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Investigation of Valence State Change in $Y_3Al_2Ga_3O_{12}$: Ce^{3+}-Cr^{3+} Persistent Phosphors

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1 Introduction

Persistent phosphors show continuous luminescence for a long duration ranging from several minutes to a few hours even after the excitation light source is removed. In 2014, we successfully developed new persistent ceramic phosphors with a new combination of lanthanide luminescent centers and transition metal trap centers in $Y_3Al_{5-x}Ga_xO_{12}$: Ce^{3+}-Cr^{3+} (x=2.5, 3, 3.5). The phosphors show Ce^{3+}:5*d*-4*f* green persistent luminescence (λ_{em}=510 nm) for several hours after blue-light excitation[1,2]. This phosphor can absorb blue light via Ce^{3+}:$4f$-$5d_1$ transition with a large cross section and the excited electron can transfer to the conduction band (CB) easily due to the small energy gap between the $5d_1$ level and the bottom of CB. In our previous work, we suggested that the Ce^{3+} ion loses an electron and the Cr^{3+} ion captures the electron under excitation, which is the main mechanism of persistent luminescence[1,2]. However, the origin of the electron donors and acceptors in $Y_3Al_{5-x}Ga_xO_{12}$:Ce^{3+}-Cr^{3+} persistent phosphors have never been directly demonstrated. In this study, the valence state change of Ce^{3+} was investigated by X-ray absorption near edge structure (XANES) spectroscopy.

2 Experiment

Polycrystalline ceramics of Ce^{3+}(0.5%) singly-doped, Ce^{3+}(0.5%)-Cr^{3+}(0.05%)-codoped and Cr^{3+}(0.2%) singly-doped $Y_3Al_2Ga_3O_{12}$ (YAGG) were synthesized by solid state reaction. The chemicals Y_2O_3 (99.99 %), Al_2O_3 (99.99 %), Ga_2O_3 (99.99 %), CeO_2 (99.99 %), Cr_2O_3 (99.9%) were used as starting materials. The powders were mixed by ball milling (Fritsch, Premium Line P-7) with ethanol and the obtained slurry was dried and pulverized. The dried powder was pressed into pellets sized 10 mm-ϕ X 2 mm thickness. The pellets were sintered at 1600 °C in air. The X-ray absorption spectroscopy (XAS) was performed at the beamline BL9A of Photon Factory (KEK, Japan). The photon flux density of X-ray at 7 keV is $4X10^{12}$ photons/sec/mm^2. The Ce L_{III} and Cr K X-ray absorption near edge structure (XANES) were recorded for all the samples in fluorescence mode with/without UV (250nm-400nm) illumination of Xe lamp (Asahi Spectra, Max 302). The reason why the sample was illuminated by UV is to cause the ionization of Ce^{3+}. As references, standard $Ce(NO_3)_3$, CeO_2, Cr_2O_3 samples were also measured.

3 Results and Discussion

Fig. 1 shows the XANES spectra for the Ce L_{III} edge of the YAGG samples under different conditions. The red and blue solid lines show the XANES spectra for the YAGG:Ce^{3+}-Cr^{3+} sample and YAGG:Ce^{3+} with UV illumination. In these XANES spectra, two main peaks were observed at 5725eV and 5735 eV. Compared with the reference XANES spectra, the peaks at 5725 eV and 5735 eV are mainly contributed by the X-ray absorption of Ce^{3+} and Ce^{4+}, respectively. From the previous results of thermoluminescence excitation spectrum for YAGG:Ce^{3+}-Cr^{3+}, it was confirmed that this persistent phosphor can be charged by UV illumination[2]. From the XANES spectrum, it is found that the valence state of Ce ion in YAGG:Ce^{3+} is almost trivalent even under UV illumination. However, in YAGG:Ce^{3+}-Cr^{3+}, a part of Ce^{3+} changes into Ce^{4+} from the XANES spectra with UV illumination. The valence state change from Ce^{3+} to Ce^{4+} can be caused by the existence of Cr^{3+} electron traps which attract the ionized electrons from Ce^{3+}.

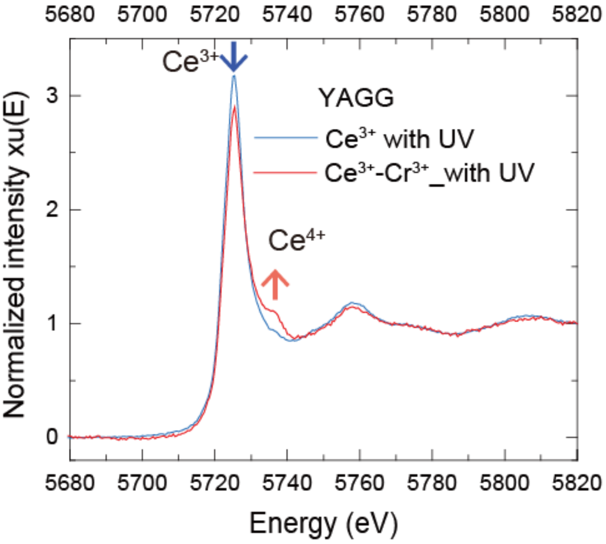

Fig. 1: XANES spectra of Ce L_{III} edge in $Y_3Al_2Ga_3O_{12}$:Ce^{3+}-Cr^{3+} illuminated with UV light and $Y_3Al_2Ga_3O_{12}$:Ce^{3+} illuminated with UV light.

References

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