

Analysis of Crystal Field near Ce Ion in Green Phosphor CSS

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The phosphor $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Ce}$ (CSS: Ce) was developed for a solid state lighting and display applications. The doped Ce is an emission center. It is excited by blue lights and then emits green lights. It is supposed in view of the ion radii that a Ce atom substitutes not a Sc site but a Ca site. However, an actual proof has not been acquired so far.

We measured Ce K-edge EXAFS spectra of CSS: Ce phosphor at BL01B1 beam line in Spring-8, using Si(111) double crystal monochromator. Ca and Sc K-edge EXAFS spectra were also measured as references.

Fourier-transformed Ce, Ca, Sc K-edge EXAFS spectra of CSS: Ce phosphors are shown in Figure 1. The first coordination shell peak (of bond distance of 1.9 Å) of Ce K-edge is assigned to a Ce-O bond. This coincides with the first coordination shell peak of Ca K-edge which is assigned to a Ca-O bond. The second and third peak of Ce K-edge (of bond distance of 2.7 to 2.8 Å and 3.1 Å, respectively) are assigned to a Ce-Si and a Ce-Sc bond, respectively. The corresponding peak of Ca K-edge shows a rather broad single peak. This is due to the low resolution of Ca RSF that is caused by

the fact that a measurement range of Ca EXAFS was limited by Sc K-edge absorption in the sample. Opposed to the similarity of Ce K-edge to Ca K-edge, Ce K-edge is different from Sc K-edge considerably.

Conclusively EXAFS results clearly showed that a Ce atom substitutes a Ca site in CSS: Ce phosphor.

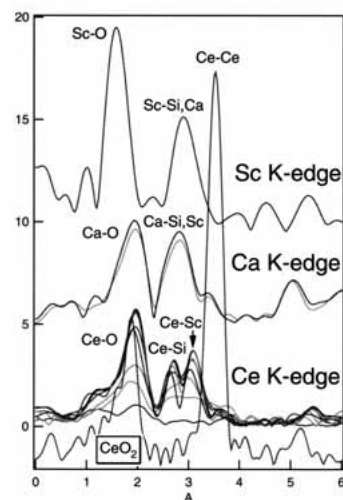


Fig. 1 FT of Sc, Ca, Ce K-edge EXAFS of CSS: Ce phosphors.

XAFS Analysis of Substitution Site of Activator Atom in the Crystal Structure of Ce-doped Gd_2SiO_5 Scintillator Materials

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Single crystal of cerium-doped gadolinium oxy-orthosilicate ($\text{Gd}_2\text{SiO}_5:\text{Ce}$), one product of our company, has been applied for a γ -ray-detecting scintillator of medical instruments such as a positron emission tomograph. Recently, Shimizu et al. reported that impurity of zirconium(4+) oxide is an effective dopant for increasing light output of $\text{Gd}_2\text{SiO}_5:\text{Ce}$.¹ We are currently developing the $\text{Gd}_2\text{SiO}_5:\text{Ce}$ scintillator to increase its performance, as well as studying the effect of the impurity. However, there is no determinate observation datum of the substitution site of activator atoms, Ce and Zr, in the crystal structure. X-ray absorption fine structure (XAFS) technique is believed as one strong tool for analyzing the local structures around those activator atoms. Therefore, we carried out XAFS measurement on Zr-doped $\text{Gd}_2\text{SiO}_5:\text{Ce}$.

All the XAFS data of this report were obtained at the beam line BL01B1 of SPring-8. Gd-K edge XAFS spectrum was recorded in transmission mode. Ce-K and Zr-K edge spectra were recorded in fluorescence mode using 19 elements of Ge-solid state detectors. The irradiation X-ray for Gd-K and Ce-K edge spectra was monochromated by two silicon (311) crystals, and it for Zr-K was monochromated by two silicon (111) crystals.

The resulted spectrum data were transformed to radial structure functions (RSFs) by the Fourier transform of the extended XAFS oscillations, as shown in

Figure 1. This figure shows (a) RSF plot of Gd from the Gd-K edge XAFS spectrum, (b) RSF plot of Ce from the Ce-K edge XAFS spectrum, and (c) RSF plot of Zr from the Zr-K edge XAFS spectrum. The three plots are similar in the shape to one another. Therefore, we concluded that the activator atoms, Ce and Zr both are in the same coordination environment with Gd that consists of Gd_2SiO_5 crystal structure. Further analysis is in progress to discuss the local structures of those atoms. We are now trying to carry out the curve fitting using various parameters of the neighbor atoms, and to compare the results with the crystal structure that is determined from the X-ray diffraction datum of Gd_2SiO_5 .²

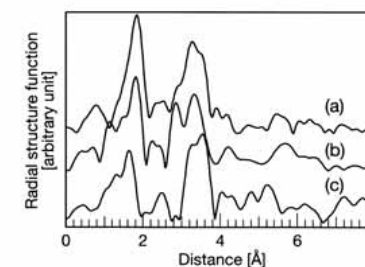


Figure 1. RSFs of (a) Gd, (b) Ce and (c) Zr of Zr-doped $\text{Gd}_2\text{SiO}_5:\text{Ce}$.

References

- (1) Shimizu, S. et al. *IEEE Trans. Nucl. Sci.* **2003**, *50*, 778.
- (2) Smolin, Y. I. et al. *Kristallografiya*, **1969**, *14*, 22.