

Site Determination of Doped Ga Ions in $\text{SrTiO}_3\text{:Pr}^{3+}$ Phosphor for Field Emission Displays by XAFS

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Abstract. The enormous enhancement of the emission intensity from $\text{SrTiO}_3\text{:Pr}^{3+}$ by addition of Al or Ga ions was found. In case of Al, it was reported that the emission enhancement is caused by charge compensation and reduction of planar faults in the host lattices. In order to clarify the mechanism of the enhancement of the emission from $\text{SrTiO}_3\text{:Pr}^{3+}$ by addition of Ga ions, we investigated the local structure of doped Ga ions in $\text{SrTiO}_3\text{:Pr}^{3+}$ (a red phosphor for Field Emission Display) by XAFS analysis. The XAFS analysis indicates that doped Ga ions substitute for Ti site in the crystal.

Keywords: phosphor, XAFS, FEFF

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INTRODUCTION

The enormous enhancement of the emission intensity from $\text{SrTiO}_3\text{:Pr}^{3+}$ by addition of Al or Ga ions was reported by H. Toki and his coworkers in 1996, although luminescence efficiency of $\text{SrTiO}_3\text{:Pr}^{3+}$ is low [1]. Recent investigations revealed that the addition of Al ions decreases the concentration of defects [2]. Therefore it is considered that Al-addition improves the carrier flow rate from SrTiO_3 lattice to Pr^{3+} [2,3]. In case of Al-addition, the impurity phase SrAl_2O_4 was found by powder X-ray diffraction [3]. On the other hand, the impurity phase such as SrGa_2O_4 was not found in the case of Ga-addition. In order to clarify the mechanism of the enhancement of the emission from $\text{SrTiO}_3\text{:Pr}^{3+}$ by addition of Ga ions, we investigated the local structure of doped Ga ions in $\text{SrTiO}_3\text{:Pr}^{3+}$ (a red phosphor for Field Emission Display [1]) by XAFS analysis. There are two kinds of possible Ga substitution sites, the Sr site and the Ti site in SrTiO_3 . Ga K-edge EXAFS spectra of Ga-doped $\text{SrTiO}_3\text{:Pr}^{3+}$ indicate that doped Ga ions substitute in the Ti site in the crystal, by comparison with Ti K- and Sr K-edges EXAFS spectra of SrTiO_3 . These results were consistent with FEFF simulations of Ga K-edge EXAFS and XANES spectra according to the models occupying the Sr and Ti sites in SrTiO_3 . Furthermore, it was also shown that Ga K-edge EXAFS spectra of Ga-doped $\text{SrTiO}_3\text{:Pr}^{3+}$ is not similar to the simulated one of SrGa_2O_4 by FEFF.

EXPERIMENTAL METHODS

For preparation of Ga-doped $\text{SrTiO}_3\text{:Pr}$ powder sample, a mixture of SrCO_3 , TiO_2 , Ga_2O_3 , $\text{Pr}(\text{NO}_3)_3$ and a small quantity of ethanol was fired in air at 1300°C for 2 hours. Purity of SrCO_3 , TiO_2 and Ga_2O_3 is four-nine. Nominal Pr and Ga concentration is 0.6 and 10 mol%, respectively.

The XAFS spectra of Ga, Sr and Ti K absorption edges were obtained in the transmission mode at BL01B1 in SPring-8 [4]. The incident X-ray was obtained using a double-crystal Si(111) monochromator. The contaminants in the higher harmonics were reduced using two rhodium-coated mirrors set at $3.6(\text{Ga-K})$, $2.6(\text{Sr-K})$ and $6(\text{Ti-K})$ mrad of incident angles. Intensities of the incident and transmitted X-rays were detected by ion chambers filled with $\text{N}_2 85\% - \text{Ar} 15\%(\text{Ga-K})$, $\text{N}_2 75\% - \text{Ar} 25\%(\text{Sr-K})$, $\text{He} 70\% - \text{N}_2 30\%(\text{Ti-K})$ and $\text{N}_2 50\% - \text{Ar} 50\%(\text{Ga-K})$, $\text{Ar} 100\%(\text{Sr-K})$, $\text{N}_2 100\%(\text{Ti-K})$ gases, respectively.

The obtained XAFS data were analyzed using REX2000 [5] and FEFF8.20 [6] codes based on the crystal structure parameters of SrTiO_3 [7].

RESULTS AND DISCUSSION

The Ga-K edge XAFS spectrum of $\text{SrTiO}_3\text{:Pr}^{3+}$, Ga was clearly observed as shown in Fig. 1. We investigated the site of Ga by comparing the radial structure function (RSF) derived from observed

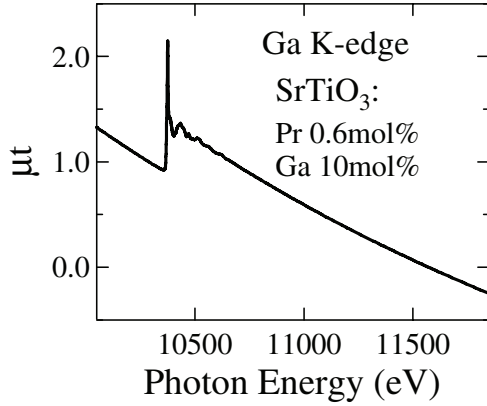


FIGURE 1. Ga K-edge XAFS spectrum of Ga-doped $\text{SrTiO}_3\text{:Pr}^{3+}$.

extended X-ray absorption fine structure (EXAFS) spectra, and we simulated RSF according to plausible structural models (Sr and Ti site occupations in SrTiO_3). The observed X-ray near edge structure (XANES) was also investigated.

Figure 2 shows $k^3\chi$ (cubed wavenumber weighted EXAFS interference function) at Sr and Ti K absorption edges of SrTiO_3 and Ga K absorption edge of Ga doped $\text{SrTiO}_3\text{:Pr}^{3+}$ derived from observed EXAFS spectra. EXAFS oscillations at Sr, Ti and Ga K absorption edges were observed up to 160 nm^{-1} .

Figure 3 shows RSFs at Sr and Ti K absorption edges of SrTiO_3 and Ga K absorption edge of Ga doped $\text{SrTiO}_3\text{:Pr}^{3+}$ derived from the observed k^3 -weighted EXAFS signals (Fig. 2) by Fourier transformation in the region of about $30\text{--}160 \text{ nm}^{-1}$ and about $40\text{--}150 \text{ nm}^{-1}$, respectively. No correction for phase shifts was made to derive these RSFs.

The RSFs at Ga and Ti K absorption edges have common characteristics. The peak positions of the first peaks in RSFs around Ga and Ti are about 0.15 nm and those of second and third peaks are about 0.3 and 0.35 nm , respectively. On the other hand, the profile of RSF around Ga differs from that around Sr. The peak position of the first peak in RSF around Sr is about 0.22 nm that is close to the second peak (0.29 nm).

Interionic distances Sr-O and Ti-O in SrTiO_3 were estimated to be 0.274 and 0.197 nm by curve fitting of the first peaks in RSFs. The estimated Ga-O distance (0.192 nm) in Ga-doped $\text{SrTiO}_3\text{:Pr}^{3+}$ is close to the Ti-O distance rather than to the Sr-O one.

The estimated valence of Ga by the bond valence sum method (BVSM) [8] also suggests that the doped Ga ions substitute for the Ti site in Ga and Pr co-doped SrTiO_3 . The nearest Sr-O and Ti-O coordination number is 12 and 6, respectively. The estimated Ga valence by BVSM is $+3.6$ or $+7.2$ for the coordination

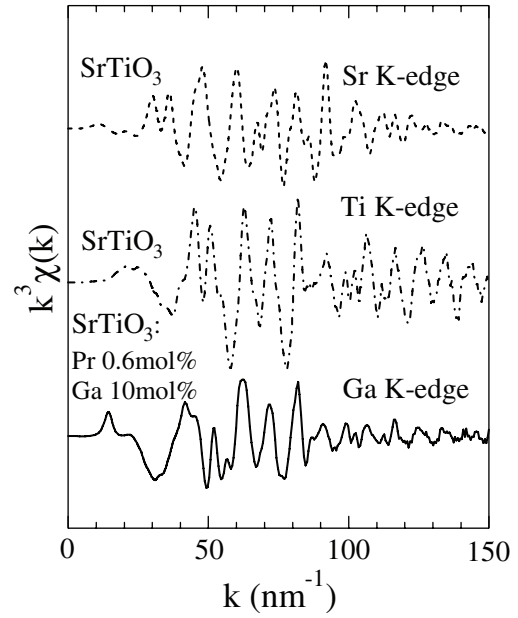


FIGURE 2. $k^3\chi$ of Sr and Ti K absorption edges in SrTiO_3 and Ga K absorption edge of Ga-doped $\text{SrTiO}_3\text{:Pr}^{3+}$.

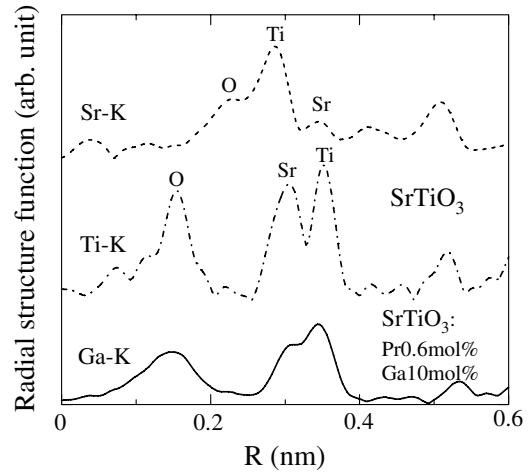


FIGURE 3. RSFs around Sr and Ti in SrTiO_3 and Ga in Ga-doped $\text{SrTiO}_3\text{:Pr}^{3+}$.

number of 12 or 6, respectively, by using the estimated Ga-O distance of 0.192 nm from the observed EXAFS oscillation. The valence of Ga is stable for $+3$ rather than $+7$. In the case of Ga^{3+} , the Ga-O coordination number is about 5 that is calculated by BVSM using the Ga-O distance of 0.192 nm estimated from the observed EXAFS oscillation. Thus, it is suggested that the coordination number of Ga-O decreases in comparison with that of Ti-O or there is disorder around the Ga ions. This may be caused by the valence discrepancy between Ga^{3+} and Ti^{4+} .

Figure 4 shows simulated $k^3\chi$'s at Ga K absorption edge according to the models occupying the Sr and Ti

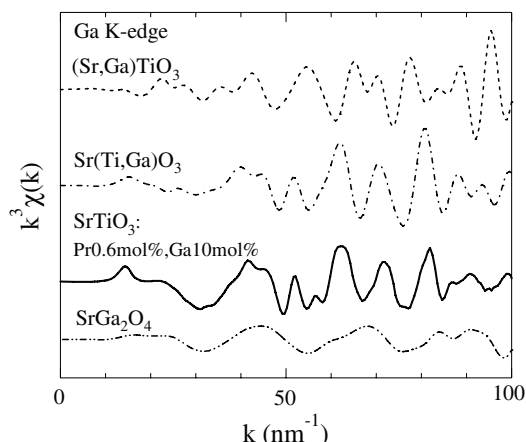


FIGURE 4. Simulated $k^3\chi$ of Ga K absorption edges of Sr and Ti site occupations in SrTiO_3 and of SrGa_2O_4 and observed $k^3\chi$ of Ga K absorption edge in Ga-doped $\text{SrTiO}_3:\text{Pr}^{3+}$.

sites in SrTiO_3 and of SrGa_2O_4 , and the observed spectrum of Ga-doped $\text{SrTiO}_3:\text{Pr}^{3+}$. The spectrum of SrGa_2O_4 is simulated based on the crystal parameters in reference [9]. As shown in Fig. 4, simulated $k^3\chi$ of the Ti site is the most similar to the observed $k^3\chi$ of Ga doped $\text{SrTiO}_3:\text{Pr}^{3+}$. This result suggests that Ga ions substitute for Ti site in the crystal.

We also focused on XANES spectrum to discuss which site doped Ga occupied (the Sr or Ti site in SrTiO_3), and simulated XANES spectra of the Sr and Ti site occupations using FEFF8.20. Radius of self-consistent field calculation of each occupation was 0.5 nm. Figure 5 shows simulated and observed Ga K-edge XANES spectra.

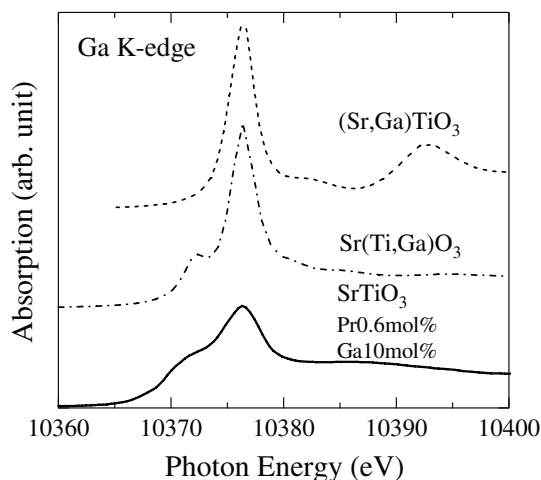


FIGURE 5. Simulated Ga K-edge XANES spectra of Sr and Ti site occupations in SrTiO_3 and observed Ga K-edge XANES spectra of Ga-doped $\text{SrTiO}_3:\text{Pr}^{3+}$.

The simulated XANES spectra are shifted in order to set simulated whiteline to observed one. The observed XANES spectrum shows a shoulder on the lower energy of the whiteline. The simulated XANES spectrum in Ti site occupation has also a shoulder in the low energy of the whiteline, but in case of Sr site occupation the spectrum show simple whiteline without a shoulder. Only the simulated XANES spectrum in Sr site occupation has broad peak around 10392 eV. Comparing to the observed XANES spectrum, the simulated XANES spectrum of Ti site occupation is more similar to the observed one than that of the Sr site occupation. This result suggests that Ga ions occupy Ti site in $\text{SrTiO}_3:\text{Pr}^{3+}$.

CONCLUSIONS

The local structure around Ga in $\text{SrTiO}_3:\text{Pr}^{3+}$, Ga red phosphor for Field Emission Display was investigated by XAFS. It is concluded that Ga ions substitute for Ti site in $\text{SrTiO}_3:\text{Pr}^{3+}$.

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