dy-doped sample was maximum among the present samples.

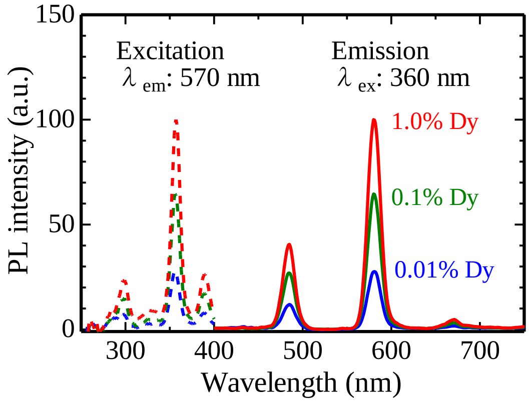

Figure 1 PL excitation and emission spectra.

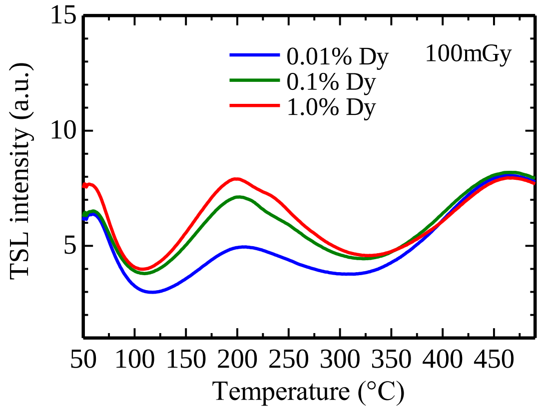

Figure 2 TSL glow curves.

References

[1] E.A. Raja et al., *J. lumin.*, **129**, 829-835 (2009)
[2] F, Khan et al., *Int. J. Lumin. Appl.*, **5**, 26-28 (2015)
[3] C, Wang et al., *Scripta Mater.*, **61**, 193-196 (2009)

Model-Free Sliding Mode Control For Shaping 800 nm Pulses Of Yb/Tm Co-Doped Laser

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Modern literature has demonstrated the use of fluorescent probes in stimulated emission depletion (STED) microscopy. Most recently, lanthanide-doped nanocrystals have been used to achieve the imaging of single up-conversion nanoparticles [1]. However, precise control of the stimulated emission at 800 nm caused by the discharge of the metastable $^3H_4$ energy level would provide enhanced imaging in modern nanoscopy. In this interdisciplinary paper, model-free control is combined with sliding mode control to shape 800 nm pulsed emission of the Yb/Tm co-doped dual-laser system. This is achieved by controlling the stimulated emission rate via automatic adjustment of the probing laser pump power. This new type of controller will not be impacted by model errors like its model-based counter parts and can be fabricated by CMOS processes paving way to photonic integration. Simulation of the controller is executed in MATLAB Simulink, which shows negligible tracking error and low power consumption. Formal mathematical analysis of this new control technique and simulation results will be presented.

References

[1] Y. Liu, Y. Lu, X. Yang, X. Zhang, S. Wen, F. Wang, X. Vidal, J. Zhao, D. Liu, Z. Zhou, C. Ma, J. Zhou, J. Piper, P. Xi and D. Jin, *Nature*, **543**, 229-233 (2017)

$SrAl_2O_4:Eu^{2+}$, Dy^{3+} ultra-small particles obtained by pulsed laser ablation in liquid and their luminescent features

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In the present study, we proposed to prepare green long persistent $SrAl_2O_4:Eu^{2+}$, Dy^{3+} (SAO) ultra-small particles by using the pulsed laser ablation in liquid (PLAL) technique. Unlike the traditional bottom-up methods, special top-down method—PLAL, has several advantages such as a one-step production, easy experimental set-up and large choice of solvent and experimental parameters [1]. PLAL method has been used for several long persistent nanomaterials such as $Ca_2Si_5N_8:Eu^{2+}$, Tm^{3+}; $ZnGa_2O_4:Cr^{3+}$ [2]. However, complicated physical and chemical processes occur over a very small-time order (ns or µs) which are not fully understood, and thus it is necessary to analyze and define the most suitable conditions to prepare different materials. To the best of our knowledge, this is the first time that this technique has been used to prepare SAO ultra-small particles.

Different solutions such as water, ethanol, and acetone and different concentration of CTAB as surfactant were used. In water, the reaction between CO_2 with the laser created Sr^{2+} ion prevents the formation of monoclinic-SAO phase. In acetone and ethanol, correct monoclinic-SAO phase is obtained but the size is difficult to control. CTAB is a cationic surfactant that can form micelles or reverse micelles which further affect the morphology of the inorganic nanomaterials [3]. The photoluminescence spectra, the persistent luminescence of the particles obtained by laser ablation in liquid (PLAL) technique are presented. We also focused our attention in the site occupancy and in the persistent luminescence properties. If controlled size particles can be obtained within this technique, this can open the path to new applications and new modality in the bio-imaging field.

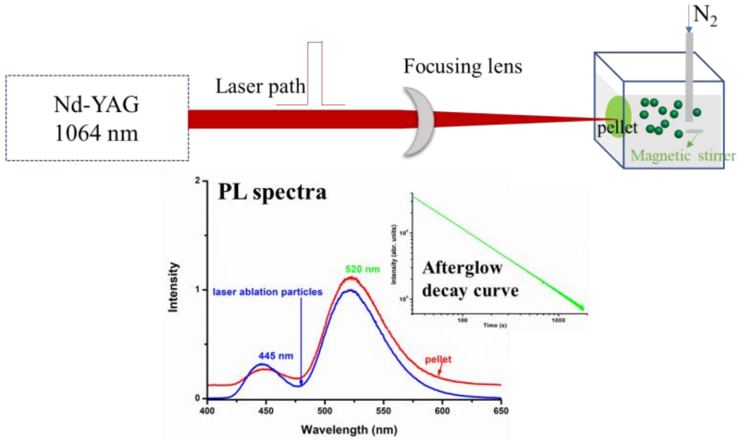

Figure1: Schematic diagram of the experimental setup used in this study and optical features.

Acknowledgments: CSC Grant and ANR Persist for their support.

References

[1] D. Zhang, et al. Chemical Reviews, 117, 3990-4103 (2017).
[2] T. Maldiney, B. Viana, et al. Optical Materials express, 2, 261-268(2012); M.S. Relvas, et al. Journal of Physics and Chemistry of Solids, 129, 413-423(2019).
[3] A. Zamiranvari, et al. Optics & Laser Technology, 97, 209-218 (2017).

Photoluminescence and scintillation properties of Ce-doped barium silicate glasses synthesized by the FZ method

Daiki Shiratori, Daisuke Nakauchi, Hiroyuki Fukushima, Noriaki Kawaguchi, Takayuki Yanagida

Nara Institute of Science and Technology

One of the ways to measure ionizing radiation is achieved by the process of converting high energy radiation into a large number of photons. The converted photons from ionizing radiation are detected by photodetectors such as photomultiplier tube or photodiode. In order to convert the ionizing radiation to photons, phosphors called a scintillator have been used. Now, the material form of a phosphor for radiation detection is mainly single crystal. However, SiO_2 glass has a high transmittance from vacuum ultraviolet to infrared regions and is excellent in low coefficient of thermal expansion and chemical durability. Therefore, SiO_2 glass can be expected as a host material for radiation measurement. In this study, to increase the sensitivity for X-rays, we focused on BaO-SiO_2 glass which contains Ba as heavy elements and evaluated its radiation response characteristics.

When photoluminescence (PL) excitation/emission spectrum was measured, we observed a broad emission band from 320 to 450 nm. Based on the PL emission wavelength, the PL decay curve was measured, and the decay time profile was approximated by a single exponential decay function. Figure 1 shows a PL decay curve of the Ce-doped glass sample. The decay time resulted 45.8 ns, and the origin was ascribed to the 5d-4f transition of Ce^{3+} [1].

Figure 2 shows scintillation spectra of the non- and Ce-doped samples under X-ray irradiation. The Ce-doped glass sample showed an intense emission from 350 to 600 nm under X-ray irradiation. This emission feature is typical for the 5d-4f transitions of Ce^{3+}. On the other hand, the undoped glass sample also showed the emission from 300 to 500 nm.

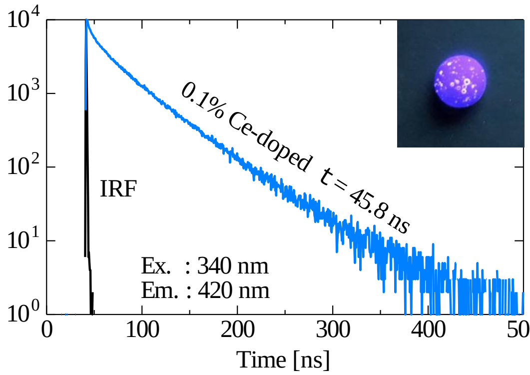

Figure 1 PL decay time profile of Ce-doped sample. Excitation and observation wavelength are 340 and 420 nm, respectively. Inset is a photograph of the Ce-doped sample under irradiation of 354 nm UV light.

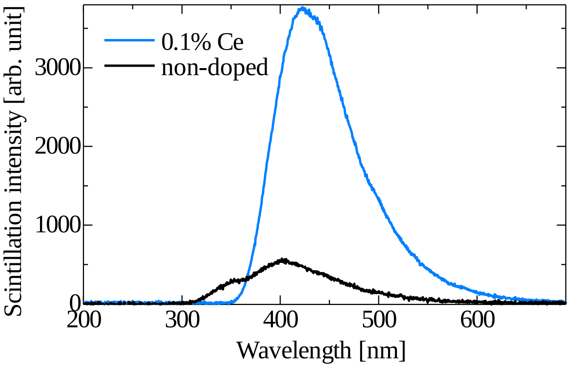

Figure 2 Scintillation spectra of the non- and Ce-doped glass samples under X-ray irradiation.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research A (17H01375) and B (18H03468), Young Scientists B (17K14911) and Early-Career Scientists (18K14158) from JSPS. The Cooperative Research Project of Research Institute of Electronics, Shizuoka University is also acknowledged.

References

[1] D. Shiratori et al., *J. Mater. Sci. Mater. El.*, **30,** 2464-2469 (2019)

Evaluation of optical and X-ray induced Scintillation properties in Ce-doped Gd_2O_3-BaO-Al_2O_3-SiO_2 glasses

Daiki Shiratori, Noriaki Kawaguchi, Takayuki Yanagida

Nara Institute of Science and Technology

A scintillator promptly converts the absorbed energy of ionizing radiations into a large number of low energy photons. It is widely applied in many scientific and industrial fields. The material form of a practical scintillator is mainly single crystal or ceramics, and at present, commercial glass scintillator is only ^{6}Li glass for neutron detection [1]. In general, most commercial glasses for optical applications compose of low atomic number elements. However, in order to detect X-rays, compositions based on heavy elements are required since the detection efficiency of the scintillator for high energy photons depends on the effective atomic number and density. In this study, to increase the sensitivity for X-rays, we focused on BaO-Gd_2O_3-Al_2O_3-SiO_2 which contains Ba and Gd as heavy elements and evaluated its radiation response characteristics.

Figure 1 exhibits photoluminescence (PL) excitation/emission map of the Ce-doped glass sample. We observed a broad emission band from 350 to 550 nm. Based on the PL map, PL decay curve of the Ce-doped sample was measured monitoring at 420 nm under 340 nm excitation. The decay time constant resulted 42 ns, and the emission origin was ascribed to the 5d-4f transition of Ce^{3+} [2].

Figure 2 shows scintillation spectra of the non- and Ce-doped samples under X-ray irradiation. The non-doped sample exhibits three emission peaks, and the line around at 300 nm is typical for the 4f-4f transitions of Gd^{3+} in the host glass. On the other hands, the Ce-doped glass sample showed an intense emission from 350 to 550 nm under X-ray irradiation. This emission feature is typical for the 5d-4f transitions of Ce^{3+}.

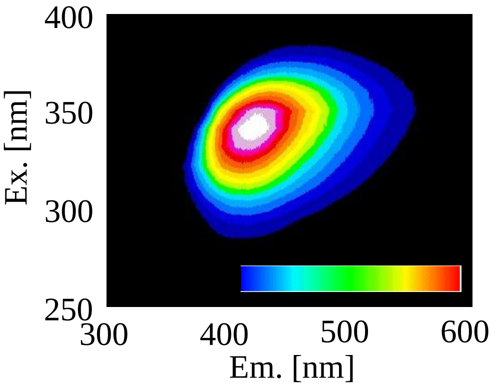

Figure 1 PL emission map of Ce-doped glass sample. Horizontal and vertical axes show emission and excitation wavelengths, respectively.

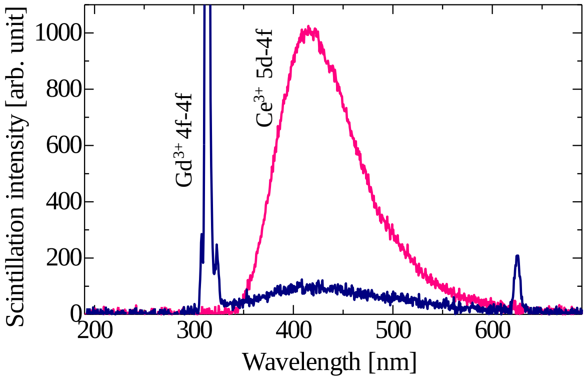

Figure 2 Scintillation spectra of the non- and Ce-doped glass samples under X-ray irradiation.

References

[1] J. Czirr, et al., *Nucl. Instrum. Meth. A*, **424,** 15-19 (1999)
[2] D. Shiratori et al., *J. Mater. Sci. Mater. El.*, **30,** 2464-2469 (2019)

Effect of La^{3+} and Gd^{3+} concentration on the NIR emission of $XNbO_4:Tm^{3+}$ for bio-labelling application

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Luminescent bioimaging is widely used in biomedical sciences for applications ranging from the morphological analysis of anatomical structure to sensitive measurements of intracellular molecular events and it is associated with several advantages like selectivity and sensitivity nature compared to conventional imaging methods[1]. Near-infrared (NIR) fluorescent probes offer advantages of, very high sensitivity, reasonably high photon penetration, low light scattering and minimal autofluorescence from living tissues. Among conventional fluorescent labels, the most used are organic dyes, fluorescent proteins, lanthanide chelates, semiconductor quantum dots and lanthanide doped inorganic nanoparticles (NP). The development of NP agents continues to receive considerable attention due to its greater biocompatibility and reduced toxicity compared to more conventional chemical agents[2]. In this context, this work reports the synthesis of $X_{(y)}NbO_4:Tm_{(3.0\%)}$, (where X = La^{3+} or Gd^{3+} and y = 1.0, 6.0 or 10.0% in mol) and its effect on the luminescent properties for bio-labelling application. The phosphors were obtained by the adapted non-hydrolytic sol-gel route and annealed at 900°C for 4 h. The results revealed that, when monitored at 811 nm, all samples presented bands in the excitation spectra at 762, 672, 462 and 358 nm ascribed to the $^1D_2 \rightarrow {}^3F_2$, $^1G_4 \rightarrow {}^3F_4$, $^3H_6 \rightarrow {}^1G_4$ and $^1G_4 \rightarrow {}^1D_2$ transitions of Tm^{3+}, respectively. For the sample containing La^{3+} ion, at least 3 unfolding were observed for the $^1G_4 \rightarrow {}^3F_4$ transition at 672 nm, while for samples prepared with Gd^{3+} ions, these unfolding were not observed. In addition, the intensity of broad band at 262 nm, which is related to the transfer charge band from O^{2-} 2p orbital to Nb^{5+} empty 4d orbital, increased in function of ion concentration for both $LaNbO_4$ and $GdNbO_4$ samples. The emission spectra (λ_{exc}: 652 nm) revealed a band at 762 nm attributed to the $^1D_2 \rightarrow {}^3F_2$ only for the $LaNbO_4$:Tm sample, in addition to the unfolded band at 811 nm related to the $^3H_4 \rightarrow {}^3H_6$. For the samples containing Gd^{3+} ion, the band at 811 nm was also observed, however, its profile was broader. Finally, when excited at deep-red wavelength (762 nm), all samples presented bands at around 811 nm related to the $^3H_4 \rightarrow {}^3H_6$ transition of Tm^{3+}, confirming that these samples are useful as NIR fluorescent probes for bio-labeling application.

Acknowledgements

The authors acknowledge FAPESP (grants: 2015/20298-0 L.A.R. and 2018/02387-3, 2019/06761-0 S.B.M.) and CNPq (grants: 304307/2015-7 L.A.R. and 302668/2017-9 E.J.N). This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and by the Grant Agency of the Slovak Academy of Sciences through project VEGA No. 2/0036/17. The authors thank Companhia Brasileira de Metalurgia e Mineração (CBMM) for donating $NbCl_5$.

References

[1] Syamchand, S. S.; Sony, G., *J. Lumin*. **2015**, 165, 190.
[2] Wang, X.; Chang, H.; Xie, J.; Zhao, B.; Liu, B.; Xu, S.; Pei, W.; Ren, N.; Huang, L.; Huang, W., *Coord. Chem. Rev.* **2014**, *273*, 201.

Poster

Luminescent properties of nanosized $LiYF_4$:Eu modified with gold nanoparticles assisted by atmospheric plasma jet

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$LiYF_4$ has been described as a highly efficient host for upconversion emission, specially compared with other fluoride or oxide hosts, exhibiting a strong emission in the visible region when excited in the near infrared providing the adequate doping ions [1]. Since Eu^{3+} can be used as a fluorescent probe, its insertion in the host could provide some insight about the structure and environment of the activator ions present in the $LiYF_4$. Gold modification of upconversion nanoparticles has been used to improve the emission of upconverted emission *via* enhancement of local electrical field [2], however, to achieve it a spacer must be present to minimize emission quenching. Nevertheless, it is possible that the luminescence quenching could be used as a way of converting the emission into heat, using the surface plasmon resonance of nanosized gold. Atmospheric plasma jet was used to reduce $HAuCl_4$ into gold nanoparticles in order to decorate the europium-doped $LiYF_4$ nanocrystals [3]. The luminescent properties of europium were obtained before and after gold functionalization, and a strong quenching was observed.

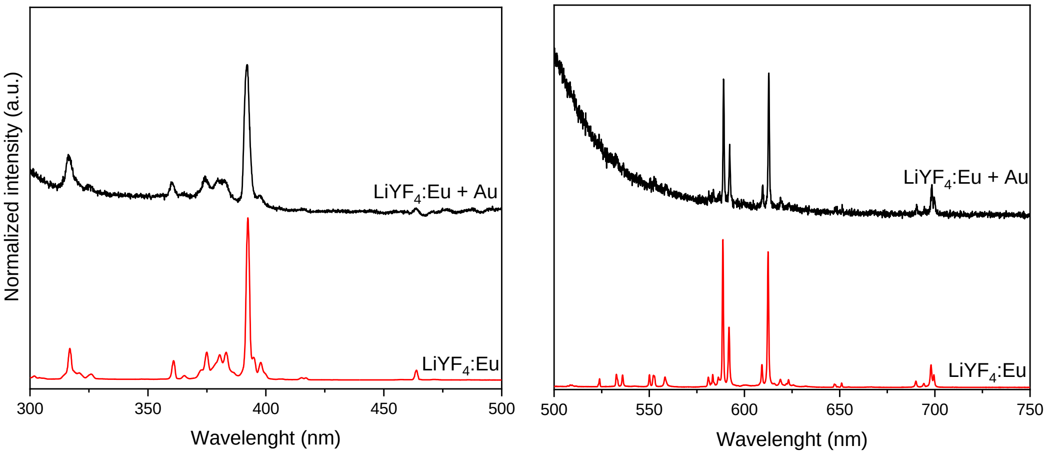

Figure 1: (a) excitation and (b) emission spectra of $LiYF_4$:Eu before and after gold nanoparticle modification.

Acknowledgements
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References

[1] Zhang, L., Wang, Z., Lu, Z. Xia, K., Deng, Y., Li, S., Zhang, C., Huang, Y., He, N., *Journal of Nanoscience and Nanotechnology*, **14**, 4710-4713 (2014).
[2] Rasskazov, I. L., Wang, L., Murphy, C. J., Bhargava, R., Carney, P. S., *Optical Materials Express*, **8**, 3797-3804 (2018).
[3] Gonçalves, J. M., Guillot, P., Caiut J. M. A., Caillier, B., *Journal of Materials Science: Materials in Electronics*, accepted paper, doi: 10.1007/s10854-019-01011-x (2019).

Evaluation of photoluminescence and scintillation properties of Ce-doped $Ca_3Hf_2SiAl_2O_{12}$ crystals

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Scintillation materials convert the energy of ionizing radiation such as gamma- or X-rays into visible or UV light. In usual, scintillators are combined with a photodetector such as photodiode or photomultiplier (PMT). The typical wavelength sensitivity range of PMT is between UV to bluish-green light region. Thus, Ce-doped materials are a good candidate for scintillators owing to 5d-4f transitions of Ce^{3+} emit suitable light (400−550 nm). In recent, hafnium oxide scintillators have been developed [1]. In usual, hafnium oxide materials have high melting point above 2,200 °C. Thus, the report of crystal synthesis using a melt-derived method is limited. $Ca_3Hf_2SiAl_2O_{12}$ (CHSA) is a new hafnium oxide material which belongs to garnet structure [2]. Hafnium oxide materials are good candidate owing to its high density and high effective atomic number. In this study, the Ce-doped CHSA crystals were synthesized using the floating zone method equipped with four xenon arc lamps and evaluated photoluminescence (PL) and scintillation properties.

Figure 1 shows the X-ray-induced scintillation spectrum of the 0.5 % Ce-doped CHSA crystal. The emission peak appears at around 480 nm due to 5d-4f transitions of Ce^{3+}. Figure 2 shows the PL decay curve of the 0.5 % Ce-doped CHSA crystal. The monitoring wavelength is 420 nm under the excitation wavelength at 365 nm. The decay curve was approximated by a sum of two exponential decay component. The primary decay component is an instrumental response function, and the secondary decay component is typical value of 5d-4f transitions of Ce^{3+} (36.3 ns). In the conference, further results including Ce concentration dependence will be presented.

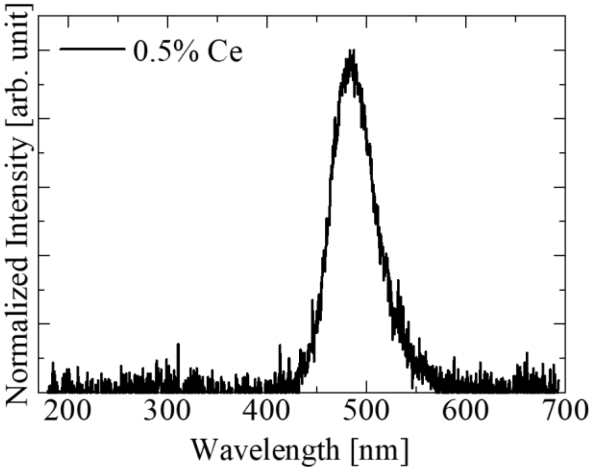

Figure 1. X-ray-induced scintillation spectra of 0.5 % Ce-doped CHSA crystal.

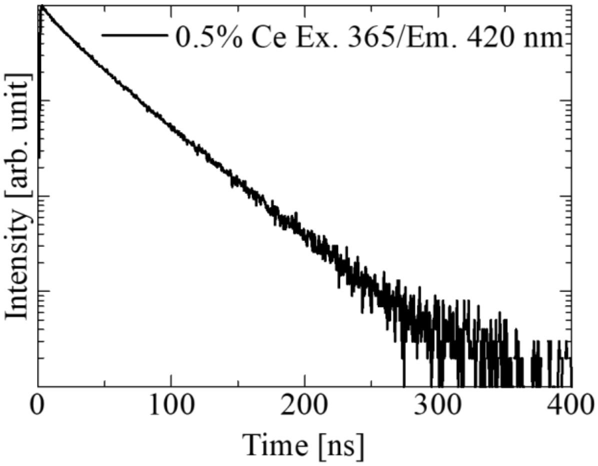

Figure 2. PL decay curve of 0.5 % Ce-doped CHSA crystal. Ex. and Em. indicates excitation and emission, respectively.

References

[1] H. Fukushima, D. Nakauchi, G. Okada, N. Kawaguchi, T. Yanagida, J. Mater. Sci. Mater. Electron. 29 (2018) 21033–21039.

[2] X. Ding, G. Zhu, W. Geng, Q. Wang, Y. Wang, CrystEngComm. 17 (2015) 3235–3242.

Photoluminescence and scintillation properties of Eu-doped $CaZrO_3$ single crystals synthesized by the floating zone method

Authors: Hiroyuki Fukushima, Daisuke Nakauchi, Noriaki kawaguchi, and Takayuki Yanagida[1]

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Scintillation materials emit thousands of photons with interactions between material and ionizing radiation such as gamma- or X-rays. The typical application fields of scintillators are medical imaging, security, oil-logging, and environmental monitoring. In recent, Ce- and Ti-doped $CaHfO_3$ crystals which have a high density and effective atomic number (Z_{eff}) have been developed as a scintillator [1,2]. The detection efficiency for high energy photons such as gamma- or X-rays depends on a density and Z_{eff}. On the analogy of $CaHfO_3$, we focused on $CaZrO_3$ which have relatively high density (5.11 g/cm^3). $CaZrO_3$ has high melting temperature (2,375 °C), thus the reports of synthesizing single crystal and scintillation properties are limited [3]. In this study, the undoped and Eu-doped $CaZrO_3$ single crystals were synthesized by the floating zone method equipped four xenon arc lamps, and their photoluminescence (PL) and scintillation properties were evaluated.

Figure 1 shows the X-ray-induced scintillation spectra of the undoped and 1.0 % Eu-doped $CaZrO_3$ single crystals. The emission peak appears at around 450 nm in the undoped $CaZrO_3$, while Eu-doped $CaZrO_3$ indicates typical emission of 4f-4f transition of Eu^{3+}. Figure 2 shows the PL decay curve of the 1.0 % Eu-doped $CaZrO_3$ single crystal. The decay curve is approximated by one exponential decay function. The primary decay component is close to typical decay time constant of Eu^{3+} (906 μs) [4]. In the conference, further results will be discussed and presented.

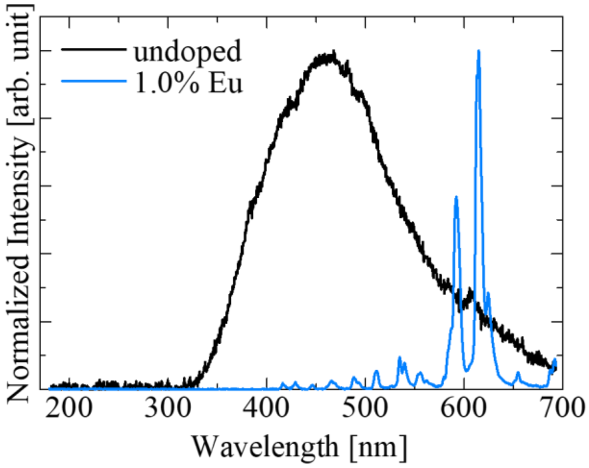

Figure 1. X-ray-induced scintillation spectra of undoped and 1.0 % Eu-doped $CaZrO_3$ single crystals.

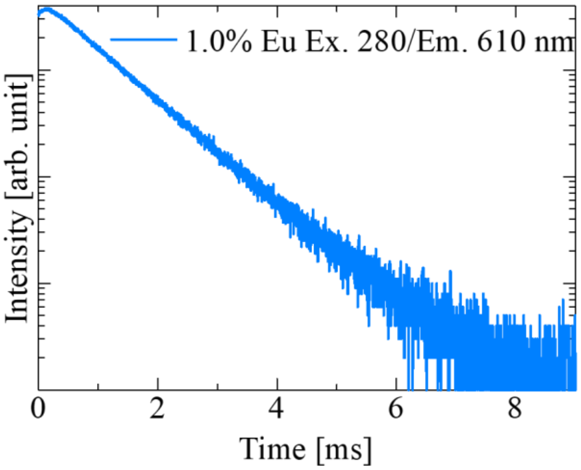

Figure 2. PL decay curve of 1.0 % Eu-doped $CaZrO_3$ single crystal.

References

[1] H. Fukushima, D. Nakauchi, G. Okada, N. Kawaguchi, T. Yanagida, J. Mater. Sci. Mater. Electron. 29 (2018) 21033–21039

[2] H. Fukushima, D. Nakauchi, N. Kawaguchi, T. Yanagida, Jpn. J. Appl. Phys. 58 (2019) 052005

[3] D.B. Gasson, B. Cockayne, Oxide crystal growth using gas lasers, J. Mater. Sci. 5 (1970) 100–104

[4] L. Guan, L. Jin, S. Guo, Y. Liu, X. Li, Q. Guo, Z. Yang, G. Fu, J. Rare Earths. 28 (2010) 292–294

Optical and radiation induced luminescence properties of $SrBr_2$ transparent ceramics doped with different Eu concentrations

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Scintillators are type of phosphors, and they have been widely used in radiation detection fields such as security, medicine and environmental monitoring. Scintillators have a function to immediately convert the absorbed energy of ionizing radiation into many low energy photons, and these photons are generally converted to electrons by photodetectors. Conventionally, most scintillator materials have been used mainly in a form of bulk single crystal because of their high optical qualities. In recent years, transparent ceramics have attracted much attention as radiation detector applications because transparent ceramic samples (e.g. GAGG:Ce, LuAG:Ce) showed superior scintillation properties than those of single crystals with the same chemical compositions in previous some literatures [1,2]. So far, Eu-doped halide scintillators have been studied, and it has been reported that SrI_2:Eu and BaBr:Eu have high light yield [3,4]. According to a previous report, $SrBr_2$:Eu has a light yield of 20,000ph/MeV and an energy resolution of 7% at 662keV [5]. However, there are no reports on scintillation properties of $SrBr_2$:Eu in the form of a transparent ceramic. In this study, we have developed $SrBr_2$:Eu transparent ceramics with different concentrations of Eu by the spark plasma sintering method and evaluated the optical and radiation induced luminescence properties.

Figure 1 shows PL excitation and emission map of $SrBr_2$:Eu (0.01%) transparent ceramic as a representative. The ceramic sample showed an emission peak around 400 nm under an excitation 280-400 nm. The spectral feature was similar to past report of $SrBr_2$:Eu single crystal sample. The PL decay curves of the $SrBr_2$:Eu samples is shown in Figure 2. The PL decay curves of all the samples were approximated by a single exponential decay function. The decay time constants of all the samples are typical values of the 5d-4f transitions of Eu^{2+} [5]. In this conference, we will report the optical and radiation induced luminescence properties in detail.

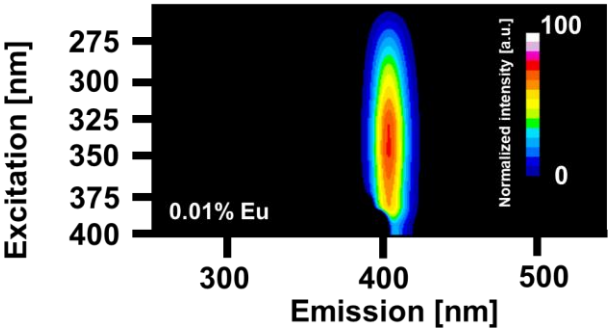

Figure 1: PL excitation and emission map of $SrBr_2$:Eu (0.01%) transparent ceramic.

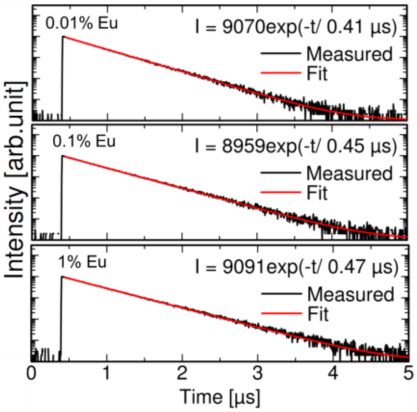

Figure 2: PL decay curves of $SrBr_2$:Eu (0.01, 0.1, 1%) transparent ceramics

References

[1] T. Yanagida, *et al.*, *Opt. Mater.*, **35**, 2480-2485 (2013) [2] T. Yanagida, *et al.*, *Radiat. Meas.*, **46**, 1503-1505 (2011) [3] J. Selling, *et al.*, *IEEE Trans. Nucl. Sci.*, **55**, 1183-1185 (2008) [4] T. Yanagida, *et al.*, *Opt. Mater.*, **61**, 119-124 (2016) [5] N. J. Cherepy, *et al.*, *IEEE Trans. Nucl. Sci.*, **56**, 873-880 (2009)

Photostimulated luminescence properties of Eu-doped Cs(Cl, Br) transparent ceramics

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Storage phosphors have a function to store incident radiation energy in the form of carrier trapping at localized trapping centers. The stored energy can be released by the stimulation of heat or light to emit photons. The resultant emission by the stimulation of heat or light are called thermally stimulated luminescence (TSL) and photostimulated luminescence (PSL), respectively. Such phosphors have been used for individual radiation monitoring devices and imaging plates (IPs). Since the late 1990s, Eu-doped CsBr has attracted much attention as the material for IPs, and many investigations on optical and PSL properties of Eu-doped CsBr have been reported on single crystals [1] and thin films [2]. In addition, the mixed anion compounds have been researched, and it has been reported that emission wavelength or lifetime can be controlled by changing the anion ratio of Eu-doped Cs(Cl, Br) in the form of single crystal [3]. In recent years, our research group has reported that transparent ceramics show better performance for radiation detection than single crystal counterparts [4]. However, there are no reports on optical and PSL properties of Eu-doped Cs(Cl, Br) transparent ceramics. In this study, we have synthesized Eu-doped Cs(Cl, Br) transparent ceramic samples with different anion ratio by the spark plasma sintering method. Subsequently, we have investigated the optical, scintillation and PSL properties.

Figure 1 shows a photograph of synthesized Eu-doped Cs(Cl, Br) transparent ceramic samples. It was confirmed that the mesh patterns on the back of the samples were clearly seen through the samples. The PSL and stimulation spectra of Eu-doped Cs(Cl, Br) transparent ceramic samples are shown in Figure 2. The peak position of stimulated spectrum shifted to long wavelength with increasing Br concentration. The PSL spectra of Eu-doped CsCl, Cs(Cl, Br) and CsBr showed a broad emission around 450 nm under the 610, 660 and 680 nm, respectively. The emission was due to the 5d-4f transitions of Eu^{2+}.

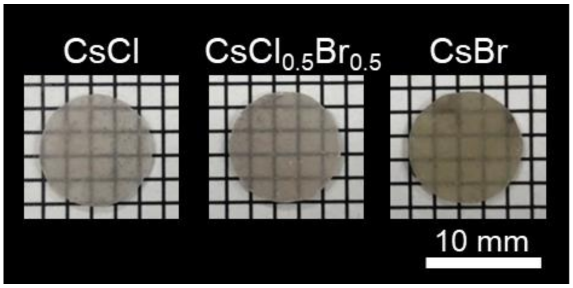

Figure 1: Synthesized Eu-doped Cs(Cl, Br) transparent ceramic samples under the room light.

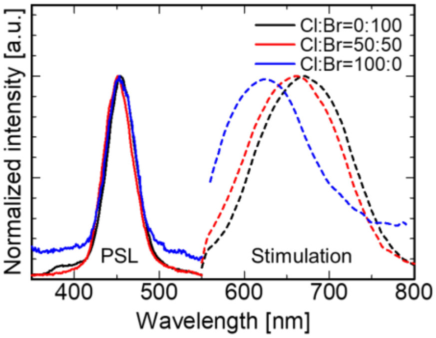

Figure 2: PSL (solid line) and stimulation (dotted line) spectra of Eu-doped Cs(Cl, Br) transparent ceramic samples.

References

[1] Y. V. Zorenko, *et al.*, *J. Appl. Spectrosc.*, **73**, 406–410 (2006) [2] H. Nanto, *et al.*, *Nicl. Instrum. Methods Phys. Sect. A*, **580**, 278–281 (2007) [3] N. Ganapathi Subramaniam, *et al.*, *J. Lumin.*, **102-103**, 807–814 (2003) [4] H. Kimura, *et al.*, *Optik.*, **157** 421–428 (2018)

Scintillation and dosimetric properties of Eu-doped $BaCaBO_3F$ ceramics

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[1] Akita University, [2] Nara Institute of Science and Technology, [3] Kanazawa Institute of Technology

Dosimeters based on phosphors have been widely used in many applications of radiation detectors such as environmental dosimetry, retrospective accidental dosimetry and individual radiation monitoring. Recently, fluoroborate compounds have been paid much attention for dosimetric applications owing to high quantum efficiency (*QE*) and high thermally-stimulated luminescence (TSL) sensitivity. For example, Ce-doped BaF_2-Al_2O_3-B_2O_3 glasses show high *QE* over 70% in photoluminescence (PL) [1]. Furthermore, the fluoroborate glasses show efficient TSL and the dynamic range are confirmed to be 0.1−1000 mGy [1]. Therefore, fluoroborate compounds are considered to be promising materials for dosimeter materials. In this study, we synthesized $BaCaBO_3F$ ceramics with different concentrations of Eu (0, 0.1, 1, 10%) by the conventional solid-state reaction. After the synthesis, we investigated their PL, scintillation and TSL properties.

B_2O_3, $Ca(OH)_2$, $BaCO_3$, BaF_2 and Eu_2O_3 were used as the starting materials. In the first step, B_2O_3, $Ca(OH)_2$ and $BaCO_3$ in a molar ratio of 1:2:1 were mixed for 1h and the mixture was sintered at 1000°C for 6 h in air. Then, $BaCa_2(BO_3)_2$ polycrystal was obtained. After that, $BaCa_2(BO_3)_2$, BaF_2 and Eu_2O_3 in a stoichiometric ratio were mixed sufficiently again, and subsequently sintered at 1000°C for 6 h in air. Finally, the undoped and Eu-doped $BaCaBO_3F$ ceramics were obtained.

The X-ray induced scintillation spectra of the undoped and Eu-doped $BaCaBO_3F$ were shown in Fig.1. The Eu-doped samples showed emissions due to the 4f-4f transitions of Eu^{3+} [2]. The 0.1% and 1% Eu-doped samples exhibited high scintillation intensity among the sample tested.

Figure.2 represents TSL glow curves of the undoped and Eu-doped $BaCaBO_3F$ after X-ray irradiation of 10 Gy. The 1.0% Eu-doped sample showed two glow peaks at 120 and 210°C while the 0.1% Eu-doped sample showed a glow peak at 120°C. Among the present samples, the 0.1% Eu-doped sample showed the highest TSL intensity. In this presentation, we also introduce PL and TSL properties in detail.

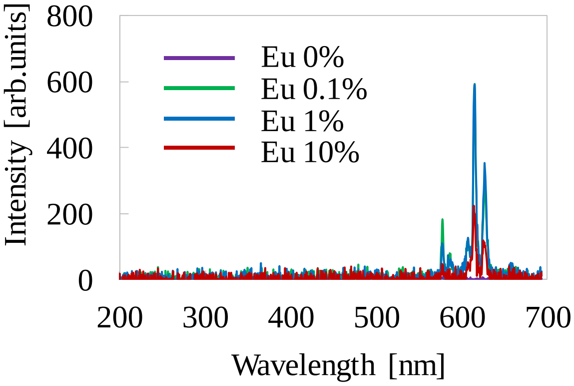

Figure 1: X-ray induced scintillation spectra.

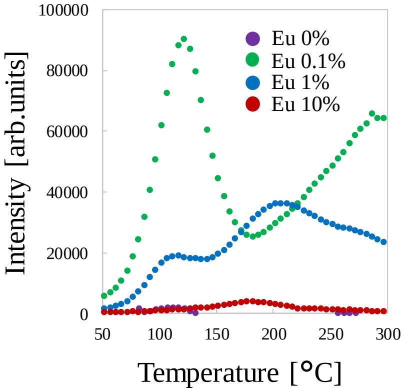

Figure 2: TSL glow curves after X-ray irradiation of 10 Gy.

References

[1] H. Samizu, K. Shinozaki, T. Kato, G. Okada, H. Masai, T. Yanagida, *Opt. Mater*. **90**, 64 (2019)
[2] C. Bensalem, M. Mortier, D. Vivien, M. Diaf, *Opt. Mater*. **33**, 791 (2011)

Scintillation properties of Nd-doped TeO_2-Al_2O_3-WO_3 glasses

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Scintillators are a type of phosphor materials for radiation measurement, and they convert a high-energy ionizing radiation to several thousands of low energy photons such as ultraviolet and visible light via energy transfer from host materials to luminescence centers. Recently, tellurite glasses have been focused on as a promising material for scintillator applications owing to many advantages such as high effective atomic number (Z_{eff}), high accommodation capability with impurity ions and chemical stability. Furthermore, a phonon energy (700–800 cm^{-1}) of the tellurite glasses are lower than that of conventional oxide glasses such as phosphate, germanite, silicate and borate glasses, thus tellurite glasses provide a low phonon energy environment to suppress non-radiative decay processes [1]. Therefore, tellurite glasses are one of the potential materials for scintillators since they are expected to show efficient emissions in both photoluminescence (PL) and scintillation owing to the suppression of non-radiative decay loss [2]. In this study, we synthesized TeO_2-Al_2O_3-WO_3 glasses doped with different concentrations of Nd (0, 0.1, 0.5 and 1.0 mol.%) by the conventional melt-quenching method. After the synthesis of the samples, we systematically investigated their PL and scintillation properties.

Figure 1 shows the X-ray induced scintillation spectra of the undoped and Nd-doped glasses. All the samples showed scintillation with peaks approximately at 900 and 1065 nm due to the 4f-4f transitions of Nd^{3+} [3]. The 1% Nd-doped sample exhibited the highest intensity among the samples.

Figure 2 represents the X-ray induce scintillation decay curves of the Nd-doped glasses. Each scintillation decay curve was fitted with two exponential decay functions. The scintillation decay time constants were approximately 6−20 μs and 110−123 μs. The faster and slower components were attributed to the instrumental response and the 4f-4f transitions of Nd^{3+}, respectively [3]. The decay time constant of the slower component was almost the constant, regardless of the concentrations of Nd. In this presentation, we will also introduce PL and afterglow properties.

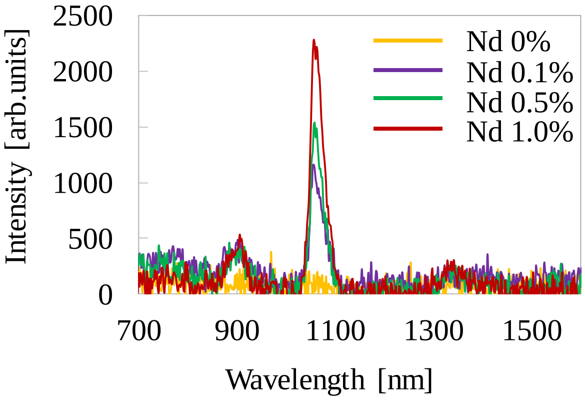

Figure 1: X-ray induced scintillation spectra.

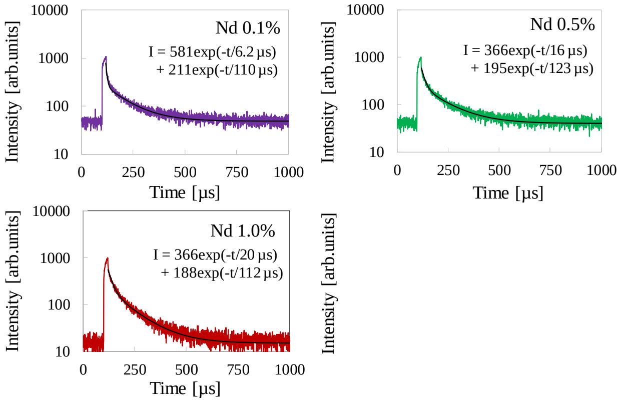

Figure 2: X-ray induced scintillation decay curves.

References

[1] M. Seshadri, V. Anjos, M.J.V. Bell, *J. Lumin*. **196**, 399 (2018)
[2] D. J. Robbins, *J. Electrochem. Soc*. **127**, 2694 (1980)
[3] D. Nakauchi, G. Okada, M. Koshimizu, T. Yanagida, *J. Rare. Earth*. **34**, 757 (2016)

Poster

Examination of luminescence initiated by ultrashort pulse excitation in $Gd_3Al_{2.5}Ga_{2.5}O_{12}$:Tm, Yb crystals.

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$Gd_3Ga_{2.5}Al_{2.5}O_{12}$ (GAGG) crystals doped with 1 at.% Tm and co –doped with 1 at.%, 3 at.% and 5 at.% Yb^{3+} were grown by the Czochralski technique. GAGG crystals belong to cubic garnet system with Ia-3d space group [1]. For Tm^{3+} and Yb^{3+} dopants various types of sites are available. Gadolinium ions reside into dodecahedral positions, surrounded by 8 oxygens while Ga^{3+} and Al^{3+} occupies tetrahedral and octahedral positions surrounded by 4 and 6 oxygen ions, respectively. In this material partial substitution of aluminum ions by gallium ions occurs and as result of that structural disorder brings about a considerable inhomogeneous broadening of luminescent ion spectral lines. Excitation of single crystal samples of Tm,Yb co-doped GAGG by femtosecond pulses results in an intense NIR-red emission originating in $^3H_4$, $^1G_4$ and $^1D_2$ thulium excited states while blue emission related to $^1G_4$-$^3H_6$ transition is characterized by lower intensity. It has been found that emission of thulium decreases effectively in GAGG:Tm,Yb crystals co-doped with higher concentrations of ytterbium. The rise time and decay time analysis was performed to examine effectiveness of population and relaxation of involved excited states. It was observed that higher Yb^{3+} concentration affects significantly relaxation of considered luminescent levels in materials under study.

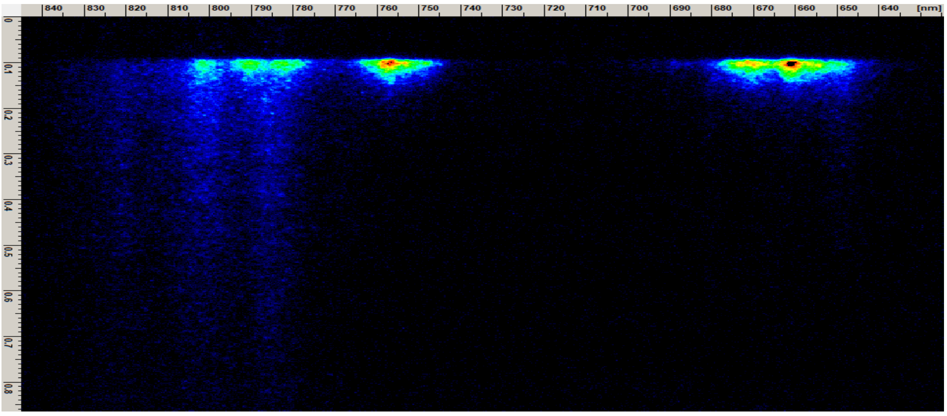

Figure 1: Image obtained with a streak camera showing details of spectral distribution of GAGG:1%Tm,1%Yb luminescence intensity in spectral region 620–840 nm.

Acknowledgements

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References

[1] Filippo Maglia, Vincenzo Buscaglia, Silvia Gennari, Paolo Ghigna, Monica Dapiaggi, Adolfo Speghini, Marco Bettinelli, *J. Phys. Chem. B* **110** 6561-6568 (2006)

Direct femtosecond laser printing of rare earth-doped silk microstructures.

Poster

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Silk fibroin (SF) is an abundant natural polymer, which in the last years has been studied as an attractive high-technology material platform [1]. Precise patterning of SF-based materials for functional microstructures has extensive applications including tissue engineering, biosensing and photonic devices. Considerable progress has been made based on lithographic methods and self-assembly approach [2]. However, most methods require chemical modification of silk fibroin to be photoreactive and demand photoinitiators, which significantly affect the optical, mechanical and biological properties of the material. At the same time, femtosecond laser induced forward transfer (fs-LIFT) has been explored as an attractive processing tool for microprinting, which can be used in the fabrication, for instance, of high-resolution complex 2D structures [3]. Herein, we were able to fabricate luminescent structures of regenerated silk fibroin (RSF) through maskless fs-LIFT technique, using a Ti:Sapphire laser oscillator delivering 50-fs pulses at 800 nm with a repetition rate of 5 MHz. Eu^{3+}/Tb^{3+} complexes were added to RSF as a gain medium, to further demonstrate the flexibility of this approach. The silk fibroin patterns were printed as hemisphere structures with diameter of 3µm and height 1 µm. Analyses of luminescence and FTIR spectroscopies confirmed that fs-LIFT does not change the optical and structural properties of silk fibroin composites. Our ability to precisely position and fabricate functionalized RSF microstructures in a repetitive and reproducible manner presents several opportunities for future innovative sensors, photonic and biomedical devices.

Acknowledgements

We acknowledge financial support from Fundação de Amparo à Ciência e Tecnologia do Estado de São Paulo (FAPESP - 2018/11039-9).

References

[1] H. Tao, D.L. Kaplan, F.G. Omenetto, Adv. Mater., 24, 2824–2837 (2012).
[2] L.D. Koh, J. Yeo, Y.Y. Lee, Q. Ong, M. Han, B.C.K. Tee, Mater. Sci. Eng. C., 86, 151–172 (2018).
[3] A. Piqué, J. Laser Micro/Nanoengineering, 9, 192–197, (2014).

Exploring the tunneling luminescence process in strontium aluminate phosphors

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Institutions: Institute of Solid State Physics, University of Latvia

Strontium aluminates doped with Eu and Dy are persistent afterglow materials, that continue to emit light up to 20 hours after irradiation, therefore can be very useful for road signs, emergency lighting and other application. The main reason for the lengthy afterglow is gradual electron migration from trapping centers to the luminescence center and resultant recombination, thus creating the well-known green afterglow. It has been shown that the electron return to the luminescence center can happen in two ways – with the aid of thermal stimulation and by electron tunneling [1, 2]. The tunneling process is not temperature dependent, therefore a possibility to increase the efficiency of the tunneling process would contribute greatly to cold weather condition applications, for example, road signs in Nordic countries. Therefore, this research is focused on linking the low temperature afterglow intensity and duration to the structure of the luminophore. The contribution of the two crystallographically different positions of the luminescence center in the tunneling process are discussed.

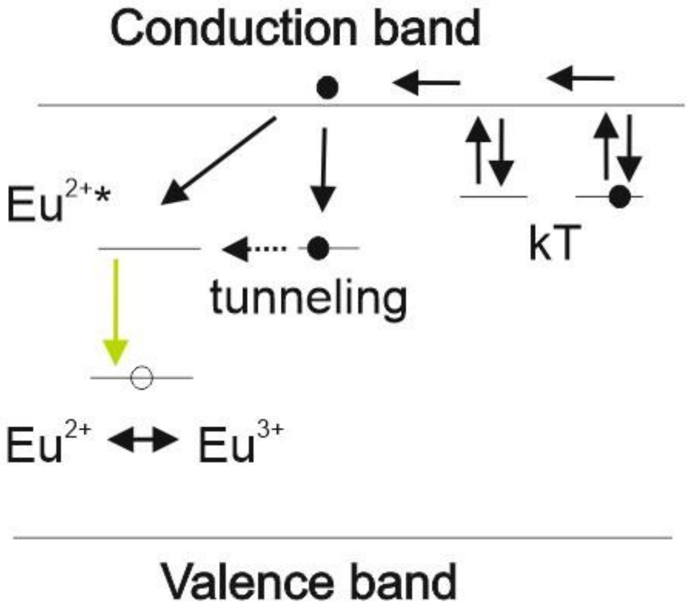

Figure 1: The mechanism of persistent luminescence in $SrAl_2O_4$:Eu, Dy material

Acknowledgements

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References

[1] V. Liepina, D. Millers, K. Smits "Tunneling luminescence in long lasting afterglow of $SrAl_2O_4$:Eu,Dy" *J. Lumin.*, **185**, 151-154 (2017).

[2] V. Liepina, D. Millers, K. Smits, A. Zolotarjovs, I. Bite "X-ray excited luminescence of $SrAl_2O_4$:Eu,Dy at low temperatures" *J. Phys. Chem. Solids*, **115**, 381-385 (2017)

Dynamic tunability of upconverting $NaYF_4$ colloidal nanoparticles by Ce^{3+} co-doping

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The possibility to tune and manipulate the UC emission color of lanthanide doped NP's is very important in case of their possible applications such as information storage, biological sensing, as well as graphics imaging and display.[1] For that reason new approaches are sought, which allow to obtain higher emission intensity or to dynamically modulate the luminescent properties of those materials. One of the possible way to obtain such goals is incorporation of passive impurities, which affect activator distribution within the UCNP, or active impurities which play an active role in energy transfer processes. Usually, such an approach leads to important modification of energy distribution and energy transfer upconversion. In consequence, the relative intensities of emission bands change and modify the overall emission color.[2,3]

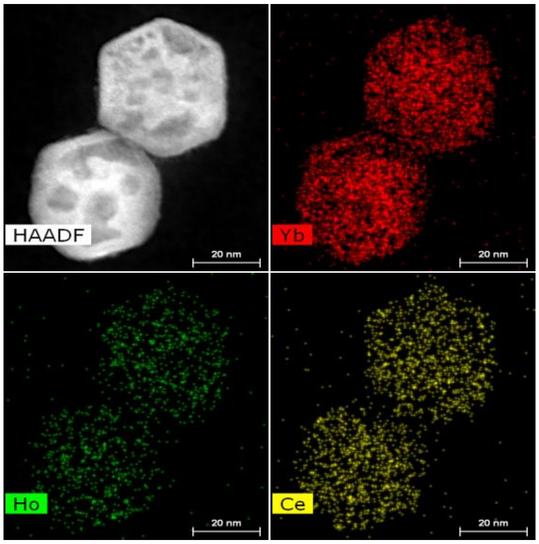

Figure 1. TEM and TEM-EDS images of $NaYF_4$:20%Yb^{3+}, 2%Ho^{3+}, 8%Ce^{3+} showing the distribution of Yb^{3+}(red) Ho^{3+} (green) and Ce^{3+} (yellow) codopants.

Several research groups observed that by the incorporating the Ce^{3+} to the NP's the red emission can be enhanced, and thus with proper selection of concentration of the co-dopants and excitation conditions the green and red emission can be obtained in Yb^{3+} /Ho^{3+} /Ce^{3+} doped systems.[4] The reason for this is that the Ce^{3+} ion has a small energy gap of about 3000 cm^{-1}, which only affects energy transfers that involve similar energy gaps.

In order to verify the influence of Ce^{3+} codoping on the luminescent properties of UCNP's based on Yb/Er and Yb/Ho co-doped doped colloidal $NaYF_4$ nanoparticles, the series of materials with different Ce^{3+} concentration was synthesized. The full structural (X-Ray Diffraction), morphological (Transmission Electron Microscopy) and spectroscopic characterization (emission spectra in function of temperature, decay and rise times) will be presented. In addition, the power dependence measurements, PWM (pulse width modulation) dependent and time resolved luminescent spectra measurements will be shown.

Acknowledgements

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References

[1] Deng, R.; Qin, F.; Chen, R.; Huang, W.; Hong, M.; Liu, X., *Nat Nanotechnol*, **10**, 237-242 (2015)

[2] Cong, T.; Ding, Y.; Yu, X.; Mu, Y.; Hong, X.; Liu, Y., *Mater. Res. Bull.*, **90**, 151-155 (2017)

[3] Kamimura, M.; Omoto, A.; Chiu, H.-C; Soga, K.; *Chem. Lett.*, **46**, 1076-1078 (2017)

[4] Chen, G.; Liu, H.; Somesfalean, G.; Liang, H.; Zhang, Z., *Nanotechnology*, **20**, 81542-81551(2009)

Photoluminescence properties of coumarins containing copolymers

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Coumarins belong to the class of heterocyclic compounds known as benzopyrones. They consist of fused pyrone and benzene rings with the pyrone carbonyl group at position 2. Coumarins are well-known for their photochemical and photophysical properties. There are also recognized due to their photoinduced cyclodimerisation properties leading to cyclobutane-based dimers with four possible isomeric configurations *syn* head-to-head, *anti* head-to-head, *syn* head-to-tail, and *anti* head-to-tail [1-4]. Coumarin system offers a unique opportunity for applications involving conjugated molecular frameworks, and photo-induced dimerisation. The photocleavage can be induced upon irradiation with higher energy photons at shorter wavelengths (see Fig. 1).

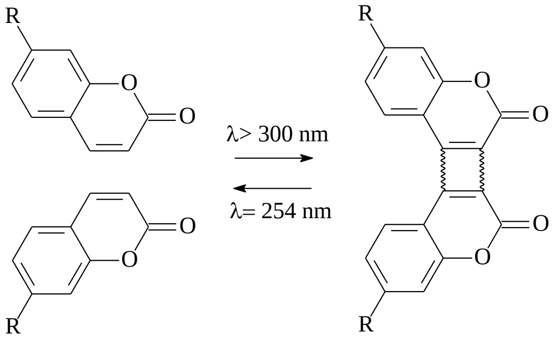

Figure 1: Reversible photoinduced cyclodimerisation of coumarins

Polymers with coumarin fragment are useful in many fields such as photoalignment of liquid crystalline molecules, photoactive surface application, electroluminescence, photovoltaic, fluorescence materials and laser dyes.
In this work, we report photoluminescence properties of thin films of coumarin containing copolymers.

Acknowledgements

The authors would like to thank M. Salle (Angers University) for support.

References

[1] D. Gindre, K. Iliopoulos, O. Krupka, E. Champigny, Y. Morille, M. Sallé, Image storage in coumarin-based copolymer thin films by photoinduced dimerization, Optics Letters 38, 4636- 4639 (2013)
[2] Z. Essaidi, O. Krupka, K. Iliopoulos, E. Champigny, B. Sahraoui, M. Sallé, D. Gindre, Synthesis and functionalization of coumarin-containing copolymers for second order optical nonlinearities, Optical Materials 35, 576-581 (2013)
[3] K. Iliopoulos, O. Krupka, D. Gindre, M. Salle, Reversible Two-Photon Optical Data Storage in Coumarin-Based Copolymers, Journal of the American Chemical Society 132, 14343-14345 (2010)
[4] L. Skowronski, O. Krupka, V. Smokal, A. Grabowski, M. Naparty, B. Derkowska-Zielinska, Optical properties of coumarins containing copolymers, Optical Materials 47, 18-23 (2015)

Microscopic parameters characterizing thermoluminescence in Ce-doped garnets

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Complex Ce-doped garnets receive a lot of attention recently as promising scintillators for medical imaging [1], phosphors for LED applications [2] and persistent phosphors [3]. The research on garnets generally consists of careful tuning of composition, stoichiometry and impurity (doping) concentrations. One of the main goals of these modifications is to influence the complex interplay between recombination and trapping/detrapping processes [4]. Extensive research has contributed to a good qualitative understanding of how traps, impurities and the presence of Ce^{4+} affect the materials properties. In this work we present a quantitative model that can explain the thermoluminescence and afterglow behavior of complex garnets.

In particular, the model allows the determination of capture rates and effective capture radii for electrons by traps and recombination centers in $Lu_1Gd_2Ga_3Al_2O_{12}$:Ce garnet ceramics. The model relies on solving a set of coupled rate equations describing charge carrier trapping and recombination in garnet ceramics doped with Ce and also co-doped with a known concentration of an intentionally added electron trap, Yb^{3+}. The model is supported by analysis of a complete set of experimental data on afterglow, rise-time kinetics and X-ray excited luminescence which show that thermoluminescence is governed by trapping/detrapping processes following interactive kinetics with dominant recombination channel. The underlying reason for dominant recombination is the presence of a small fraction of Ce^{4+} (~2 ppm in the 0.2 % Ce-doped sample) which have a very high capture cross-section (~2.7 Å effective radius) because of the Coulomb attractive nature of this recombination center.

The quantitative insights on capture cross-sections and concentrations of Ce^{4+} help to better understand the optical properties of Ce-doped garnet scintillators and persistent luminescent materials and serves in optimizing synthesis procedures by tuning the Ce$^{3+/4+}$ ratio by co-doping with divalent cations and annealing in an oxygen containing atmosphere.

References

[1] C. W. E. van Eijk, *Phys. Med. Biol.*, **47**, R85 (2002)

[2] Z. Xia, A. Meijerink, *Chem. Soc. Rev.*, **46**, 275–299 (2017)

[3] J. Ueda, P. Dorenbos, A. J. J. Bos, K. Kuroishi, S. Tanabe, *J. Mater. Chem. C*, **3**, 5642–5651 (2015)

[4] M. Nikl, V. Babin, J. A. Mares, K. Kamada, S. Kurosawa, A. Yoshikawa, J. Tous, J. Houzvicka, K. Blazek, *J. Lumin.*, **169**, 539-543 (2016)

Alkali cations effects on structural, morphological and photoluminescence properties of zinc oxide materials (ZnO) synthesized from seed growth by hydrothermal process.

Poster

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One-dimensional semiconducting nanostructures have stimulated great interest due to their interesting properties that differ from those of the bulk or spherical nanoparticles of the same composition. ZnO is one of the most attracting semiconductors due to its intrinsic properties that are enhanced at the nanoscale. In particular, one can cite the wide direct band-gap (3,37 eV), the large exciton binding energy (60 meV) at room temperature and an excellent chemical and thermal stability. Moreover, it is a versatile smart material with unique applications in sensors, photovoltaic, surface acoustic wave devices, light emitting diodes and luminescent devices, transparent conductive coatings and others [1-4].

In the present work, we describe the seed growth hydrothermal method of different shaped ZnO nano/microrods. Alkaline colloidal solutions are prepared separately and added with different quantities to the principal solution. The growth ZnO particles are ended hydrothermally in autoclave. The impact of colloidal solutions volume added as well as alkali cation's type on the morphology, crystallite size and their distributions is presented and discussed. Furthermore, the vibrational and optical properties of the obtained particles are also investigated.

[1] Z.W. Pan, Z. R. Dai, Z. L. Wang, *Science*, **291,** 1947 (2001).
[2] C. Klingshirna, J. Fallerta, O. Gogolinb, M. Wissingera, R. Hauschilda, M. Hausera, H. Kalta, H. Zhoua, *J of luminescence*, **128,** 792 (2008).
[4] D.Vanmaekelbergh and L. K. van Vugt, *Nanoscale*, **3**, 2783 (2011).
[5] V.Kumar, O. M. Ntwaeaborwa, T. Soga, V. Dutta and H. C. Swart, *ACS Photonics*, 4 (11), 2613 (2017).

Poster

Visualizing the infection dynamics of pathogenic bacteria labelled by upconverting nanoparticles inside mouse gut

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This study intends to show the potential use of near-infrared light (NIR) triggered luminous nanoparticles, also known as upconverting nanoparticles (UCNPs), to investigate the colonization and infection dynamics of a natural murine intestinal pathogen, *Citrobacter rodentium* (*C.rodentium*), which colonizes in mice GI tract, and induces inflammation. Remarkably, this pathogen expresses genetic similarities to human pathogens, including enteropathogenic *Escherichia coli* (EPEC) and enterohemorrhagic *E.coli* (EHEC) that are well associated with significant human gut diseases including inflammatory bowel disease (IBD) development. Although the exact causes of IBD are still unknown, the recent studies show that gut microbiota is a contributing factor to IBD [1]. Although the role of intestinal pathogens in the development of IBD in animals is revealed, the interaction mechanisms between the host and pathogen are still to be defined precisely. *C. rodentium* infection model is considered as a useful preliminary method to understand these interactions *in vivo* [2]. It has been studied by different optical imaging techniques *in vivo*, including fluorescence imaging (FI) and bioluminescence (BL) [3, 4]. FI employs custom designed organic fluorophores as contrast markers, whereas BL rely on genetically modified pathogen strains that are able to catalyse luciferin molecule by luciferase enzyme. However, using organic fluorescent dyes *in vivo* suffers tissue autofluorescence and photobleaching. In the case of BL, it is not always possible to genetically engineer all types of bacteria strains for BL use. Nevertheless, in this study, NIR light triggered lanthanide (Ln) doped UCNPs are employed as both labelling and contrast agents to visualise the infection dynamics of *C.rodentium*. First, surface of ligand free Ln-UCNPs are functionalized through citrate modification method for further antibody (Ab) conjugation. Next, anti-*C.rodentium*-Ab are bioconjugated with Ln-UCNPs to label *C.rodentium*. Upconversion (UC) photoluminescence from Ab-UCNP labelled *C.rodentium* in mouse is imaged by a commercial imaging system (IVIS Lumina III, *Perkin Elmer*). Herein, it should be noted that major optical design modifications has been done to IVIS Lumina III to make it use in NIR region. Ln-UCNPs with unique optical properties yield noticeable advantages including free tissue autofluorescence, high penetration depths, and high photochemical stability. Finally, the infection profile of *C.rodentium* has been mapped through UC emission from labelled bacteria *in vivo*.

Acknowledgements

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References

[1] Wirtz S., and Neurath M. F., *Advanced drug delivery reviews*, **59,** 1073-1083 (2007).
[2] Silberger D.J., Zindl C.L., and Weaver C.T., *Mucosal Immunology*, **10**, 1108 (2017).
[3] Leevy W. Matthew, et al., *Journal of the American Chemical Society*, **128,** 16476-16477 (2006).
[4] Andreu N., Zelmer A., and Wiles S., *FEMS microbiology reviews*, **35,** 360-394 (2011).

Upconversion emission studies of structural phase flips in Er^{3+}/Yb^{3+}: $KLaF_4$ bio-compatible nanoparticles

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Abstract

Up-conversion nanoparticles (UCNPs) are emerging as exciting alternatives to conventional organic dyes and quantum dots in the field of bio-imaging and targeted drug delivery. Due to the superior properties, it is more advantageous and effective to develop these UCNPs as a possible replacement of conventional imaging organic/inorganic light emitters. Herein, we report up-conversion emission monitoring of structural phase flips from cubic to hexagonal ordered $KLaF_4$ UCNPs doped with Er^{3+} and Yb^{3+} as sensitizer, fabricated from conventional chemical synthesis route[1, 2]. Morphological studies were carried out on these UCNPs to demonstrate their crystal phase and purity. Under the infrared (CW and femtosecond) laser excitation, these UCNPs emit intense up-converted green to red ($^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$) color emission, based on the structural transformation from cubic to hexagonal phases. Details of up-conversion emission process based on double photon excitation, energy transfer (ET) and Ground/Excited states absorption (GSA/ESA) processes are discussed. Finally, we demonstrate that these UCNPs are potential host lattices for low-cost bio-imaging and targeted drug delivery applications.

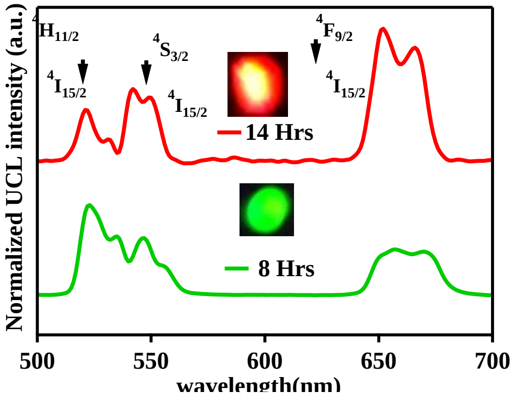

Figure 1: Up-conversion Emission spectra of $KLaF_4:Er^{3+}/Yb^{3+}$ UCNPs. λ_{exe}= 980nm.

Acknowledgements:

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References:

1. M. Gupta , M. Adnan, R. Nagarajan , G. Vijaya Prakash, *ACS Omega*, **4**, 2275 (2019)
2. A. Prasad, A. Srinivasa Rao, M. Gupta, G Vijaya Prakash, *Mater. Chem. Phys*, **219**, 13(2018)

Structural and spectroscopic properties of thermally stable Eu^{3+} doped barium zinc orthophosphate phosphor for w-LEDs

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Monoclinic crystalline structure of europium (Eu^{3+}) activated barium zinc orthophosphate (BZP) phosphor has been synthesized via solid-state reaction method in ambient atmosphere. The phase purity, structural and emissive characteristics have been analyzed by recording X-ray diffraction pattern and photoluminescence (PL) spectra, respectively. The diffraction pattern demonstrated the single phase formation of BZP sample and is similar with the standard data (JCPDS-16-0554). The results indicate that BZP sample consist of monoclinic structure with space group $P2_{1/}c$ and the lattice constant a, b and c values are 8.59, 9.76 Å, and 9.15 Å, respectively. Scanning electronic micrograph of BZP powder specifies the uniform spherical shape with some agglomeration of the synthesized particles. The particle size for BZP powder sample varies from 2 to 8 μm. The PL spectra exhibit the most intense emission peak centered at 616 nm owing to $^5D_0 \rightarrow {}^7F_2$ transition of europium ions under the 393 nm (n-UV) and 466 nm (blue) excitations. Emission spectra reveal that the PL intensity improves with the concentration of Eu^{3+} ions up to 4.0 mol% and beyond that, the PL intensity decreases. The CIE coordinates evaluated for the as-synthesized phosphor, which lies in the red region and close to commercial red phosphors Y_2O_2S: Eu (0.647, 0.343). The average decay time of the Eu^{3+} doped BZP phosphor is in the millisecond range and the value decreases with increasing Eu^{3+} concentration. The emission intensity remains to 68.41% at 423 K of that at room temperature, which indicates good thermal stability in the BZP phosphor. All these results indicate the suitability of the as-synthesized phosphors for white light emitting (w-LEDs) devices [1, 2].

References

[1] T. Pulli, T. Dönsberg, T. Poikonen, F. Manoocheri, P. Kärhä, E. Ikonen, *Light Sci Appl.*, **4(9)**, e332 (2015).
[2] J. Chen, W. Zhao, J. Wang, N. Wang, *J. Mater. Sci. Mater. Electron,*. **27**, 237–244 (2016).

Poster

Photoluminescence studies on Er^{3+}-doped sodium-bismo-phosphate glasses for optoelectronic applications

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Erbium (Er^{3+}) ion doped Na_2O - Bi_2O_3- P_2O_5- SrO glasses were fabricated by using melt quenching technique and studied the influence of Er^{3+} ion concentration on the photoluminescence (PL) performance using the spectroscopic techniques to understand the utility of the titled glasses for optical fiber amplifiers. The XRD pattern reveals amorphous nature of the as-synthesized glass. The emission spectra exhibit intense band at around 535 nm corresponding to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition under near ultraviolet (n-UV) excitation. The chromaticity coordinates of the glasses are calculated by evaluating the tristimulus values from the emission spectra when excited at 376 nm wavelength. The PL decay curves for $^4S_{3/2}$ (visible) level are discussed and they are exhibiting non-exponential nature for the as prepared glasses. Optimum value for green emission intensity was obtained at dopant concentration 1.0 mol%. The above-mentioned studies show potentiality of the as-synthesized Er^{3+} doped Na_2O - Bi_2O_3- P_2O_5- SrO glasses in optoelectronic applications.

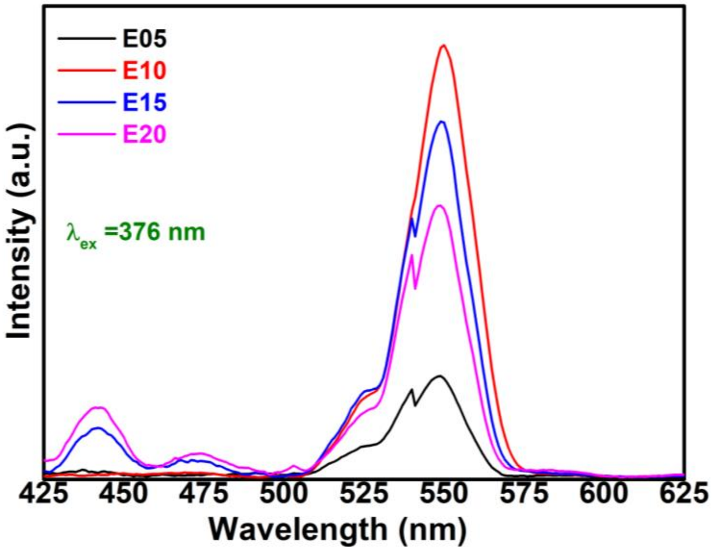

Figure 1: Photoluminescence spectra of Er^{3+} for NBSP glasses under 376 nm excitation.

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References

1. Rupesh A. Talewar, Sk. Mahamuda, A. Vyas, A.S. Rao and S.V. Moharil, *J. Alloys Compds*, **775,** 810-817 (2019).