

Synthesis of SrAl₂O₄: Eu, Dy-based phosphors by coprecipitation and characterization of their photoluminescence

Jung-Sik Kim*

Department of Materials Science & Engineering, The University of Seoul, Seoul 130-743, Korea

In this study, the long photoluminescence phosphor, SrAl₂O₄: Eu²⁺, Dy³⁺ was synthesized by a coprecipitation method in which metal salts of Sr(NO₃)₂, Al(NO₃)₃·9H₂O, were dissolved in a (NH₄)₂CO₃ solution with Eu(NO₃)₃·5H₂O and Dy(NO₃)₃·5H₂O added as an activator and co-activator, respectively. The coprecipitated products were separated from the solution, washed, dried in a vacuum and heated at 800-1400 °C for 3 h under a reducing ambient atmosphere of 95%Ar +5 %H₂. For the synthesized SrAl₂O₄: Eu²⁺, Dy³⁺, the properties of photoluminescence such as emission, excitation and decay time were examined. Monitored at 520 nm, the excitation spectrum showed a maximum peak intensity at 313 nm with a broad band from 200-500 nm. The shift of main peaks of excitation toward shorter wavelengths for the phosphors prepared by the coprecipitation method occurred due to the quantum size effect of the nano-sized particles, compared with those produced by the solid-state reaction method. The emission intensity increased as the annealing temperature increased and showed a maximum peak intensity at 510 nm with a broad band from 400-650 nm. The decay time of SrAl₂O₄: Eu²⁺, Dy³⁺ increased as the heat treatment temperature increased.

Key words: Photoluminescence, Long phosphorescence phosphor, Decay time.

Introduction

Phosphorescent materials have a great potential for various device applications and have been widely studied by many researchers. The ZnS-based phosphors have been extensively employed in many displays. However, the sulfide compound is very unstable to moisture or carbon dioxide during standby and has a short durability. Compared with the alkaline earth sulfides, alkaline earth aluminates are chemically stable in an ambient environment, and are used as new host materials in recent years[1].

The characteristic broad band luminescence originates from transitions between the ⁸S_{7/2}(4f⁷) ground state and the crystal field components of the 4f⁶5d¹ excited state configuration[2]. The luminescence is very strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electromagnetic spectrum. In addition to the initial very short decay time, the photoluminescence of Eu²⁺-doped alkaline earth aluminates, MA₂O₄: Eu²⁺ (M = Ca, Sr, Ba), also show luminescence with a very long lifetime in the same characteristics blue/green visible range as the photoluminescence itself [3, 4]. Since the lifetime greatly exceeds that of any other material known to date [5], this offers an unexpectedly large field of applications for the use of these aluminates. The long-lasting characteristic of alkaline earth aluminates phosphors have attracted

considerable attention for their potential applications in such fields as luminous paint, safety indicators on emergency devices, electronic instrument dial pads, lighting apparatus and switches, automobile dials and panels, writing and printing inks, plasma display phosphors, etc.[6, 7] Up to now, alkali-earth aluminate phosphors with excellent properties, such as blue CaAl₂O₄: (Eu²⁺, Nd³⁺), green SrAl₂O₄: (Eu²⁺, Dy³⁺) and BaAl₂O₄: (Eu²⁺, Dy³⁺), have been developed for various applications [8, 9].

Thus far, long afterglow phosphors were mainly prepared through solid-state reactions, which led to a large grain size. Normally, the grain size is more than 10 μm by this routine. Since the emitting center will be affected by the surrounding lattice environment, the phosphorescent properties of long-lasting phosphors are greatly affected by the grain size. When the grain size reaches the nanoscale, many new properties will be observed, such as a peak shift either in the excitation or the emission spectrum [10, 11]. However, the preparation of phosphors at a nano or sub-micrometer scale and their related properties have scarcely been reported.

In the present study, nanocrystalline powders of SrAl₂O₄: (Eu²⁺, Dy³⁺) phosphor were prepared by a coprecipitation method, and their properties of photoluminescence and long-phosphorescence were examined as a function of heat treatment temperature.

Experimental Procedure

For the coprecipitation process, precursor materials were prepared from Sr(NO₃)₂, Al(NO₃)₃·9H₂O, (Aldrich,

*Corresponding author:
Tel : +82-2-2210-2758
Fax: +82-2-2215-5863
E-mail: jskim@uos.ac.kr

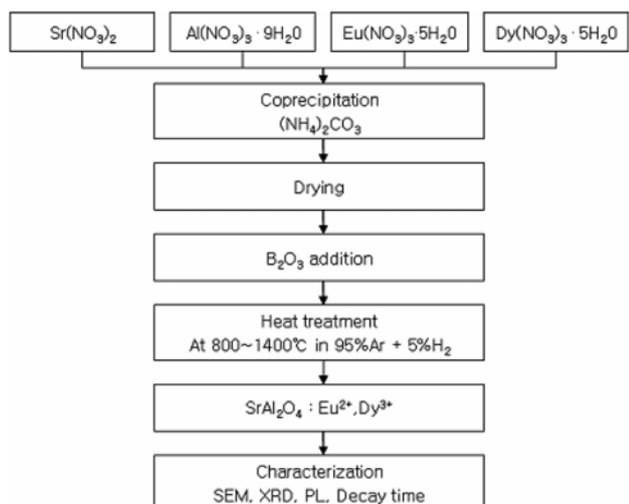


Fig. 1. Flow chart for the preparation of $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ and its characterization.

99.% purity), $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with a mole ratio of 0.97 : 2.0 : 0.01 : 0.02, respectively. The nitrates were weighed stoichiometrically and dissolved in deionized water and stirred well for 20-25 minutes to get a clear solution. The solutions were then titrated with $(\text{NH}_4)_2\text{CO}_3$ to completely precipitate. The colloidal precipitates were dried at 100 °C for 20 hours in a dry oven and then annealed at 300 °C for 5 hours in order to completely remove water and remnant nitrates.

A small amount of B_2O_3 (2 wt%) was added to the calcined powders as a flux. Finally, the powders were heated in the temperature range of 800-1400 °C for 3 hours in a reducing atmosphere of Ar-5% H_2 gas. Phase identification of the sample was carried out by an X-ray Diffractometer (Rigaku D/max-2200/pc) with Cu-K α radiation. The morphology of the powders was observed by a SEM (FE-SEM, Hitach S-1400). Photoluminescence (PL) spectra were obtained using a photo-luminescence spectrometer (Hitach, F-4500) with a pulse a Xe lamp. The decay curve of afterglow was measured by the same instrument after the specimens were sufficiently irradiated by a standard D56-lamp for 10 minutes.

The experimental procedure of this study is summarized in Fig.1.

Results and Discussion

Fig. 2 shows a high magnification SEM micrograph of phosphor powders annealed at 300 °C for 5 h. The micrograph shows a uniform distribution of particles with an average size of 20-30 nm in diameter.

Fig. 3 shows a low magnification SEM micrographs of $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors synthesized by coprecipitation and heat treated at 800 °C-1400 °C for 3 h in a 95%Ar + 5% H_2 atmosphere. As the heat treating temperature increased, the particle size increased from submicrometer at 800 °C to 50 μm at 1400 °C. The inset

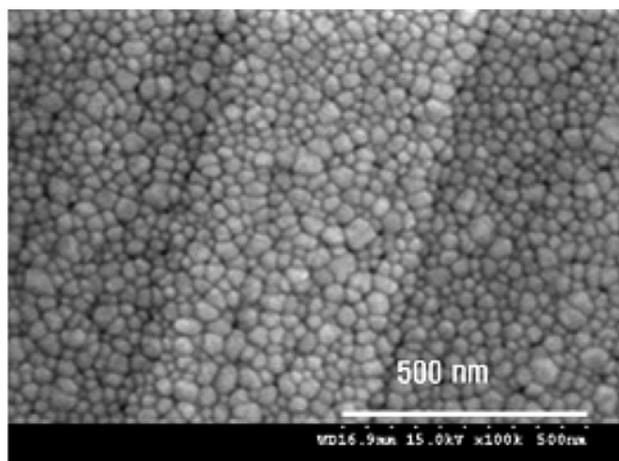


Fig. 2. SEM micrograph of the $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor synthesized by coprecipitation and calcined at 300 °C.

SEM micrograph at the left top is a high magnification micrograph of the particle surface and show an evidence of coalesced nanoparticles. According to the results of both low and high magnification micrographs, thousands of nanosized particles coalesce to be large clusters decades of micrometers in size.

Fig. 4 shows XRD patterns of $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors after heat treatment at various temperatures. When the heat treatment temperature is below 1000 °C, some peaks from second phases such as $\text{Sr}_3\text{Al}_2\text{O}_6$ (principal peak, $2\theta = 35.1^\circ$) occurred. However, above 1200 °C a single phase of SrAl_2O_4 was only observed without any peaks from second phases. The principal peak of $\text{Sr}_3\text{Al}_2\text{O}_6$ ($2\theta = 28.4^\circ$) is shifted slightly towards smaller θ values as the heat treatment temperature was increased, which is related with the effects of Eu, Dy and B ions. It is generally considered that Eu^{2+} and Dy^{3+} ions enter into the Sr ion sites in the $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ host. Because the radii of Eu^{2+} (0.130 nm) and Dy^{3+} (0.117 nm) ions, is approximately equivalent to that of the Sr^{2+} ion (0.127 nm), their substitutions will not involve a significant distortion of the lattice parameter. It is possible for B^{3+} (0.02 nm) ions to enter into the Al ion sites or any interstitial sites in the $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ host. If B^{3+} ions substitute into the Al^{3+} ion sites, the principal peak of $\text{Sr}_3\text{Al}_2\text{O}_6$ ($2\theta = 28.4^\circ$) should shift toward a higher θ value since the radius of B^{3+} (0.02 nm) is smaller than that of Al^{3+} (0.057 nm). Thus, it is concluded that B^{3+} ions might occupy the interstitial sites in the $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ crystal.

Fig. 5 shows the excitation spectra of $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors prepared by coprecipitation (a) and solid state reaction methods (b) which exhibit slightly different excitation behaviors. The major peaks of the $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor prepared by the coprecipitation method shift to shorter wavelengths than those of the phosphor prepared by the solid-state reaction method (example; from 258 to 249 and 326 to 313 nm). This is related to the quantum size effect of nano-sized particles

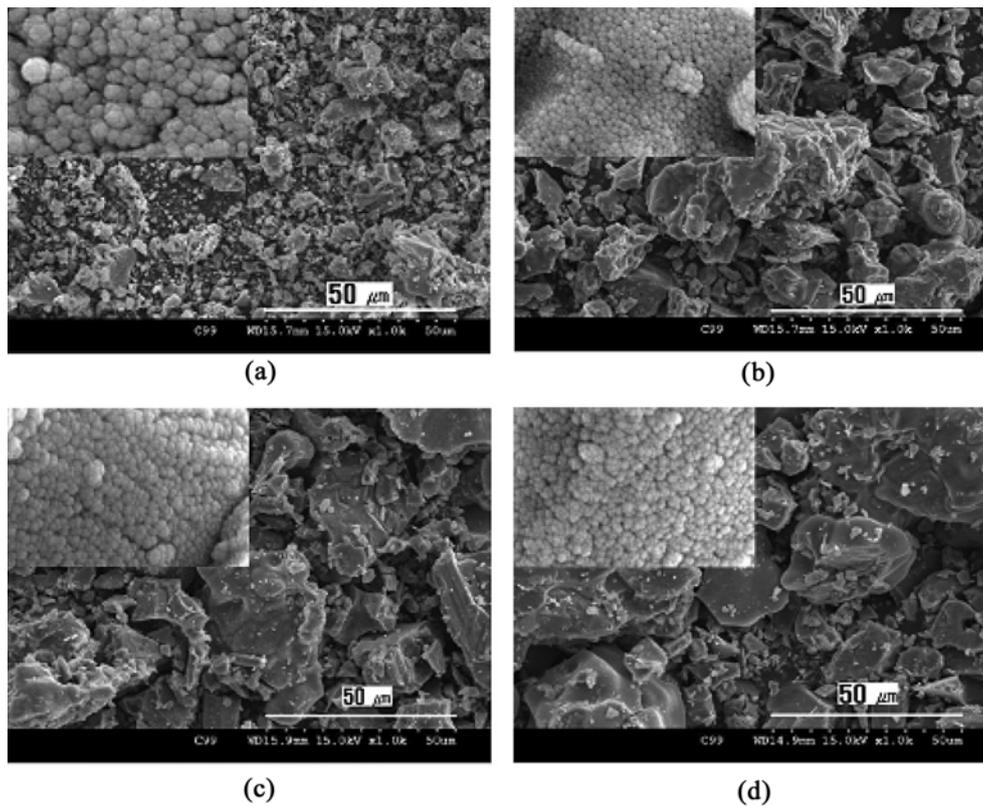


Fig. 3. SEM micrographs of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors synthesized by coprecipitation method and heat treated for 3h in a 95%Ar + 5% H_2 atmosphere at; (a) 800 °C, (b) 1000 °C, (c) 1200 °C, and (d) 1400 °C.

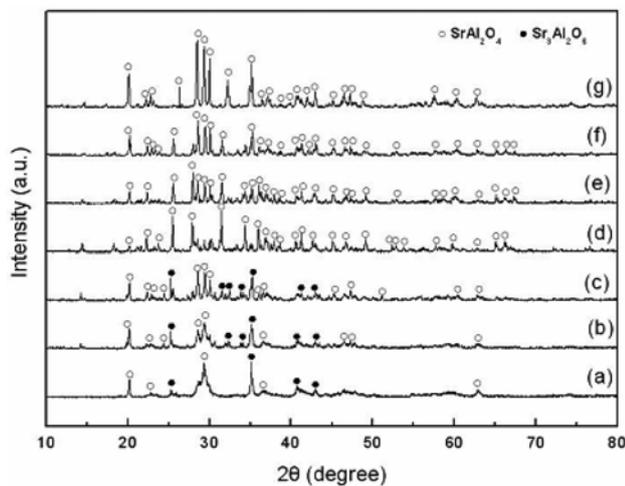


Fig. 4. X-ray diffraction patterns of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ long phosphorescence phosphor heat treated for 3 h at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C, (e) 1200 °C, (f) 1300 °C, and (g) 1400 °C.

for the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor prepared by the coprecipitation method. The nano-particles of phosphors increase the kinetic energy of electrons, resulting in a larger energy band gap, and thus require a higher excitation energy for luminescence[12].

Fig. 6 shows the emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors prepared by the coprecipitation method and heat treated at various temperatures from 800 °C-

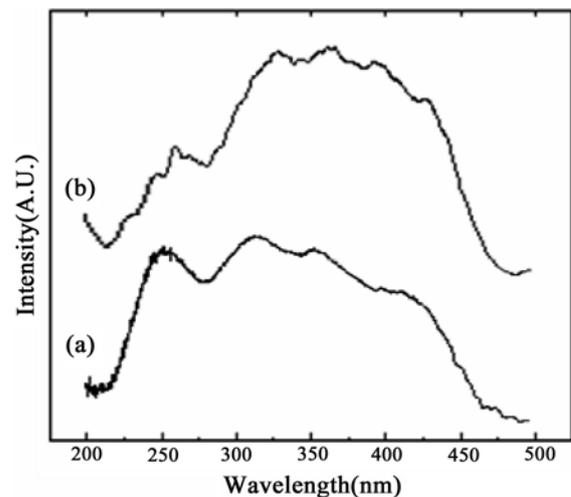


Fig. 5. Excitation spectra of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ long phosphorescence phosphors synthesized by the coprecipitation (a) and solid state reaction methods (b) and heat treated at 1400 °C in a 95%Ar - 5% H_2 atmosphere.

1400 °C for 3 h in a 95%Ar + 5% H_2 atmosphere. It is well known that the emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ have a broadband character due to 4f-5d transitions of Eu^{2+} ion, and the emission peak is at about 520 nm resulting in a green light [13]. In this study the emission spectra exhibit bright green luminescence at $\lambda_{\text{max}} = 510$ nm and a single broad band emission. As the heat-treatment temperature increases, the emission intensity increases.

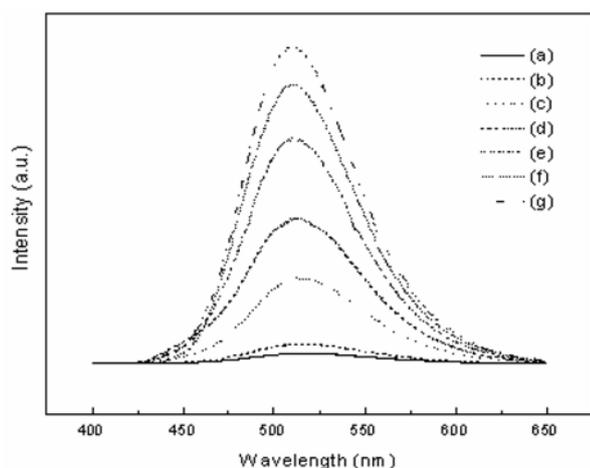


Fig. 6. Emission spectra of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ long phosphorescence phosphors heat treated for 3 h at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C, (e) 1200 °C, (f) 1300 °C, and (g) 1400 °C.

The low emission intensity at a low heat treatment temperature is mainly due to the formation of second phases as shown in the XRD patterns of Fig. 4.

Moreover, the emission maximum peak of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors prepared by coprecipitation in this study shifted to a shorter wavelength ($\lambda_{\text{max}} = 510$ nm), compared with the reported data for samples obtained by a solid-state reaction method (520 nm) [14]. The slight shift of the emission peak towards a shorter wavelength may result from the changes of the crystal field around Eu^{2+} as the phosphor crystals decrease in size to be nano-sized. Since the excited $4f^65d^1$ configurations of Eu^{2+} ion are highly sensitive to the lattice environment and 5d electrons can be strongly coupled with the lattice, the mixed states of 4f and 5d will be split by the crystal field, which may lead to the shift of the emission peak toward shorter wavelength.

Fig. 7 shows the afterglow decay curves of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors prepared by the coprecipitation method as a function of heat treatment temperature. The initial luminescent intensity and decay speed of the afterglow of phosphors are different from each other with a change of heat-treatment temperature. As the heat-treatment temperature increases, the initial intensity increases and the decay speed decreases.

It is well-known that in a $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphor, Eu^{2+} ions are the luminescent centers [13], the photo-excited luminescence is considered to be due to the transition from the 5d level to the 4f level of Eu^{2+} and holes in the traps are responsible for the long afterglow. Dy^{3+} ions play an important role and work as hole traps lying in between the excited state and the ground state of Eu^{2+} . After excitation by the light photons, electrons of an Eu^{2+} ion in the 4f level transfer to the 5d level, and holes are produced in the valence band. Some holes created are captured by the Dy^{3+} hole traps, then thermally released slowly to the valence band, and returned to the

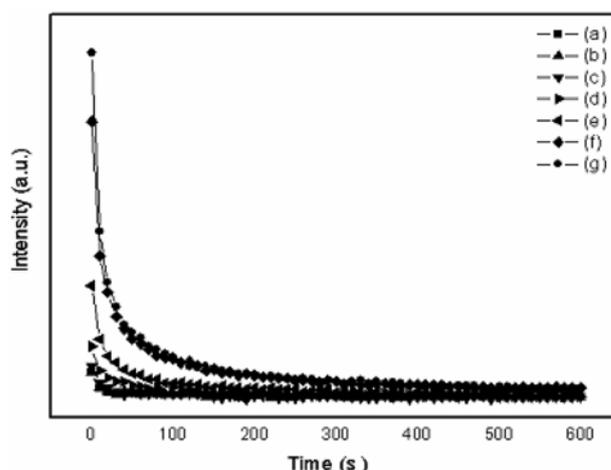


Fig. 7. Afterglow decay curves for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ long phosphorescence phosphor heat treated for 3 h at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C, (e) 1200 °C, (f) 1300 °C, and (g) 1400 °C.

ground state of Eu^{2+} accompanied with the emission of light photons. Furthermore, the hole mobility may also play an important role and need to be taken into account. A low rate of hole mobility and electron-hole recombination will increase the retrapping probability and further slow down of the decay process [15].

Conclusions

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ long persistence phosphors as nano-sized particles were prepared by a co-precipitation method in this experiment.

1. The synthesized phosphor powders showed a uniform distribution of particles with an average size of 20-30 nm in diameter. As the heat treatment temperature increased, nanosized particles coalesced to be large clusters several decades of micrometers in size.

2. The single phase of SrAl_2O_4 was formed at heat treatment temperatures above 1200 °C below which second phases such as $\text{Sr}_3\text{Al}_2\text{O}_6$ occurred. According to the slight shift of Bragg's angle (2θ) toward a smaller value, it is concluded that B^{3+} ions occupy interstitial sites in the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ host.

3. A shift of the main excitation peaks towards a shorter wavelength for the phosphors prepared by the coprecipitation method occurred due to the nano-sized particles, compared with those prepared by the solid-state reaction method.

4. The phosphors prepared showed an emission peak at 510 nm which is slightly shifted towards a shorter wavelength, compared with the phosphor prepared by a solid-state reaction method due to the decrease in particle size.

5. As heat-treatment temperature increased, the peak intensity of the emission spectra increased, the initial intensity of the decay curves increased, and the decay speed decreased.

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