

Report form of Joint Research Project at ZAIKEN (FY2022)

Title of Project	Study on the local structure around dilute dopants in optical materials		
Priority Area	I-C, III-C		
Continuation of 2021project			
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

1. Several series of Mn^{4+} doped double perovskites (La_2MgMO_6 , $M=\text{Ti, Sn, Zr, Hf}$) 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 ($A=\text{Ca, Sr, Ba}$, $B=\text{Mo, W}$) samples doped with the Er^{3+} ions were synthesized and their upconversion properties were studied.
3. First-principles calculations of the Na^+ and Er^{3+} energy levels in CaSnO_3 were performed.
4. The hybrid organic-inorganic perovskite materials were synthesized and their photovoltaic properties were studied.
5. Machine-learning methods were applied to identify correlations between the structural and electronic properties of large classes of isostructural materials; this is a very popular topic of modern research and these works will be actively continued.
6. First-principles calculations of the structural, electronic, elastic properties of the Mn^{4+} -doped phosphor materials were continued. The most important parameters, such as the energy of the ${}^2\text{E}-{}^4\text{A}_2$ emission transition and the crystal field strength were calculated. This is important for a deeper understanding of red phosphors performance.
7. A visit to Prof. T. Yamamoto laboratory was arranged between January 16 and 27, 2023. Several meetings with Prof. T. Yamamoto group members were organized, where the students presented 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 also presented a tutorial lecture “Electronic properties of transition metal and rare earth ions”. 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 3, 2022. Prof. M.G. Brik gave a presentation entitled “ Mn^{4+} -doped red phosphors for white LED: first-principles calculations”.
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)

An invited talk: “Experimental and theoretical investigations of local environment of Mn ions in red phosphors” (Tomoyuki Yamamoto, Mekhrdod Subhoni, Umar Zafari, Musashi Sagayama, Mikhail G. Brik), presented at the EMRS Fall Meeting, Warsaw, Poland, September 19-22, 2022. (A paper based on this presentation has been recently accepted by Physica Status Solidi B).

A paper: “Influence of co-doping of divalent ions on the photoluminescence intensity of Mn^{4+} doped $\text{CaAl}_{12}\text{O}_{19}$ ” (Umar Zafari, Musashi Sagayama, Mekhrdod Subhoni, Alok M. Srivastava, William W. Beers, William E. Cohen, Chong-Geng Ma, Michal Piasecki, Mikhail G. Brik, Tomoyuki Yamamoto), Optical Materials X 16 (2022) 100197.