Project No. 02507

Report form of Joint Research Project at ZAIKEN (FY2025)

Title of Project	**Experimental and first-principles studies of the electronic properties of dopants in optical materials**		
Priority Area	**III－B Energy Saving & Structures; III－C Energy Saving & Properties**		
New proposal or Continuation of 2024			
Name of Main Applicant	**Mihail G. Brik**		
Institution	**Centre of Excellence for Photoconversion, Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia**	**title**	**Professor**
Name of the host faculty at Waseda	**Prof. Tomoyuki Yamamoto**		

Aim of the research project

Development of advanced optical materials is very important for many technological applications. The phosphor materials based on the transition metal or rare earth ions doped crystalline solids are used for lighting, sensing, bioimaging etc. Performance and limitations of such phosphors is determined by a combination of the properties of dopants and host materials. Thoroughly performed studies of their structural and electronic properties are of paramount importance for a meaningful development of phosphor materials. In this continued project with Prof. Yamamoto we extend our activities on the combined experimental and theoretical studies of the Mn^{4+}- and Cr^{3+}-doped phosphors and photon up-conversion in the rare-earth ions doped materials. These materials are vital for lighting, e.g. the Mn^{4+}-doped red phosphors improve properties of white LEDs, increase their efficiency and reduce their cost; in addition, they are also beneficial for plant growth. They can also be used for noncontact temperature measurements. We shall study the properties of the synthesized phosphor materials in the powder form (focusing on the perovskites and double perovskites), study their properties by the X-ray diffraction, UV-Vis, photoluminescence, ESR measurements and complement these experimental findings by the theoretical density functional theory (DFT)-based calculations to interpret the obtained results and elucidate the main factors affecting the materials' performance.

Contents and results of the research
(Please indicate to which extent the expected objectives in your proposal have been achieved.)

1. Experimental and first-principles studies of Mn^{4+}-, Cr^{3+}- and rare-earth-ion-doped optical materials were continued through the collaboration between Prof. Tomoyuki Yamamoto's group at Waseda University and Prof. Mihail G. Brik's group at the University of Belgrade. Experimental characterization and density functional theory (DFT)-based calculations were carried out to clarify the relationships between crystal structures, electronic structures, and optical properties of phosphor materials.
2. First-principles DFT calculations were performed to investigate the electronic structures and optical transition energies of Cr^{3+}- and Mn^{4+}-activated phosphors. New computational schemes based on the ΔSCF-DFT approach were developed to evaluate the emission energies of Cr^{3+}-activated fluoride phosphors, providing improved theoretical models for analyzing luminescence mechanisms.
3. The thermal quenching mechanism of Mn^{4+}-doped fluoride phosphors was systematically investigated by combining first-principles calculations with available experimental data. The study clarified the relationships among crystal structure, lattice stability, electronic structure, and luminescence efficiency, and proposed predictive design principles for high-performance phosphor materials suitable for energy-saving lighting applications.
4. Comparative theoretical studies on Cr^{3+}-activated oxide and fluoride phosphors revealed systematic relationships between local coordination environments, chemical bonding, and zero-phonon-line transition energies. These results provide useful guidelines for designing new near-infrared phosphors with improved optical performance.
5. Several joint papers were published in international journals during FY2025, and the research results were presented at international conferences held in Spain, Romania, and Latvia. These achievements further strengthened the long-term international collaboration between Waseda University and the University of Belgrade and expanded scientific exchanges with collaborating researchers in Europe, North America, and Asia.
6. Comparing the initial research plan with the obtained results, the expected objectives of the project were successfully achieved.

Outputs of the project (publications, presentations, patents)

Invited talks were given by Prof. M.G. Brik at several International Conferences, e.g., 22nd International Conference on Radiation Effects on Insulators (REI-22), Madrid, Spain, June 8–13, 2025, Functional Materials and Nanotechnologies (FMNT 2025), Riga, Latvia, 8th International Conference on Advanced Elecrtromaterials, November 25-28, Jeju, Korea.

The following joint papers were published in peer-reviewed international journals:

1. Zafari Umar, Oleg Khyzhun, Alexander Platonenko, Tomoyuki Yamamoto, Mikhail G. Brik, Michal Piasecki, Different calculating schemes for evaluating the transition emission energies in a Cr^{3+}-activated $KMgF_3$ phosphor: ΔSCF-DFT approaches, Computational Condensed Matter 47 (2026), e01274.
2. Mekhrdod S. Kurboniyon, Alok M. Srivastava, William W. Beers, William E. Cohen, Mohammad Bagheri, Bibo Lou, Tomoyuki Yamamoto, Mikhail G. Brik, Chong-Geng Ma, First-principles study of thermal quenching mechanism of Mn^{4+}-doped fluoride phosphors: Electronic structure, optical properties and phosphor design principles, Chemical Engineering Journal 525 (2025), 170227.
3. Zafari Umar, Oleg Khyzhun, Mekhrdod S. Kurboniyon, Tomoyuki Yamamoto, Mikhail G. Brik, Anatoli I. Popov, Michal Piasecki, Electronic structure and energy transitions in oxides and fluorides doped by octahedrally surrounded Cr^{3+} ions, Optical Materials 160 (2025), 116681.
4. Mekhrdod S. Kurboniyon, Shamsulkhak Nurulkhakov, Bibo Lou, Khaiyom Rahmonov, Alok M. Srivastava, Mikhail G. Brik, Tomoyuki Yamamoto, Chong-Geng Ma, Influence of the First Cation A of $A_2SiF_6:Mn^{4+}$ (A = K, Rb, Cs) Phosphors on Their Geometric Structures and the Optical Transition Energies: First-Principles Analysis, Journal of Electronic Materials 54 (2025), 962–969.
5. Mekhrdod S. Kurboniyon, Alok M. Srivastava, Bibo Lou, Yang Wang, Dan Zhang, Dzhumakhon M. Sharifov, Dulat H. Daurenbekov, Tomoyuki Yamamoto, Mikhail G. Brik, Chong-Geng Ma, Effect of Chemical Composition on the Optical Properties of Cr^{3+} Impurity in $A_3B_5O_{12}$ Garnets (A = Lu, Y, Gd, La; B = Al, Ga, Sc), ACS Applied Optical Materials 3 (2025), 422–430.