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Effect of surface modification on UV induced valence change in $Ca_2MgSi_2O_7$ persistent phosphorescence phosphors

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1 Introduction

Long-persistent phosphorescence phosphors are indispensable materials for ensuring safety and security, even in the event of a power outage. They are widely used, for example, as phosphorescent pigments. The essence of the long-persistent phosphorescence phenomenon is belived to be the valence change of the dopant, caused by light irradiation.

Photo-induced changes in the valence of dopant have been investigated by XAFS experiments [1]. Some groups confirmed the change from Ce^{3+} to Ce^{4+} and from Eu^{2+} to Eu^{3+}. However, the magnitude of this change is relatively small. This may be due to the difference in the penetration depth between the excitation light and the X-rays into the phosphor particles of about 1 micron in size. Unless the penetration depths match, it is difficult to observe a large spectral change due to the photo-induced valence change of the dopant. The discrepancy is due to the scattering of the excitation light on the phosphor particle surface. To suppress this effect, it is essential to modify the phosphor particle surface. If the discrepancy in the penetration depth is resolved by using surface-modified phosphor particles and a large spectral change occurs under photo-irradiation, it may be possible to find out whether there is a correlation between the local structural change and the valence change through the analysis of EXAFS oscillations.

In the present study, Eu L_3-edge XANES spectra of $Ca_2Mg_2SiO_7$:Eu,Dy were measured at 290 K under irradiation and non-irradiation with a UV laser-diode (380 nm). $Ca_2Mg_2SiO_7$:Eu,Dy is one of the persistent phosphorescence phosphors. The effect of surface modification on the photo-induced valence change of Eu ions in this phosphor was investigated.

2 Experiment

We prepared powder various samples $Ca_2MgSi_2O_7$:Eu,Dy by a solid state reaction and crystal crushing. Hereafter, the former and latter are named as the sample #1 and #2, respectively. The sample #1 was washed in a dilute nitric acid solution. It was confirmed that these powders have the crystal structure of $Ca_2MgSi_2O_7$ and that they exhibit a persistent phosphorescence.

Eu L_3-edge XANES were measured at the BL12C in PF. The XANES spectra were obtained at 290 K in fluorescence mode. Pulsed UV light around 800 nm from a laser diode was irradiated to the samples to induce the valence change of Eu ions. The light source distribution of the incident X-ray was measured using an ionization chamber in front of the samples. The measured XANES spectra were corrected for the light source distribution and temporal fluctuation.

3 Results and Discussion

In Fig. 1, two prominent peaks are observed in Eu-L_3 XANES spectra of $Ca_2MgSi_2O_7$:Eu,Dy powders washed with a dilute nitric acid solution (left). The low- and high-energy peaks are indication of 2+ and 3+ states of Eu ions. The valence change of Eu ions induced by UV irradiation are clearly observed.

The difference in Eu-L_3 edge XANES spectra between UV irradiation and non-irradiation is negligibly small (right). Unfortunately, the chemical cleaning using a few acids was ineffective for modifying phosphor particle surface. Further investigations would be required to observe a large valence change in XANES spectra and a large structure change in EXAFS spectra under UV irradiation. Currently, improvements are being performed in both sample surface modification and experimental techniques.

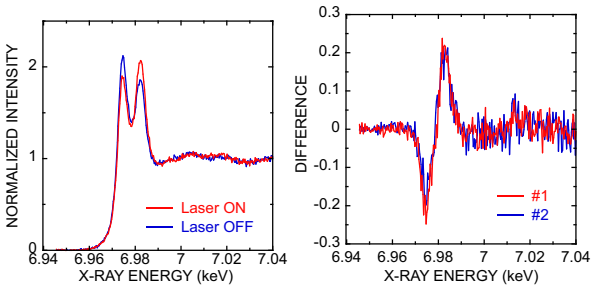

Fig. 1: UV irradiated (red) and non-irradiated (blue) Eu-L_3 XANES spectra of $Ca_2MgSi_2O_7$:Eu,Dy powders washed in dilute nitric acid solution (left) and difference in Eu-L_3 edge XANES spectra between UV irradiation and non-irradiation for the samples #1 and #2.

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References

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