Project No. 02115 / Grant No. JPMXP0621467974

Report form of Joint Research Project at ZAIKEN (FY2021)

Title of Project	**Study on the local structure around dilute dopants in optical materials**		
Priority Area	**I-C, III-C**		
New proposal			
Name of Main Applicant	**Mikhail G. Brik**		
Institution	**University of Tartu, Estonia**	**title**	**Professor**

Aim of the research project

The advanced optical materials have gained great attentions to realize sustainable societies. To get efficient optical materials, a doping technique is often employed. To understand their efficiency of light emission and absorption mechanisms, it is essential to know the geometric and electronic structures. In particular, local structure around dopants is of paramount importance for enhancement of the phosphors' brightness. The main aim of the proposed research is to understand the mechanisms of the emission enhancement of the Mn^{4+}-doped phosphors and photon up-conversion in the rare-earth ions doped materials. These topics are now extremely actively studied by many research groups worldwide, which is explained by numerous practical applications of these materials for solid state lighting, photovoltaics, agriculture etc. Despite high research activity in this field, the mechanisms underlying these phenomena have not yet been understood with strong experimental and theoretical evidences. In the present joint research with Prof. Yamamoto, we would like to focus on the experimental and theoretical studies of the Mn^{4+} -doped (and co-doped with other cations) phosphor materials and rare-earth ions doped oxide powders, which will include the X-ray diffraction, UV-Vis, photoluminescence, ESR measurements and theoretical density functional theory (DFT)-based calculations to understand the local structure effects on the optical properties.

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

1. Several series of Mn^{4+} and rare-earth ions doped (as well as co-doped with various cations) materials with varying stoichiometry, and different hexafluorides and rare-earth doped oxide perovskites were fabricated with conventional solid-state reaction method. Their structure was confirmed by the X-ray diffraction (XRD) experiments, and their excitation and photoluminescence spectra were recorded in the ultra-violet and visible spectral regions. Special attention was paid to the upconversion properties of the prepared samples.
2. The valence states of the impurity ions were probed by the X-ray absorption spectra and electron spin resonance (ESR) measurements. The experiments were conducted at SPring-8 and KEK-PF (X-ray) and Waseda University (ESR).
3. First-principles calculations of the structural, electronic, elastic properties of the Mn^{4+}-doped phosphor materials were performed and published in two papers and one book chapter. It was demonstrated that the Mn^{4+} ions form the localized energy levels in the band gap of the host materials. doping and to understand the electronic structure of the matrix materials. Calculations of the total energy (per supercell) of $CaAl_{12}O_{19}$ (where there are several crystallographic sites available for the Mn^{4+} ions) allowed to identify the preferable position of impurity.
4. After the position of the Mn^{4+} ions in $CaAl_{12}O_{19}$ was identified, the crystal field calculations for the Mn^{4+} ions were performed and the calculated energy levels were compared with the experimental excitation spectra.
5. Consistent calculations of the structural and electronic properties of $K_2SiF_6:Mn^{4+}$ at the ambient and elevated pressures allowed us to model the pressure effects on the positions of the Mn^{4+} states in the band gap, as well as on the variation of the host band gap value.
6. We continue working on preparation of the structural database for the garnet materials to develop a structural model linking together the ionic radii and electronegativities of the constituting ions and the lattice constants of the considered crystals.
7. Like in the previous year, no usual “on site” meetings and discussions were held; therefore, the electronic means were used for communications and data exchange between the project participants. Active cooperation with the research groups from the USA, Poland, China and Tajikistan was developed during this project implementation.
8. Comparing the initial plan of our activities with the summary of the obtained results, we can conclude that the expected objectives of the project were to a large extent achieved.

Outputs of the project (publications, presentations, patents)

Book chapter:

Mikhail G. Brik, Chong-Geng Ma, Tomoyuki Yamamoto, Michal Piasecki, and Anatoli I. Popov, “First-Principles Methods as a Powerful Tool for Fundamental and Applied Research in the Field of Optical Materials”, in: Phosphor Handbook: Experimental Methods for Phosphor Evaluation and Characterization, Eds. Ru-Shi Liu, Xiao-Jun Wang, 2022 Taylor & Francis Group, LLC, pp. 1-25.

Papers in international journals:

1. Musashi Sagayama, Umar Zafari, Mekhrdod Subhoni, Alok M. Srivastava, William W. Beers, William E. Cohen, Mikhail G. Brik, and Tomoyuki Yamamoto, “Theoretical and Experimental Investigations of Mn^{4+} Site Occupation in $CaAl_{12}O_{19}$”, ECS Journal of Solid State Science and Technology 10 (2021) 076004.
2. Mekhrdod Subhoni, Umar Zafari, Chong-Geng Ma, Alok M. Srivastava, William W. Beers, William E. Cohen, Mikhail G. Brik, Michal Piasecki and Tomoyuki Yamamoto, “Influence of Isostatic Pressure on the Elastic and Electronic Properties of $K_2SiF_6:Mn^{4+}$”, Materials 15 (2022) 613.