The temperature-dependent structural and optical properties of SrAl₂O₄-based phosphor

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Abstract. This research studied the thermal stability of SrAl₂O₄ : Eu⁺, Dy⁺ phosphor for the fabrication of luminescent glasses. The temperature-dependent structural and optical properties of the phosphor were investigated. The results showed that SrAl₂O₄ : Eu⁺, Dy⁺ phosphor could emit the green light when excited by ultraviolet (UV) light. It was also found that annealing could induce further growth of SrAl₂O₄ crystals, which gave rise to more intense green-light emission. However, at high annealing temperature, the luminescence attained a maximum and started decreasing. An intense luminescence was observed for the SrAl₂O₄ : Eu⁺, Dy⁺ phosphor annealed at 750°C. The phosphor degradation at temperatures above 750°C could be because of the formation of secondary phases and the oxidation of the rare-earth atoms that were doped in phosphor. The results showed that, with proper fabrication processes, phosphors could be considered as promising materials for various applications.

1. Introduction

Phosphors are materials that can emit an intense and long-lasting light when absorbing high external energy. Thus, they are widely used in many applications such as lighting and display devices. In the fabrication of phosphors, rare-earth and transition-metal ions are typically doped in wide-bandgap host compounds such as silicates, phosphates, aluminates, and borates. SrAl₂O₄ is one of the promising host materials for long persistent phosphors.²⁻³ It is usually co-doped with europium ion (Eu⁺) and dysprosium ion (Dy⁺) to exhibit a prolonged afterglow performance, which could be more than ten times compared to other phosphors.²⁻³ However, many phosphors including SrAl₂O₄-based phosphors tend to lose their luminescence efficiency at high temperatures, which is undesirable for many applications.⁴

Glass-based phosphors are materials containing phosphor powders in glass matrices. These materials have been recently commercialized for their advantages over conventional polymer-based phosphors used in optical devices such as light emitting diodes (LEDs).⁵⁻⁶ They are prepared from a mixture of glass powders (or frits) and phosphor powders. The typical fabrication processes, however, involve the
annealing or sintering at high temperatures to obtain the desired products. As a consequence, various approaches have been attempted to overcome the thermal degradation and to improve the stability of phosphors.

In this study, the temperature-dependent properties of green-emitting SrAlO$_2$-based phosphor powders were studied. The samples were characterized using X-ray diffraction (XRD), photoluminescence (PL) spectroscopy, Raman spectroscopy, and scanning electron microscopy (SEM).

2. Experimental Procedure

The commercial green-emitting SrAlO$_2$: Eu$^+$, Dy$^3+$ phosphor powders (45-55 µm, Fluorescent glow powder, Amhere Intertrade, Ltd) were used as received. The phosphor powders were first dried in an oven at 120°C for 24 h to evaporate the moisture, and, then, annealed from 700°C to 900°C for 30 min in air to study the temperature stability.

After annealing, the powders were characterized by XRD on a Shimadzu XRD-6100 diffractometer with CuKα radiation (λ=0.154056 nm, 40 kV and 30 mA). The morphology of the samples was examined by scanning electron microscopy (TM3030, Hitachi). Raman measurements were performed at room temperature by The Senterra Raman spectroscopy (Bruker). The optical properties were measured on a photoluminescence spectrometer (AvaSpec-2048TEC, Avantes).

3. Results and Discussion

![Figure 1. XRD patterns of SrAl$_2$O$_4$-based phosphor powders annealed at various temperatures from 700°C to 900°C for 30 min.](image-url)
The phase purities and the crystal structures of the phosphor powders annealed at different temperatures (700°C, 750°C, 800°C, 850°C, and 900°C) were characterized by XRD, and the results were shown in figure 1. All of the samples exhibited monoclinic SrAl$_2$O$_4$ crystal structure as a dominant phase, which could be characterized by five main peaks corresponding to (001), (-221), (220), (221), and (031) planes (JCPDS: 34-0379). The presence of the hexagonal polymorph of SrAl$_2$O$_4$ was also observed in annealed samples, as indicated by the different intensity ratios of the main peaks. In general, SrAl$_2$O$_4$ has monoclinic and hexagonal polymorphs with the phase transition occurring at about 650°C.[7] These two polymorphs have the most intense XRD peaks overlapped, and, therefore, it could be difficult to distinguish the two phases. Nevertheless, the result revealed that the presence of dopants had no effect on the crystal structure of SrAl$_2$O$_4$. This was because the ionic radius of the common Eu$^{2+}$ dopant in SrAl$_2$O$_4$-based phosphor was similar to that of Sr$^{2+}$ ion, and as a result Eu$^{2+}$ ion tended to be substituted at the Sr$^{2+}$ sites.[8]

![Figure 2](image-url)

**Figure 2.** Raman spectra of SrAl$_2$O$_4$-based phosphor powders annealed at various temperatures from 700°C to 900°C for 30 min.

With increasing annealing temperatures, the particle size and the crystallinity of the phosphor were found to increase and reached the maximum at 750°C. When the annealing temperatures was raised to 800°C, it could be seen that the XRD patterns contained additional peaks other than those of SrAl$_2$O$_4$, indicating the formation of a mixed oxide phase. The XRD peaks of secondary phases (Sr$_x$Al$_y$O$_z$) became sharper with an increase in annealing temperatures, indicating the higher crystallinity. Previous studies establish that the luminescent efficiency is a function of the SrAl$_2$O$_4$ phase, the degree of crystallinity, as well as the existence of secondary phases.[7]
Figure 2 shows Raman spectra of SrAl$_2$O$_4$-based phosphor powders at room temperature. For non-annealed sample, the spectrum exhibited 7 peaks around 400-1400 cm$^{-1}$. The bands at a frequency higher than 600 cm$^{-1}$ could be attributed to the Al-O stretching vibrations, while the peak at 465 cm$^{-1}$ to the bending vibration of the O-Al-O groups in corner-sharing tetrahedral.[8] However, for the annealed samples, only the peak at 465 cm$^{-1}$ was clearly observed, which was the characteristic peak of the SrAl$_2$O$_4$ structure. On the contrary, the other peaks depended on the defects or impurities in the crystal lattices.[8-9]

Surface morphology of samples was analyzed using SEM (figure 3). The average particle size of SrAl$_2$O$_4$-based phosphor powders before annealing was about 128 micrometers. With increasing annealing temperatures, the particle sizes were increased. In addition, the morphologies of the phosphor particles changed from sharp surfaces to irregular and rough surfaces. This could be associated with the particle agglomeration and secondary-phase formation at high annealing temperatures.

![SEM micrographs of SrAl$_2$O$_4$-based phosphor powders annealed at various temperatures from 700°C to 900°C for 30 min.](image)

Figure 3. SEM micrographs of SrAl$_2$O$_4$-based phosphor powders annealed at various temperatures from 700°C to 900°C for 30 min.

Figure 4 shows the PL spectra of phosphor powders with the excitation wavelength of 345 nm. The PL spectrum of non-annealed powders showed a maximum at 520 nm, which corresponded to the green-light emission band. This luminescence could be ascribed to the typical 4f$^5$5d$^1$-4f$^7$ transition of Eu$^{2+}$ ion in the SrAl$_2$O$_4$. However, the spectrum shape was slightly asymmetric due to the emission of fluorescent pigment, which was contained in the phosphor. For annealed samples, PL intensity obviously increased with increasing annealing temperatures and reached the maximum intensity at around 750°C. Further
increase in annealing temperatures led to decreasing luminescent intensity due to the phase transformation and the oxidation of Eu\(^{2+}\) ion. In addition, two emission peaks at 500 nm and 524 nm were also observed after annealing. This could be explained in terms of a change in the oxidized Eu\(^{2+}\) environment. Previous researches have reported that the allowed 4f-5d transitions are strongly influenced by the chemical environment of Eu\(^{2+}\) ion, and, as a result, the emission of Eu\(^{2+}\) ion can vary from ultraviolet to red for the aluminates.\(^9\)\(^\text{-}\)\(^10\) It has been reported that the Eu\(^{2+}\) emission shifts to longer wavelength with increasing Sr/Al ratio.\(^10\)

\[\text{Figure 4. PL spectra of SrAl}_2\text{O}_4\text{-based phosphor powders annealed at various temperatures}\]

Figure 5 shows the physical appearance and the glowing effect of SrAl\(_2\)O\(_4\)-based phosphor powders. The samples were exposed to the UV light for 15 min to enable the glowing effect in the dark. It could be clearly seen that the phosphor powders exhibited green-light emission, and the intensity of the emitted light was strongly a function of annealing temperatures. The optimal performance was obtained with the phosphors annealed at 750°C, and the greenish glow was completely lost at 900°C. The main reason for the drastic reduction of luminescent intensity at high annealing temperatures was the thermal oxidation of Eu\(^{2+}\).
Figure 5. SrAl$_2$O$_4$-based phosphor powders annealed at various temperatures in daylight and under UV light.

Figure 6. (Left) The fabrication of glass-based phosphors using a granular-molding machine, (Middle, Right) Luminescent cements in Daylight and under UV light.

The application of the SrAl$_2$O$_4$-based phosphor powders as glass-based phosphors and luminescent aggregates in cement is shown in figure 6. Luminescent aggregates were produced by mixing glass frits (SiO$_2$-CaO-Na$_2$O-Al$_2$O$_3$-MgO) and SrAl$_2$O$_4$-based phosphor powders (15% by weight) in granular-molding machine. The resultant spherical-like aggregates were then annealed at 750°C and decorated onto the cement block. The products were found to glow after UV exposure and had good chemical and thermal stabilities.

4. Conclusions

In this study, the temperature-dependent properties and the optimum temperature of commercial SrAl$_2$O$_4$-based phosphor powders were investigated. The temperature-dependent luminescence of the samples was largely determined by their crystallinity, secondary phases, as well as thermal oxidation of doping rare-earth atoms. The powders annealed at 750°C was found to show the most-efficient green
luminescence and could be utilized to produce glass-based phosphors, which required high-temperature fabrication processes.

5. References

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