

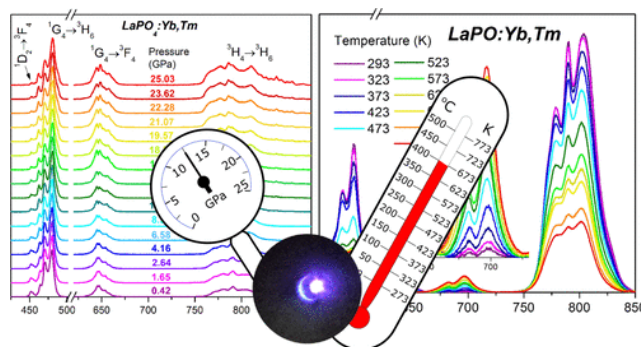
Inorganic nanoluminophores and their functionalized systems based on rare earth ions: application potential and new research perspectives

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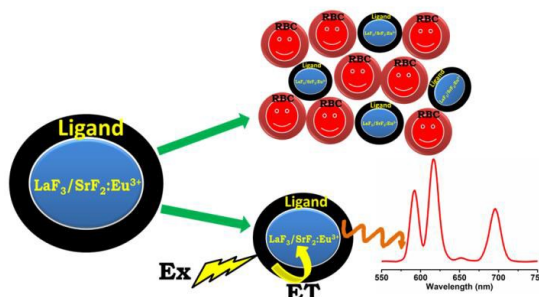
Luminescent nanomaterials containing rare earth (RE) ions are of great interest and due to their unique properties they can be applied in various fields, such as optoelectronics, plasma displays, lasers, solar cells, lighting, forensic and security materials, as well as materials bio-related areas.

In my lecture I will present the results of our own investigations concerning selected nanomaterials based on inorganic matrices (e.g.: fluorides, borates, phosphates, vanadates, silicates, etc.) doped with the luminescent RE ions, which are characterized by high thermal and photochemical stability. As application materials, they should show: phase purity, high crystallinity and homogeneity, small particle size and narrow particle size distribution, and should not be agglomerated. Synthesized, under intentionally designed and optimal experimental conditions, nanoluminophores (NLs) and up-converting luminophores (UCNLs), core-shell surface functionalized nanoparticles (NPs) and multifunctional (e.g. luminescent-magnetic) hybrids have been characterized structurally and spectroscopically in detail. Selected NPs showing effective luminescence (of RE) and superparamagnetism (of Fe_3O_4) have been successfully applied as multifunctional materials, e.g. as modifiers (luminescent/magnetic) incorporated into cellulose materials, which confirms the concept of advanced, multimodal protection of documents (clothing) against counterfeiting, or functionalized by chains of helical complexes of various lanthanide ions as building blocks in the design novel multifunctional nanosystems.



The successful application of the luminescent RE^{3+} /(and/or RE^{2+})-doped NPs as optical and multifunctional optical sensors for nanomanometry and nanothermometry (e.g. fluorides, phosphates, borates, vanadates) will be discussed.

Our research on luminescent (Eu^{3+} -doped) NPs functionalized with the desired organic (e.g. Aspirin, ibuprofen, aspirin) ligand molecules for hemocompatibility studies proved that the tested nanomaterials are highly biocompatible compounds in vitro and can be further investigated for biomedical application in vivo. In recent studies we demonstrated that luminescent NPs of $\text{CaF}_2:\text{Tb}^{3+}(\text{Eu}^{3+})$ -capped organic ligands, can be successfully used luminescent probes, for the determination of metal species (WO_4^{2-} , MnO_4^- , Cu^{2+}) in water samples, using highly selective fluorescence methods, based on energy transfer from the analyte ion to the Tb^{3+} , (or Eu^{3+}) ions.



References

- W. T. Carnall, Handbook on the Physics and Chemistry of Rare Earths, (Eds.) K. A. Gschneidner, L.R. Eyring, Vol.3, 1979, Vol.21, 1995, North Holland, Amsterdam.
- S. Lis, Luminescence Studies of Lanthanide(III) Ions in Solution, *J. Alloys Comp.*, 341 (2002) 45-50.
- A. M. Kłonkowski, S. Lis, M. Pietraszkiewicz, Z. Hnatejko, K. Czarnobaj, M. Elbanowski, Luminescence Properties of Materials with Eu(III) Complexes. Role of Ligand, Coligand, Anion, and Matrix, *Chem. Mater.*, 15 (2003) 656-663.
- T. Grzyb, S. Lis, Structural and Spectroscopic Properties of LaOF:Eu³⁺ Nanocrystals Prepared by the Sol-Gel Pechini Method, *Inorg. Chem.*, 50 (2011) 8112–8120.
- T. Grzyb, A. Gruszczyńska, R. J. Wiglusz, S. Lis, The effects of down- and up-conversion on dual-mode green luminescence from Yb³⁺- and Tb³⁺-doped LaPO₄ nanocrystals, *J. Mater. Chem. C*, 1 (2013) 5410-5418.
- A. Szczeszak, A. Ekner-Grzyb, M. Runowski, L. Mrówczyńska, T. Grzyb, S. Lis, Synthesis, photophysical analysis and in vitro cytotoxicity assessment of the multifunctional (magnetic and luminescent) core@shell nanomaterial based on lanthanide doped orthovanadates, *J. Nanoparticle Research*, 17 (2015) 143, 11 pages.
- M. Runowski, A. Ekner-Grzyb, L. Mrówczyńska, S. Balabhadra, J. Paczesny, A. Zep, T. Grzyb, S. Lis, Synthesis and organic surface modification of lanthanide doped, luminescent core/shell nanomaterials – LnF₃@SiO₂@NH₂@organic acid, *Langmuir*, 30 (2014) 9533–9543.
- P. Kulpiński, A. Erdman, T. Grzyb, S. Lis, Luminescent cellulose fibers modified with cerium fluoride doped terbium particles, *Polymer Composites*, 37 (2016) 153-160.
- Q. Guo, C. Zhao, L. Liao, S. Lis, H. Liu, L. Mei, Luminescence investigations of novel orange–red fluorapatite KLaSr₃(PO₄)₃F:Sm³⁺ phosphors of high thermal stability, *JACerS*, 100, (2017) 2221-2231.
- M. Runowski, A. Shyichuk, A. Tyminiński, T. Grzyb, V. Lavin, S. Lis, Multifunctional Optical Sensors for Nanomanometry & Nanothermometry: High-Pressure and Temperature Upconversion Luminescence of Lanthanide Doped Phosphates - LaPO₄/YPO₄:Yb³⁺-Tm³⁺, *ACS Appl. Mater. Interfaces*, 10 (2018) 17269-17279.
- M. Skwierczyńska, M. Runowski, P. Kulpiński, S. Lis, Modification of cellulose fibers with inorganic luminescent nanoparticles based on lanthanide(III) ions, *Carbohydrate Polymers*, 206 (2019) 742-748.
- M. Runowski, N. Stopikowska, D. Szeremeta, S. Goderski, M. Skwierczyńska, S. Lis, Up-Converting Lanthanide Fluoride Core@Shell Nanorods for Luminescent Thermometry in the First and Second Biological Windows - β-NaYF₄: Yb³⁺, Er³⁺@SiO₂ Temperature Sensor, *ACS Appl. Mater. Interfaces*, 11 (2019) 13389–13396.
- T. Zheng, M. Runowski, P. Woźny, S. Lis, V. Lavin, Huge Enhancement of Sm²⁺ Emission via Eu²⁺ Energy Transfer in a SrB₄O₇ Pressure Sensor, *J. Mater. Chem. C* 8, (2020) 4810-4817.
- S. Goderski, S. Kanno, K. Yoshihara, H. Komiya, K. Goto, T. Tanaka, S. Kawaguchi, A. Ishii, J. Shimoyama, M. Hasegawa, S. Lis, Lanthanide Luminescence Enhancement of Core–Shell Magnetite–SiO₂ Nanoparticles Covered with Chain-Structured Helical Eu/Tb Complexes, *ASC Omega* 5, 51 (2020) 32930–32938.
- N. Stopikowska, M. Runowski, P. Woźny, S. Goderski, S. Lis, Improving temperature resolution of luminescent nanothermometers working in the near-infrared range using non-thermally coupled levels of Yb³⁺ & Tm³⁺, *J. Luminescence*, 228 (2020) 117643.
- S. Goderski, M. Runowski, P. Woźny, V. Lavin, S. Lis, Lanthanide Upconverted Luminescence for Simultaneous Contactless Optical Thermometry and Manometry–Sensing under Extreme Conditions of Pressure and Temperature, *ACS Appl. Mater. Interfaces*, 12, 36 (2020) 40475–40485.
- V. Adusumalli, L. Mrówczyńska, D. Kwiatek, Ł. Piosik, A. Lesicki, S. Lis, Ligand sensitised LaF₃:Eu³⁺ and SrF₂:Eu³⁺ nanocrystals and their in vitro haemocompatibility, *ChemMedChem*, 16 (2021) 1-12.