Project No. 31008

Report form of Joint Research Project at ZAIKEN (2019)

Title of Project	**Development of efficient rare-earth phosphor oxide doped with Mn ions**		
Priority Area	**Energy conversion materials with environmental consciousness**		
Continuation of joint research in 2018			
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Aim of the research project

The white light-emitting diode (w-LED) has been recognized as one of the energy efficient technologies due to their main features for energy-saving capacity. The current commercial w-LED is basically composed of the blue LED, e.g., InGaN, and the yellow conversion phosphor, e.g., YAG: Ce^{3+}. The red emission intensity of the w-LEDs with YAG: Ce^{3+} is very weak and this deficiency leads to a deterioration in the quality of color rendering index and higher color correlated temperature. One of the best ways to overcome above mentioned problem is adding some high efficient red phosphor materials with strong blue absorption into the commercial white LED system, as red luminescence center.

In view of the above strategy, rare earth ions doped nitrides red phosphor materials for w- LED was designed. Among such rare earth ions doped materials, Eu doping in the nitride hosts with the wide band-gap satisfied the requirements of practical application for red emission in w-LED. However, in addition to the usual strong reabsorption of photons in the green or yellow region of the spectrum due to 4f-5d transition in Eu ion, there are still some disadvantages, i.e., the requirements of extremely high temperature, high pressure reaction conditions, and/or strict synthesis procedures. At last, but not at least, rare-earth free phosphors are cheaper than those with the rare-earth ions, which has also an important economic impact on the LEDs prices for the consumers and all relevant research costs involved. Therefore, the design of new inexpensive and efficient red phosphors is of particular interest.

Improvement of quantum efficiency of w-LED is required to design new red phosphor based on rare-earth free systems. 3d transition elements are also good emission center for such purpose, in which Mn^{4+} ion is the promising candidate for the red-emitting phosphor in the coming generation as an emitting center in the matrix materials. Recently, considerable amounts of works have been devoted to the development of the Mn^{4+} ion doped red phosphors for w-LEDs. When additional ions M^{2+} (Zn, Mg) included into some kinds of Mn^{4+} doped phosphors, e.g., $CaAl_{12}O_{19}$ and $Sr_4Al_{12}O_{25}$, the photoluminescence emission intensity has been enhanced. However, the mechanism of such enhancement is still remains unclear, therefore experimental and computational investigations are necessary to elucidate the mechanism.

Contents and results of the research

Investigation of effects of additional doping on the electronic structure, local environment and optical properties of Mn^{4+} doped phosphors, in which Mn^{4+} is an activated red emission center, makes the mechanism of the enhancement clear. In the current research, we investigated the preferable site occupancy for the dopants, electronic structure and local environment of Mn^{4+} and M^{2+} (M= Mg, Cd and Zn) co-doped $CaAl_{12}O_{19}$ and influence of the additional doped ions on the red emission intensity of $CaAl_{12}O_{19}$: Mn^{4+}. We found that the inclusion of Cd^{2+}, Zn^{2+} and Mg^{2+} can enhance the PL emission intensity of $CaAl_{12}O_{19}$: Mn^{4+}.

All the samples were fabricated with the conventional solid-state reaction method, whose crystal structures were examined by the X-ray diffraction technique. The electronic structures of the sample powders were examined by the diffuse reflectance spectra using integration sphere equipped with the UV-Vis spectrometer. Change in band-gap and absorption states created by the Mn doping were determined.

The electronic and geometric structures of the pure host, Mn^{4+} doped and co-doped M^{2+} (M= Mg, Cd and Zn) and Mn^{4+} $CaAl_{12}O_{19}$ were investigated using the first-principles calculations within a DFT. The detailed theoretical study was conducted on the effect of the Coulomb coupling interaction energy parameter U for d-d orbital interaction on the t_{2g} and e_g states and d-d orbitals interaction of Mn^{4+} ions in $CaAl_{12}O_{19}$ system using DFT+U method.

Analyses of the site occupancy of Mn^{4+} ions into the pure host $CaAl_{12}O_{19}$ and additional doped divalent ions into $CaAl_{12}O_{19}$:Mn^{4+} system was also theoretically done within DFT methods.

In addition, we determined here the dependence of PL intensity of $CaAl_{12}O_{19}$:Mn^{4+} on the various kinds of concentrations of additional divalent ions. We found that the optimized concentration of additionally doped ions, in which $CaAl_{12}O_{19}$: Mn^{4+} system has the strongest intensity among the materials with additional doped ions.

Based on DFT calculations it was found that the Al(2) site is the most favourable for Mn^{4+} substation in $CaAl_{12}O_{19}$ and Al(3) site is the best for the additional doped divalent ions substation in $CaAl_{12}O_{19}$:Mn^{4+}. The DFT results confirmed the suggestion about formation of the new O-Mn^{4+}↔Mg^{2+}-O, O-Mn^{4+}↔Cd^{2+}-O and O-Mn^{4+}↔Zn^{2+}-O ions pairs by replacing the O-$Al(3)^{3+}$↔$Al(4)^{3+}$-O ions pairs.

Outputs of the project (publications, presentations, patents)

We have published a following joint paper.

Z. Umar, M. Subhoni, T. Yamamoto and R. Farhod, “Theoretical investigation of the electronic structure of $LaScO_3$:Mn^{4+} within density functionality theory”, Reports Academy of Science of Republic of Tajikistan, 2019, 62, 3-4, pp.176-181.

Several presentations were given at the international conferences

1. M. Subhoni, U. Zafari and T. Yamamoto, “Electronic structure analysis of of Mn-doped $CaMO_3$ perovskites”. he 6th International Symposium on Advanced Microscopy and Theoretical Calculations. 14 -15 June, 2019, Nagoya, Japan.
2. M. Sagayama, U. Zafari, M. Subhoni, M. G. Brik, and T. Yamamoto, “Influence of Additional Doping of Divalent Ions on Emission Intensity of Mn-doped $CaAl_{12}O_{19}$”, Pacrim13, Oct. 27-Nov. 1, 2019, Okinawa, Japan.
3. Y. Togashi, U. Zafari, M. Subhoni, M. G. Brik, and T. Yamamoto, “Dependence of Excitation Wavelength on the Photoluminescence Spectra of Mn-doped $Mg_2A_{1-x}B_xO_4$”, Pacrim13, Oct. 27-Nov. 1, 2019, Okinawa, Japan.
4. M. Subhoni, U. Zafari, M. Sagayama, Y. Togashi, H. Taki and T. Yamamoto, “Electronic Structure Calculations of Mn-doped Oxide Phosphors”, 29th MRS-J, Nov. 27-29, Yokohama, Japan.

Some experimental and calculated results of the current joint research are under preparation to be submitted to the international journals as joint papers.