Project No. 02411

Report form of Joint Research Project at ZAIKEN (FY2024)

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		
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

Aim of the research project

Development of advanced optical materials is very important for many technological applications. Among various optical materials, phosphors play a special role for lighting, sensing, bioimaging etc. Their applications are based on introduction of impurity ions into crystalline solids. Performance of phosphors crucially depends on the interplay of the properties of dopants and host materials. To understand the mechanisms of those interactions, detailed studies of their structural and electronic properties are necessary. In the proposed project with Prof. Yamamoto we shall focus 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 important for lighting, in particular, the Mn^{4+}-doped red phosphors improve properties of white LEDs, increase their efficiency and reduce their cost. In addition, their emission spectra can be used for noncontact temperature measurements. We shall perform synthesis of 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 with the main aim of deeper understanding of the obtained results and highlighting the most important factors affecting the materials' performance.

Contents and results of the research

1. Several series of Mn^{4+} doped double perovskites (RE_2MgMO_6, *RE*=La, Y, *M*=Ti, Sn) were synthesized. Influence of chemical composition on the Mn^{4+}-emission spectra was studied. The samples were characterized by the X-ray diffraction (XRD) and optical spectroscopy methods.
2. The ABO_4 (*A*=Ca, Sr, Ba, *B*=Mo, W) samples doped with the Er^{3+} ions were synthesized and their upconversion properties were studied. Influence of local symmetry and codopants on the emission intensity was considered.
3. First-principles calculations of the Mn^{4+} energy levels in $CaMO_3$ (M=Ti, Zr, and Sn) were performed with detailed analysis of the local symmetry and energy levels of impurities in the band gap of the host materials.
4. The hybrid organic-inorganic perovskite materials were synthesized and their photovoltaic properties were studied experimentally and by means of the first principles calculations.
5. Machine-learning methods were applied to identify correlations between the structural and electronic properties of garnets. In addition, the same methods were used to describe and predict emission energy of the red phosphors based on the Mn^{4+} and Cr^{3+} ions. These works are in progress now.
6. First-principles calculations of the structural, electronic, elastic properties of the Mn^{4+}- and Cr^{3+}-doped phosphor materials were continued. The most important parameters, such as the energy of the ^2E-$^4A_2$ emission transition and the crystal field strength were calculated. This is important for a deeper understanding of red phosphors performance, in particular, thermal quenching effects.
7. A visit to Prof. T. Yamamoto laboratory was arranged between January 20 and 31, 2025. Several meetings with Prof. T. Yamamoto group members were organized, where the students presented and discussed their recent results. Active discussions were held; the plans for publications of those results and for the future research were outlined. Prof. M.G. Brik presented a tutorial lecture "Impurity ions in solids: theoretical modeling of optical properties". The visit was very fruitful for the development of joint research plans.
8. An online meeting for the joint research at ZAIKEN, Waseda University was held on March 7, 2025. Prof. M.G. Brik gave a presentation entitled "Spin-forbidden emission transitions of 3d ions and their applications".
9. Active cooperation with the research groups from the USA, Poland, China and Tajikistan was strengthened further during this project implementation.
10. Comparing the initial plan of our activities with the summary of the obtained results, we conclude that the expected objectives of the project were achieved.

Outputs of the project (publications, presentations, patents)

Invited talks were given by Prof. M.G. Brik at the International Conference on the Physics of Optical Materials and Devices (ICOM), Becici, Montenegro, August 26-30, 2024, and 1st Sino-Poland ECS-LDM Meeting and the 2nd International School on Smart Light Conversion Materials and Technology (ISSLCMT), Chongqing, China, November 23-35, 2024, and by Prof. T. Yamamoto at the 12th International Conference on Luminescent Detectors and Transformers of Ionizing Radiation, June 16-21, 2024, Riga, Latvia, and 11th International Workshop on Advanced Materials Science and Nanotechnology, September 22-25, 2024, Danang, Vietnam. Some joint works were presented by the students in Prof. Yamamoto's group at the PRiME2024, October 6-11, 2024, Honolulu, USA, and 11th International Workshop on Advanced Materials Science and Nanotechnology, September 22-25, 2024, Danang, Vietnam.
The following papers were published in the international journals:

1. Zafari Umar, Mekhrdod S. Kurboniyon, Oleg Khyzhun, Tomoyuki Yamamoto, Chong-Geng Ma, Mikhail G. Brik, Michal Piasecki, "*First-principles calculations of the*

electronic structure and mechanical properties of non-doped and Cr^{3+}-Doped K_2LiAlF_6 under pressure", Journal of Luminescence 266 (2024) 120278.

2. Mekhrdod S. Kurboniyon, Alok M. Srivastava, Bibo Lou, Dilshod D. Nematov, Amondulloi Burhonzoda, Tomoyuki Yamamoto, Chong-Geng Ma, and Mikhail G. Brik, "*Thermal Quenching Mechanism of Mn^{4+} in Na_2SiF_6, $NaKSiF_6$, and K_2SiF_6 Phosphors: Insights from the First-Principles Analysis*", Inorganic Chemistry 63 (2024) 21212−21221.

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, Alok M. Srivastava, Bibo Lou, Yang Wang, Dan Zhang, Dzhumakhon M. Sharifov, Dulat H. Daurenbekov, Tomoyuki Yamamoto, Mikhail G. Brik, and Chonggeng 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.

5. 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.