Research Letter

Effects of Particle Size and Type of Alumina on the Morphology and Photoluminescence Properties of Sr₄Al₁₄O₂₅:Eu²⁺/Dy³⁺ Phosphor

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 $Sr_4Al_{14}O_{25}:Eu^{2+}/Dy^{3+}$ phosphor with high luminescence intensity and long afterglow duration was synthesized using 1.0 μ m (α), 0.1 μ m (α), and 0.05 μ m (γ) particle sizes of Al_2O_3 . SEM observation results showed that spike-like thin particles were formed when 0.05 μ m γ -Al₂O₃ was used as raw material. Hexagonal thick particles were observed when 0.1 μ m α -Al₂O₃ was used. But irregular, thin particles were observed while using 1 μ m α -Al₂O₃. Photoluminescence measurements showed that both the initial intensity and the long persistency were much higher for the phosphor prepared using γ -Al₂O₃ of 0.05 μ m particle size.

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1. Introduction

Of the phosphors, the alkali earth aluminates containing rare earth ions are functional inorganic materials with strong luminescence in blue to red regions [1–3]. These materials are widely used in various fields; to highlight a few, one may include emergency signs, low level lightening escape systems, military applications, textile fibers, lightening apparatus, exit signboards, and many more [4]. These materials, due to better safe, chemical stability, excellent photo resistance, very high brightness, and long-lasting afterglow with no radio active radiations [5], form the important materials in various ceramics industries [6].

In recent years, $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$ doped with Eu^{2+} and Dy^{3+} have been regarded as an excellent phosphor and attracted the researcher's interest. For the improvement of phosphorescence, many researches have been focused on regarding additives, molar ratio of constituents, and the preparation methods [6–8]. It was found that the shape and size of phosphor particles play important role for the phosphorescence properties. When the particle size reaches the nanoscale, new properties are appeared like the blue shift of emission intensity [9]. If the phosphor particles are regular and flat plate-like, they are expected to give a better light absorption and form a dense compact by their orientation, resulting in higher phosphorescence intensity. The shape and size of the phosphor particles may depend on the crystal type and particle size of the starting materials as well as the method of preparation. This letter reports the effect of raw Al_2O_3 type and size on the formation of regular particles for the higher luminescence intensity of $Sr_4Al_{14}O_{25}$:Eu²⁺, Dy³⁺ phosphor.

2. Experimental

Strontium aluminates doped with Eu^{2+} and Dy^{3+} (Sr₄Al₁₄O₂₅:Eu²⁺/Dy³⁺) were prepared by the reaction between strontium carbonate (SrCO₃; Sigma-Aldrich, Inc., Mo, USA), aluminum oxide (Al₂O₃ Sigma-Aldrich, Inc., Mo, USA), europium oxide (Eu₂O₃; Sigma-Aldrich, Inc., Mo, USA), europium oxide (Eu₂O₃; Sigma-Aldrich, Inc., Mo, USA, 99.9+ %), and dysprosium oxide (Dy₂O₃; Sigma-Aldrich, Inc., Mo, USA, 99.9+ %). Boric acid (H₃BO₃; Katayama Chemicals, Japan) was used as a flux. The powders were mixed according to the nominal composition of 4SrCO₃ + 7Al₂O₃ + 0.4 B (as H₃BO₃) + 4 at% Eu and 8 at% Dy. In this work, different particle size alumina of γ and atypes (0.05 μ m γ -type, 0.1 μ m, and 1.0 μ m, α -type) were used to reveal the effect of raw alumina powder. The mixing was performed thoroughly by mortal and pestle with the help of ethanol. Pellets were prepared and preheated in air atmosphere at 1000°C for 4 hours, pulverized and then heated at 1300°C for 5 hours in a reducing atmosphere of $H_2/N_2 = 1/9$.

Phase identification was carried out using a Shimadzu XRD-6300 instrument with CuK α radiation at room temperature. Scanning electron microscopy (SEM) observations were carried out using a JEOLJSM-5510LV instrument. Photoluminescence (PL) spectra were measured using USB 4000 UV-VIS miniature fiber optic spectrometer (Ocean Optics, Fla, USA). The decay curves were obtained at room temperature using a brightness meter (Konica Minolta LS-100). Before decay curves measurement, the samples were exposed to standard 60 W xenon lamps for 25 minutes. All measurements were carried out at room temperature.

3. Results and Discussion

The X-ray diffraction patterns of the specimens prepared from the different particle sizes and crystal types of Al_2O_3 were almost the same as shown in Figure 1. The same $Sr_4Al_{14}O_{25}$ phase was formed (except very small impurities of $SrAl_4O_7$ phase in all three samples as in Figure 1) which was confirmed when compared with standard JCPDS card data (52–1876). This result indicates that the reaction conditions under this work were enough for the formation of $Sr_4Al_{14}O_{25}$ phase. Also the change of particle size and crystal type of starting Al_2O_3 did not affect the phase formation.

Figure 2 shows the SEM microstructure of the three samples prepared using Al₂O₃of different particle sizes: (a) $0.05 \,\mu\text{m}$ (γ), (b) $0.1 \,\mu\text{m}$ (α), and (c) $1.0 \,\mu\text{m}$ (α). Although the same phase was observed as in XRD observations, their microstructures were quite different. When γ -Al₂O₃ of smaller particle size was used as precursor powder, a ball-like microstructure composed of spikes or elongated plates was observed. The average size of the plate particle was roughly $1 \,\mu m$ long, $0.2 \,\mu m$ wide, and $20 \,nm$ thick. Due to the formation of regular and smaller particles, these small plates overlapped with each other, forming compact ball-like structure. The size of the ball was about $3 \mu m$ in diameter. When $0.1 \,\mu m \,\alpha$ -Al₂O₃ was used, irregular porous microstructure composed of bigger and thicker hexagonal plates with $1\,\mu m$ long, $0.75\,\mu m$ wide, and $0.5\,\mu m$ thick was formed as in Figure 2(b). These plates connected with each other and form walls, making the spongy structure. While, using α -Al₂O₃ of 1.0 μ m particle size, much bigger but thinner, irregular flat plates of $3 \mu m \log 2 \mu m$ wide, and 30 nm thick were observed as in Figure 2(c). Due to the high aspect ratio of the irregular plates, porous microstructure was formed. The porous microstructure was further supported by the density of the prepared pellets that decreased on increasing the particle size of raw alumina powder and also the phosphor particles $(0.05 \,\mu$ -1.909 g/cm³ > $0.1 \,\mu$ -1.87 g/cm³ > 1.0 μ -1.803 g/cm³). The particle shape dependency according to the starting alumina powder may be explained on the basis of dissolution and precipitation



FIGURE 1: X-ray diffraction pattern of Sr₄Al₁₄O₂₅:Eu²⁺/Dy³⁺ phosphor prepared using (a) 0.05 μ m; γ -Al₂O₃, (b) 0.1 μ m; α -Al₂O₃, and (c) 1.0 μ m; α -Al₂O₃.

mechanisms [10]. The detail mechanism for the explanation of different shapes according to the starting material is under progress.

Figure 3 shows the excitation and emission spectra of $Sr_4Al_{14}O_{25}:Eu^{2+}/Dy^{3+}$ phosphor prepared using $0.05 \,\mu m$, $0.1 \,\mu\text{m}$, and $1.0 \,\mu\text{m}$ Al₂O₃ as starting materials. All samples prepared from these three types of Al₂O₃ were excitated by the light of wavelength ranging from 220 to 440 nm. These samples gave the similar emission spectra with peaks at ~500 nm showing blue-green color. However, there was a small blue shift in the case of phosphor prepared using $0.05 \,\mu$ Al₂O₃. It is obvious that the decrease in particle size increases the surface energy, which results in the distortion of atomic structure around the Eu²⁺, and consequently, the blue shift in the emission peak is observed [9]. The emission intensity of these phosphors, however, varied drastically according to the used raw alumina powder as shown in the inserted graph in Figure 4. The initial emission intensities of the products from $0.05 \,\mu\text{m}$, $0.1 \,\mu\text{m}$, and $1.0 \,\mu\text{m}$ Al₂O₃ were 2316, 137,9 and 1025 mcd \cdot m⁻², respectively. The emission intensity increased with the decreasing of Al₂O₃ particle size and became the highest for the phosphor prepared using $0.05 \,\mu m$ Al₂O₃. The decrease in phosphorescence intensity might be due to the formation of bigger particles with much porous microstructure on increasing the Al₂O₃ particle



(c)

 $1 \,\mu m$

FIGURE 2: SEM microstructure of $Sr_4Al_{14}O_{25}$:Eu²⁺/Dy³⁺ phosphor prepared using (a) 0.05 μ m; γ -Al₂O₃, (b) 0.1 μ m; α -Al₂O₃, and (c) 1.0 μ m; α -Al₂O₃.



FIGURE 3: Excitation (normalized) and emission spectra of $Sr_4Al_{14}O_{25}:Eu^{2+}/Dy^{3+}$ phosphor using (a) 0.05 μ m; γ -Al₂O₃, (b) 0.1 μ m; α -Al₂O₃, and (c) 1.0 μ m; α -Al₂O₃.

size as explained in the SEM microstructure observations. Obviously, as the packing density decreases, the volume content of the phosphor decreases leading to the decrease of the emission intensity of the phosphor.

Figure 4 shows the change in the afterglow emission intensity of the phosphor products with time. The afterglow intensity was decreased by >1/100th of the initial intensity within 1 hour. The afterglow emission intensity and duration were higher for the phosphor prepared using $0.05 \,\mu\text{m} \,\gamma$ -Al₂O₃, and its afterglow duration over the value



FIGURE 4: Effect of Al_2O_3 particle size on the photoluminescence properties of $Sr_4Al_{14}O_{25}$:Eu²⁺/Dy³⁺ phosphor. Inserted figure shows the variation of emission intensity with particle size of Al_2O_3 .



FIGURE 5: The mechanism of long afterglow of $Sr_4Al_{14}O_{25}$:Eu²⁺/ Dy³⁺ phosphor.

of $5 \text{ mcd} \cdot \text{m}^{-2}$ was more than 20 hours. The longer afterglow duration of the smaller particles phosphor may be explained as, upon exposure to light source, the direct excitation of Eu^{2+} due to 4f to 4f5d transition occurs (Figure 5), and a great numbers of holes are generated near the valence band. Some of these free holes are released thermally to the valence band, migrate through the valence band, and captured by the Dy^{3+} -borate complex [6, 11]. When the excitation source is removed, the trapped holes are released thermally to the valence band, migrate to the excited Eu²⁺, and consequently, the recombination takes place, which leads to the long afterglow. So, the long afterglow duration depends on the number of captured holes. The numbers of captured holes, in turn, depend on the concentration of Dy-borate complexes and the trap depth of it. With the decrease of particle size, the blue shift of the trap depth occurs [9] that leads to increase in the afterglow duration. The detailed explanation of the mechanism with other supporting information is under progress.

4. Conclusions

Long-afterglow Sr₄Al₁₄O₂₅:Eu²⁺/Dy³⁺ phosphor was synthesized by solid phase reaction method using α and γ types Al₂O₃ of different particle sizes. Though the same Sr₄Al₁₄O₂₅ phase was formed on changing the alumina precursors, quite different structures were observed. When $0.05 \,\mu m \,\gamma$ -Al₂O₃ was used, spike-like phosphor particles were observed with minimum particle size, which agglomerated to form a ball-like structure. When $0.1 \,\mu m \,\alpha$ -Al₂O₃ was used, bigger particles with the shape of hexagon were observed, while using $1.0 \,\mu m \,\alpha$ -Al₂O₃ much bigger but thinner irregular particles were observed, that is, the shape and size of phosphor particles can be controlled by changing the alumina precursor under the experimental conditions. The better phosphorescence intensity and persistency were observed for the phosphor prepared using $0.05 \,\mu m \,\gamma$ -Al₂O₃ that might be due to the smaller and regular particles formation.

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