Project No. 02214 / Grant No. JPMXP0621467974

Report form of Joint Research Project at ZAIKEN (FY2022)

Title of Project	**Development of efficient sustainable phosphor materials with the aid of quantum chemical calculations**		
Priority Area	**I-B, I-C, III-B, III-C**		
New proposal			
Name of Main Applicant	**Tagoimurod Kh. Solekhov**		
Institution	**Tajik National University, Republic of Tajikistan**	**title**	**Professor**

Aim of the research project

The white light-emitting diode (w-LED) has been recognized as one of the energy efficient technologies. Rare-earth doped nitrides, oxides and fluorides with large band-gaps have been applied for the red luminescence center in the w-LED. As rare-earth ions are limited and expensive, rare-earth free phosphors are demanding nowadays to stabilize supply of the efficient phosphors for the use of w-LED. Mn doped nitrides, oxides and fluorides are one of the rare-earth free red phosphors. In the current research, we focus on the search of the efficient red-emitting phosphors by doping with Mn ions in nitrides, oxides and fluorides. For this purpose, various kinds of materials with efficient red-emitting property without rare-earth ions are synthesized and cutting-edge first principles calculations are carried out to study electronic and geometrical structures of the materials. At Waseda collaborating with professor Yamamoto, advanced analyses such as X-ray diffraction, SEM-EDX, AES, XPS, UV-Vis, PL, ESR will be performed.

Contents and results of the research

In the current project, we would like to synthesize various kinds of matrix materials and perform a series of analyses, i.e., X-ray diffraction for structure analysis, UV-Vis for electronic structure analysis, photoluminescence (PL) analysis, to search efficient Mn-doped red-emitting phosphors without any rare-earth ions.
At first, we have studied the influence of additional co-dopings of divalent ions on the photoluminescence of Mn-doped $CaAl_{12}O_{19}$ [1]. Samples were synthesized by a research group of Prof. Yamamoto using the solid-state reaction method. Their Crystal structures were examined by the XRD and optical properties, such as photoluminescence and photoabsorption, were observed. To study local environment of Mn ions, electron spin resonance (ESR) was also measured. The PL intensities of Mg and Zn coped ones are three time stronger than Mn mono-doped $CaAl_{12}O_{19}$, while Cd and Sr codopings did not show such extensive enhancement.
In addition to the above experiments, we have performed the first principles calculations for the Mn-doped $CaAl_{12}O_{19}$ with additional codopings of divalent ions such as Mg^{2+}, Zn^{2+}, Sr^{2+} and Cd^{2+}, using the Vienna Ab-initio Simulation Package, vasp, within a density functional theory level. Prior to the calculations of divalent ion co-doped models, most preferable substitution site for Mn in $CaAl_{12}O_{19}$ was examined in Mn mono-doped one. After the confirmation, Mn is doped at one of the distorted octahedron site, Al(2), and the divalent ion was doped at all the possible Al sites. From the results of total electronic energies, the most preferable substitution sites for the additionally doped divalent ions were determined. In these codoped models, we focused upon change in local environment of Mn ion due to the divalent ions codopings. This is because ESR measurements suggested significant change in local environment of Mn ions due to the doping of Mg^{2+} and Zn^{2+}, while only slight change was seen in the case of Sr^{2+} and Cd^{2+} codopings. ESR is quite sensitive to change in local environment of the ion of interest, here Mn^{4+}, then the current ESR results suggest that Mg^{2+} and Zn^{2+} codopings influence much on the local environment of Mn^{4+} ion, but just slight effect has been applied by Sr^{2+} and Cd^{2+} codopings. From the results of the first principles calculations, these local environment changes were confirmed in an atomic scale.

[1] U. Zafari, M. Sagayama, M. Subhoni A. M. Srivastava, W. W. Beers, W. Cohen, C.-G. Ma, M. Piasecki, M. G. Brik, T. Yamamoto, Opt. Matter: X16 (2022) 100197. https://doi.org/10.1016/j.omx.2022.100197

Outputs of the project (publications, presentations, patents)

Publication
[1] U. Zafari, M. Sagayama, M. Subhoni A. M. Srivastava, W. W. Beers, W. Cohen, C.-G. Ma, M. Piasecki, M. G. Brik, T. Yamamoto, Opt. Matter: X16 (2022) 100197. https://doi.org/10.1016/j.omx.2022.100197