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# Enhancement of photoluminescence properties of $SrAl_2Si_2O_8:Eu^{2+}$ by a large amount of $SiO_2$ addition

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SiO<sub>2</sub> added phosphors, SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>:Eu<sup>2+</sup> + xSiO<sub>2</sub> (x = 0, 1, 2 and 3 mol) were synthesized by a novel liquid phase precursor (LPP) method. The photoluminescence properties of phosphor added by 2 mol of SiO<sub>2</sub> showed 71% increase in the emission intensity compared with the SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>:Eu<sup>2+</sup> phosphor. A broad emission and excitation wavelength was observed approximately from 400 nm to 600 nm centered at 430 nm and from 300 nm to 400 nm centered at 350 nm, respectively. Photoluminescence intensity of the phosphors increased continuously by SiO<sub>2</sub> addition up to x = 2 mol and then it decreased at 3 mol of SiO<sub>2</sub>. The observed photoluminescence properties of the phosphors were discussed by their crystalline structure and morphology.

Key words: Optical materials, X-ray diffraction, Luminescence, Optical properties.

### Introduction

Since the first reported light emitting diodes (LEDs) in 1960s, there have been significant advances in LEDs [1]. LEDs are a promising candidate for next generation solid lighting material owing to their higher energy efficiency, longer lifetime, better environmental friendliness and reliability compared to previous light sources [2-3]. On the other hand, as the main materials in LED, the phosphors have a difficult problem to overcome a series of environmental decrease of luminescence property and thermal quenching during LED operation. High emission efficiency and stability has been required importantly for LED development [4].

Generally, the divalent europium ion  $(Eu^{2+})$  is used widely as an activator in phosphors.  $Eu^{2+}$  ions show a broad emission band ranging from the ultraviolet (UV) to red spectral region arising from a 4f<sup>6</sup>5d<sup>1</sup>-4f<sup>7</sup> allowed transition, which is strongly dependent on the crystal fields of the 5d orbital in the host lattice [5, 6]. In the present study, SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>:Eu<sup>2+</sup> phosphors are synthesized to satisfy above requirement. The SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> crystalline structure is composed of a rigid framework of tetrahedral silicates and aluminates, in which Sr<sup>2+</sup> ions occupy the interstitial sites of the framework.

Most of the studies with respect to phosphor have utilized conventional solid state reaction (SSR) method [7-8]. The precursor of SSR obtained by hand-grinding of oxide raw materials is not homogeneous. In contrast, the precursor prepared by liquid phase precursor (LPP) method is considerably homogenous since an aqueous solution of homogeneously mixed raw materials was impregnated into the cellulose fiber cell [9]. Samples using LPP method are synthesized for comparably short time at relatively low temperature compared to SSR method. Therefore, we carried out to synthesize a system of  $xSiO_2$  added  $SrAl_2Si_2O_8$ :Eu<sup>2+</sup> (x = 0, 1, 2 and 3 mol) phosphors by using a novel LPP method. We confirmed that photoluminescence (PL) intensity of obtained phosphors is fairly enhanced by  $SiO_2$  addition. The mechanism of this PL enhancement is discussed in this paper.

# **Experimental**

The SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>:Eu<sup>2+</sup> + xSiO<sub>2</sub> phosphors (x = 0, 1, 2) and 3 mol) were prepared using the LPP method. The 30 wt% Sr(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O (Junsei chemical Co., Japan), 50 wt% Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O (Samchun chemical Co., 98%), 20 wt% SiO<sub>2</sub> (sol, 20 nm, snotex-O, Nissan chemical) and 50 wt% EuCl<sub>3</sub> · 3H<sub>2</sub>O (Aldrich grade) solutions were mixed together and impregnated into a crystalline cellulose powder (avicel, Asahe). The impregnated cellulose precursors were rapidly calcined in a box furnace at 500 °C for 3 hrs in air. This process evaporates the crystalline cellulose as CO<sub>2</sub> and H<sub>2</sub>O gas. The samples were fired at 1200 °C for 2 hrs in air. Crystalline phosphor materials were obtained by this firing process. The obtained samples were again fired at 1000 °C for 10 hrs under a N<sub>2</sub>/H<sub>2</sub> (95/5) reduction atmosphere to reduce from Eu<sup>3+</sup> to Eu<sup>2+</sup>. The crystalline phases of the obtained phosphors were examined by XRD (CuK $\alpha$ ,  $\lambda = 1.5406$ , 40 kV, 20 mA, Rigaku, Japan). The photoluminescence properties of the phosphors were measured using a PL

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spectrometer (SINCO, FS-2, Korea) equipped with a 500W Xenon discharge lamp. The particle morphology was observed by FE-SEM (JEOL, JSM7500F, Japan).

# **Results and discussion**

### X-ray diffraction analysis

Fig. 1 shows the XRD patterns of  $SrAl_2Si_2O_8Eu^{2+}+$ x SiO<sub>2</sub> (x = 0, 1, 2 and 3 mol) phosphors synthesized at 1000 °C for 12 hours under reduced atmosphere. The phosphors exhibit mainly SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> (JCPDF card #038-1354 Monoclinic) and SiO<sub>2</sub> (JCPDF card #082-0512 Cristobalite) phases. Fig. 2 shows the XRD intensity of SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> and SiO<sub>2</sub> phases of the phosphors with the increasing of SiO<sub>2</sub> concentrations (x value). The intensity of SiO<sub>2</sub> phase increased further with the increase of SiO<sub>2</sub> concentration. However, the intensity of  $SrAl_2Si_2O_8$  phases decreases when x = 3 mol. It implies that additional SiO<sub>2</sub> flux contribute to the formation of crystalline SiO<sub>2</sub> phase. In general, the increase of the SiO<sub>2</sub> concentration decreased the SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>:Eu<sup>2+</sup> phase and increased the SiO<sub>2</sub> phase. This observation suggests that the extra SiO<sub>2</sub> in the phosphors could exist in the crystalline forms. The results indicate that Eu<sup>2+</sup> doped SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> crystal was more stable than the  $SiO_2$  crystal.



**Fig. 1.** XRD patterns of  $SrAl_2Si_2O_8:Eu^{2+} + xSiO_2 (x = 0, 1, 2 and 3)$  and phosphor fired at 1000 °C in reduction atmosphere.



**Fig. 2.** Intensities of XRD peaks of monoclinic  $(SrAl_2Si_2O_8)$  and cristobalite  $(SiO_2)$  as a function of added  $SiO_2$  concentrations (x value).

# **FE-SEM** images

Fig. 3 shows the FE-SEM images of  $SrAl_2Si_2O_8:Eu^{2+}$ + x SiO<sub>2</sub> (x = 0, 1, 2 and 3 mol). The FE-SEM images indicate the surface morphology of the phosphors. The size and shapes are not uniform and also the surface is not clear as there are many small particles. It could be assumed that amount of small SiO<sub>2</sub> crystals are covered on the surface of SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>:Eu<sup>2+</sup> phosphors. By increasing the SiO<sub>2</sub> concentrations, the surface of phosphor particle become clear which means that abundant SiO<sub>2</sub> crystals are enough to cover the surface of phosphor particle. It could be assumed that SiO<sub>2</sub> and phosphors are forming nano-composite.

### **Photoluminescence properties**

Fig. 4 shows the photoluminescence spectra of the  $SrAl_2Si_2O_8:Eu^{2+} + xSiO_2$  (x = 0, 1, 2 and 3 mol) phosphors. The PL spectra showed a broad excitation and emission spectra. The broad excitation spectra exhibits a couple of overlapping peaks centered at 320 nm ( $t_{2g}$ ) and 370 nm ( $e_g$ ), which is due to the result of 5d orbital separation caused by crystal field splitting peaks in fig. 5 [10]. The emission spectra showed a broad emission



Fig. 3. FE-SEM images of  $CaAl_2Si_2O_8$ : $Eu^{2+} + xSiO_2$  (x = 0, 1, 2, 3, 6 and 13 mol) phosphors.



**Fig. 4.** Excitation (left) spectra and emission (right) spectra of  $SrAl_2Si_2O_8:Eu^{2+} + xSiO_2$  phosphors fired at 1000 °C in reduction atmosphere. Inset shows normalized emission intensity of  $SrAl_2Si_2O_8:Eu^{2+} + xSiO_2$  phosphors at 430 nm.



Fig. 5. The effect of crystal field splitting on energy level of  $Eu^{2+}$  in  $SrAl_2Si_2O_8$  host lattice.

centered at 430 nm. The emission spectra showed two closely overlapped peaks (430, 470 nm). Although it could be considered that  $Eu^{2+}$  substituted the Si<sup>4+</sup> site in SiO<sub>2</sub> crystal,  $Eu^{2+}$  couldn't be occupy the Si<sup>4+</sup> site, since the charge and coordination numbers were different (Si<sup>4+</sup>:4-coordination,  $Eu^{2+}:6 \sim 10$ -coordinations). Moreover, the ionic size of  $Eu^{2+}$  (1.17 ~ 1.35 Å) was

too large to substitute Si<sup>4+</sup> site (0.26 Å) or occupy into the interstitial site in SiO<sub>2</sub> crystal. Therefore, the overlapped peaks are due to two Eu<sup>2+</sup> site in the SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> crystal since different sites make different environment to Eu<sup>2+</sup> ion [11]. Inset in Fig. 3 displays the effect of SiO<sub>2</sub> addition on the emission intensity. The PL intensities were increased with increasing SiO<sub>2</sub> concentration (from x = 0 to 2 mol) and also the SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>:Eu<sup>2+</sup> phosphor with 2 mol of SiO<sub>2</sub> exhibited 71% enhanced emission intensity when compared with the phosphor without any  $SiO_2$  addition. The extra  $SiO_2$ encourage a strong reduction atmosphere supporting electrons into the phosphor. The supported electrons reduce Eu<sup>3+</sup> to Eu<sup>2+</sup>, because of abundant electrons are at the edge of tetrahedral silicate crystal [12]. Therefore, the increase of PL intensity is caused by the increased ratio of  $Eu^{2+}$  to  $Eu^{3+}$  ions. However,  $SrAl_2Si_2O_8:Eu^{2+}+x SiO_2$ phosphors with higher  $SiO_2$  concentration (x = 3 mol) showed, rapidly decreased emission intensities and red shift. In this case, it could be considered that there exists a saturation concentration for the enhancement of PL intensity by SiO<sub>2</sub> addition. A decrease of luminescence material (Eu<sup>2+</sup> doped SrAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) induced a drop of PL intensity at high SiO<sub>2</sub> concentration.

#### Conclusion

 $SrAl_2Si_2O_8:Eu^{2+} + x SiO_2$  (x = 0, 1, 2 and 3 mol)

phosphors were prepared using the LPP method. X-ray diffraction patterns indicated that phosphors have mixed phases of both cristobalite (SiO<sub>2</sub>) and Monoclinic  $(SrAl_2Si_2O_8)$ . The Eu<sup>2+</sup> ion was well occupied in monoclinic crystalline structure. The intensity of cristoblaite phase increased and monoclinic phase decreased with the addition of SiO<sub>2</sub>. Photoluminescence intensity increased with the increase of  $SiO_2$  concentration from x = 0 to 2 mol. On the other hand, the PL intensity decreased at higher  $SiO_2$  concentrations (x = 3 mol). The highest intensity of PL was observed at 430 nm (blue) when 3 mol of  $SiO_2$  was added to the phosphor. The enhancement of PL intensity is could be explained by abundant electrons on the edge of SiO<sub>2</sub>, which could help the reduction from  $Eu^{3+}$  to  $Eu^{2+}$ . The FE-SEM measurements demonstrated that the SiO<sub>2</sub> crystals are formed on the surface of the phosphors.

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