

Synthesis and Photoluminescence Studies on $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$

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ABSTRACT

Strontium-substituted $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ compositions were prepared by the solid state synthesis method. These compositions were characterized for their phase, crystallinity and morphology using powder x-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Photoluminescence properties were investigated by measuring excitation spectra, emission spectra and decay time for varying Ba/Sr concentrations. Photoluminescence results show higher luminescence and long decay time for $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ ($x=0$). This is probably due to the influence of the 5d electron states of Eu^{2+} in the crystal field. Long persistence was observed for these compositions due to Dy^{3+} co-doping.

Key words: Solid-solution, X-ray diffraction, SEM, Photoluminescence

1. Introduction

Phosphors with long persistence can light up for a longer time in the darkness after irradiation with sunlight or artificial light. Eu^{2+} doped alkaline earth $\text{MAl}_2\text{O}_4 : \text{Eu}^{2+}$ (M: Ca, Sr, Ba) with strong photoluminescence in the blue-green visible region have been studied extensively.^{1,2)} The persistence time in these materials is much longer than that of doped sulfides.³⁾ Several aluminates have been investigated and used as photoluminescence, cathodoluminescence and plasma display panel phosphors for their high quantum efficiency in the visible region. Eu^{2+} doped phosphors usually show intense broad band photoluminescence (PL) with a short decay time the order of tens of nanoseconds.⁴⁾ The valence state of the activator ion dictates the emission wavelength.^{5,6)} The trivalent Eu^{3+} ions show red luminescence properties in highly stable lead-based heavy metal oxide glasses.^{7,8)} The emission of Eu^{2+} strongly depends on the host lattice and can occur from the ultraviolet to the red region of the electro-magnetic spectrum. This is because the $5d \leftrightarrow 4f$ transition is associated with the change in electric dipole and the 5d excited state is affected by crystal field effects. Strontium aluminates doped with Eu show very high quantum efficiency, long persistence and better stability than the other alkaline earth aluminates. In the $\text{SrO} - \text{Al}_2\text{O}_3$ system, four well-known phosphor hosts exist:

SrAl_2O_4 , $\text{SrAl}_{12}\text{O}_{19}$, $\text{Sr}_2\text{Al}_6\text{O}_{11}$ and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$.⁹⁻¹¹⁾ Green-emitting SrAl_2O_4 has good brightness, long-persistent phosphorescence and greater chemical stability than the traditional $\text{ZnS} : \text{Cu}, \text{Co}$ phosphor. SrAl_2O_4 is not radioactive; therefore, this material can be safely used as the phosphorescent pigment for luminous watches and clocks. The phosphorescence characteristics of $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ have been explained in terms of the trapping and thermal release of the charge carriers (holes) at room temperature wherein Eu^{2+} is an activator and Dy^{3+} serves as a trapping center. Among the four strontium aluminates mentioned above, only the crystals of the first two compounds have been found to exhibit phosphorescence when co-activated with Eu^{2+} and Dy^{3+} , with emission peaks around 520 and 400 nm, respectively.^{12,13)} Low energy emission due to Eu^{2+} was reported in the solid solutions of $\text{BaAl}_2\text{O}_4 : \text{Eu}^{2+}$ and $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}$.¹⁴⁾

It is expected that the substitution of Sr for Ba in $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4 : \text{Eu} : \text{Dy}$ will yield tunable emissions. In view of this expectation we have prepared phosphor compositions in the series $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4$ (for $x=1, 0.5$ and 0) with Eu^{2+} and Dy^{3+} ions as activators and trapping centers, respectively, to achieve long persistence decay. Prepared phosphors were investigated for single phase and crystallinity using XRD and SEM techniques. The PL and decay time measurements were done on the synthesized compositions.

2. Experimental Details

The solid solubility of Sr is reasonably good in Ba compounds. Particularly in oxides and aluminates they substitute for each other and make solid solutions quite easily.

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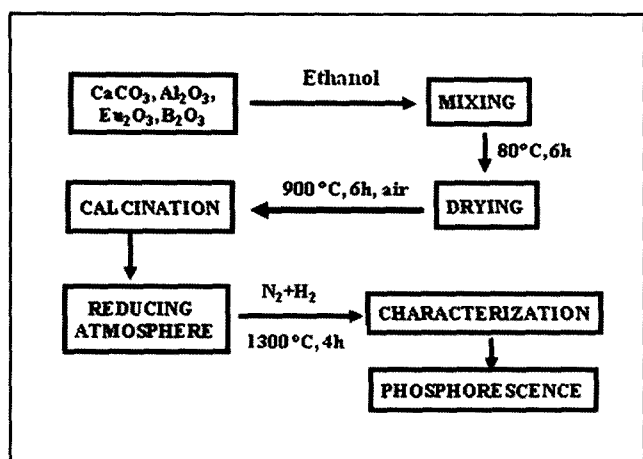


Fig. 1. Flow chart for solid state synthesis process.

Compositions in the series $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x=1, 0.5$ and 0) were prepared using the solid state synthesis method. High purity (4N) raw materials of Aldrich make, $\text{BaCO}_3, \text{SrCO}_3, \text{Al}_2\text{O}_3, \text{Eu}_2\text{O}_3, \text{Dy}_2\text{O}_3$ and B_2O_3 were used for charge preparation. Composition in stoichiometric ratios for each material was weighted and mixed thoroughly with ethanol in an agate mortar. The resulting slurry was dried at 80°C in a vacuum oven for 4 h. Each composition was co-doped with 0.25 mol% Eu_2O_3 and 0.25 mol% Dy_2O_3 . The mixed and grounded charge was sintered at 1200°C for 6 h in an air atmosphere. The sintered charge was annealed at 1300°C for 4 h in a reducing atmosphere (5% H_2 and 95% N_2) to ensure complete reduction of Eu^{3+} to Eu^{2+} . The flow chart describing the solid state preparation route is shown in Fig. 1. The crystallinity, phase and morphology of the synthesized compositions were investigated by powder XRD and SEM techniques. Photoluminescence (PL) emission spectra were taken on a Perkin-Elmer LS50B luminescence spectrometer. Each sample was excited with a 254 nm light source and the emission spectra were scanned in the wavelength range from 360 to 700 nm. To measure the excitation spectra, the analyzer monochromator was set to the maximum wavelength of the emission spectra and then an excitation monochromator was used in the range 200 to 400 nm. The decay time on these synthesized compositions was recorded using a pulsed Xenon lamp.

3. Results and Discussion

Compositions in the series $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, with $x=1, 0.5$ and 0 , were synthesized. Eu^{2+} and Dy^{3+} concentrations in $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4$ were optimized and kept constant at 0.25 mol% in the present study. Fig. 2 shows the representative powder XRD patterns for series $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ with $x=1, 0.5$ and 0 . The XRD patterns show the monoclinic phase diffraction peaks for SrAl_2O_4 (b, for $x=0$). The XRD pattern shows a hexagonal phase for the BaAl_2O_4 (a, for $x=1$). The representative pattern for the intermediate composition (c, for $x=0.5$) is given for compari-

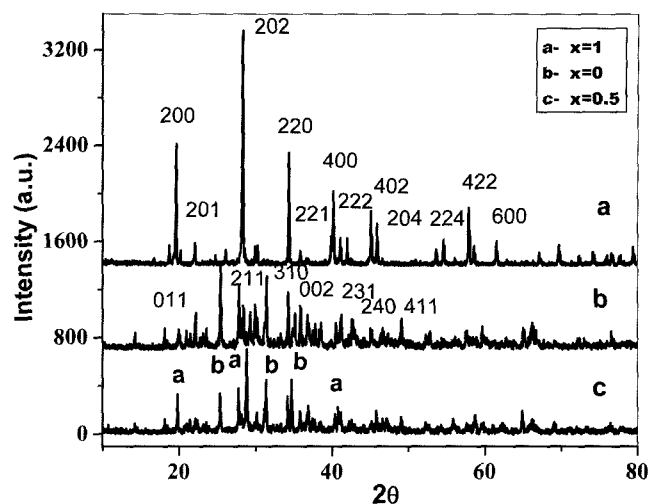


Fig. 2. Powder XRD patterns for $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x=1, 0$ and 0.5).

son. The XRD peaks for this composition are a mixture of both the end members, apart from some unknown peaks. These peaks are assigned as 'a' (hexagonal) and 'b' (monoclinic) to match with the end members. This suggests that the composition is mainly the mixed phase of both the end members, apart from some small amount of unknown phase. The lattice parameters for the parent BaAl_2O_4 and SrAl_2O_4 were calculated from XRD patterns and found to match closely with the JCPDS data (PDF#17-0306 and PDF# 74-0794). The calculated lattice parameters were: for hexagonal BaAl_2O_4 , $a=b=10.401 \text{ \AA}$, $c=8.788 \text{ \AA}$; for monoclinic SrAl_2O_4 , $a=8.441 \text{ \AA}$, $b=8.812 \text{ \AA}$ and $c=5.158 \text{ \AA}$. Small quantities of the doped rare earth active ions Eu^{2+} and Dy^{3+} had a negligible effect on the basic crystal structure. The samples reduced at 1300°C became crystalline and these were used for SEM study. Fig. 3 (a, b, c) shows the representative SEM micrographs taken for $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ where $x=1, 0.5$ and 0 , respectively. The micrographs show that the crystallite sizes vary from few a microns to several tens of microns. It was observed that the crystallite sizes are nearly the same regardless of the composition.

The Ba and Sr aluminates phosphor exhibit green emission when excited by UV light. This indicates that the activator ion Eu is in a divalent (Eu^{2+} , green emission) rather than a trivalent (Eu^{3+} , red emission) state. Excitation and emission spectra for $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ (for $x=1, 0.5$ and 0) at an excitation wavelength of 254 nm from a pulsed xenon lamp are shown in Fig. 4 (a, b). The excitation spectrum in Fig. 4(a) shows a broad band at 250 to 400 nm that corresponds to the crystal field splitting of the Eu^{2+} d-orbital. The emission spectrum in Fig. 4(b) is a symmetrical band near 500 nm. The emission band has a peak at 492 nm, 495 nm and 488 nm for the compositions when $x=1, 0.5$ and 0 , respectively. These emissions are attributed to the typical $4f^65d^1-4f^7$ transition of the Eu^{2+} ion. Dy^{3+} ion doping in the phosphor creates the deep trapping levels.¹²⁾ Blue shift was observed in the emission spectra when the compo-

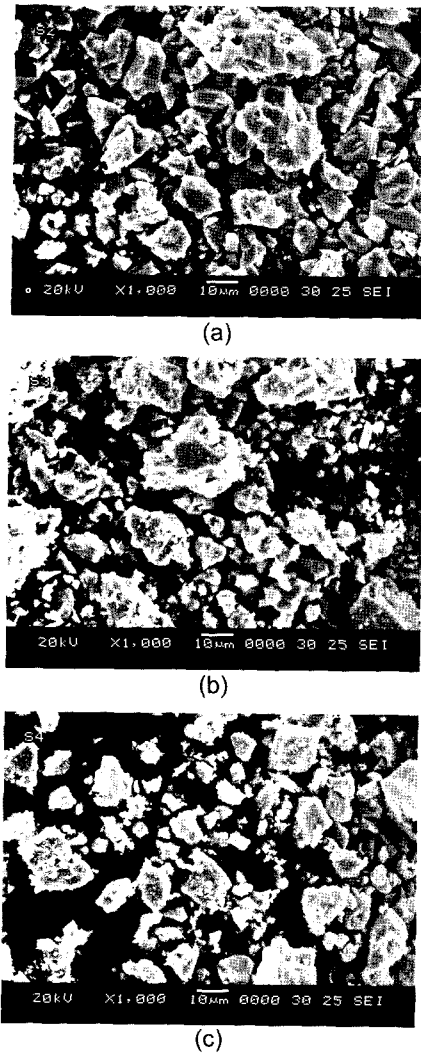


Fig. 3. SEM micrographs for $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x=1, 0.5$ and 0).

sition moved from BaAl_2O_4 (492 nm) to SrAl_2O_4 (488 nm). The emission intensity increased as Sr concentration increased, and was highest for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x=0$). The emission intensity was found to be lowest for the mixed phase. This is because the composition is not a single phase, but rather a mixture of the two phases. This was expected from the mixed phase composition. Fig. 5 shows the decay time curves for $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ solid solution compositions for ($x=1, 0.5$ and 0). All the samples showed long decay time when the powders were efficiently excited by a pulsed Xenon lamp for 15 min. When the source lamp was switched off, the intensity of the persistence decreased rapidly and finally formed a stable long-persistent emission for several minutes. Long-persistence time for this doubly-doped phosphor was found to be due to the doping with a second sensitizer ion, Dy^{3+} . Incorporation of the Dy^{3+} ion creates deep traps in the energy band gap of the host material. These traps act as hole trapping levels near the valence band.¹⁵⁾ When the excitation source is switched off, the relaxation of these secondary ions from deep traps is very

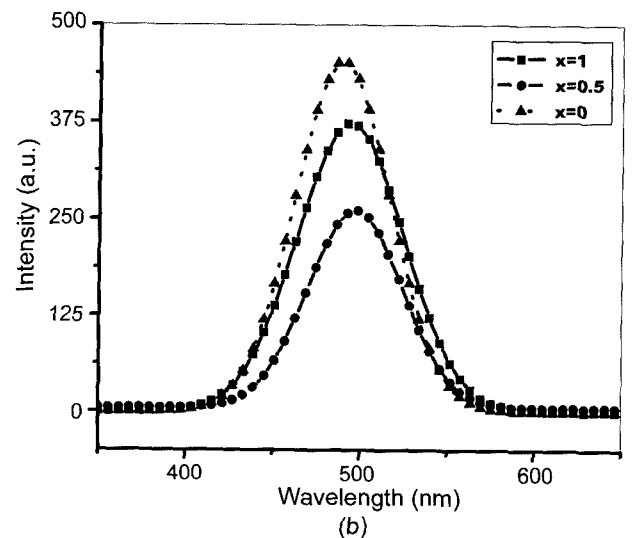
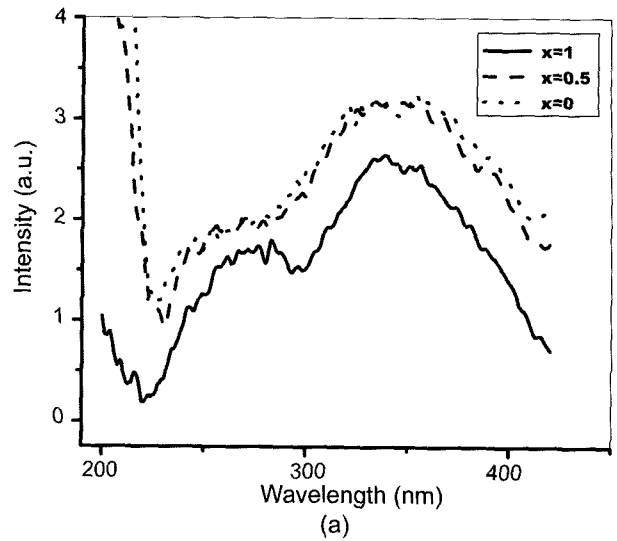


Fig. 4. Excitation (a) and emission (b) spectra for $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x=1, 0.5$, and 0).

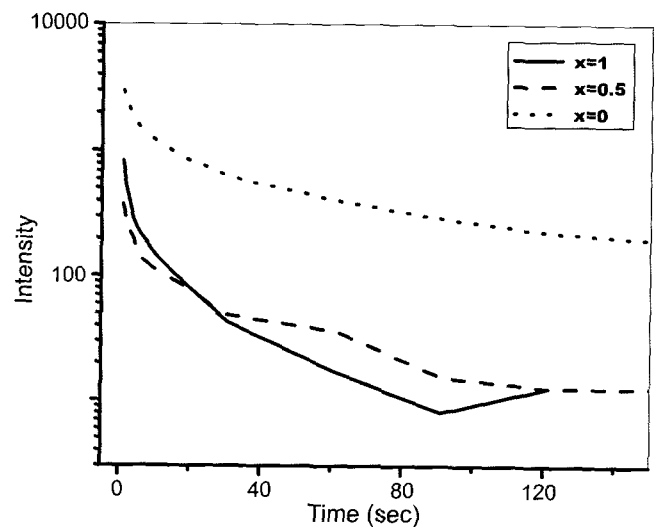


Fig. 5. Decay time for $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x=1, 0.5$ and 0).

slow, which leads to the long persistence.

4. Conclusions

Compositions with varying Ba/Sr in the series $\text{Sr}_{1-x}\text{Ba}_x\text{Al}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ were synthesized. Powder XRD was done to investigate the prepared compositions for their phase and crystallinity. The structural change from hexagonal BaAl_2O_4 to monoclinic SrAl_2O_4 was observed. Blue shift was observed in the emission spectra when the composition moved from BaAl_2O_4 to SrAl_2O_4 . Higher emission intensity and longer decay time was found for Sr-rich compositions, and was highest for SrAl_2O_4 . The long persistence time observed for doubly-doped phosphor was due to the creation of the deep traps generated by the sensitizer ion Dy^{3+} .

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