Long Persistence in Sr/BaAl$_2$O$_4$: Eu$^{2+}$: Dy$^{3+}$ Green Phosphor

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Abstract
Solid solution of barium strontium aluminate, Sr/BaAl$_2$O$_4$: Eu$^{2+}$ co-doped with Dy$^{3+}$ was prepared by solid state reaction method. The prepared phosphor compositions with varying Dy$^{3+}$ compositions were investigated by powder X-ray diffractometer (XRD), SEM, TEM and photoluminescence (PL) excitation and emission spectra. Long persistent luminescence was observed in these phosphor materials. The broad band UV excited luminescence of the Sr/BaAl$_2$O$_4$:Eu$^{2+}$:Dy$^{3+}$ was observed in the green region ($\lambda_{\text{max}}=500\,\text{nm}$) due to transitions from the 4f$^5$5d$^1$ to 4f$^7$ configuration of the Eu$^{2+}$ ion. Effects of co-doping of Dy$^{3+}$ on the photoluminescence properties of these compositions were investigated.

1. Introduction
Several aluminate compositions are investigated and used as photoluminescence, catholuminescence 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 of the order of tens of nanoseconds$^3$. The emission of Eu$^{2+}$ is strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electromagnetic spectrum. This is because the 5d$\leftrightarrow$4f transition is associated with the change in electric dipole and the 5d excited state is affected by crystal field effects. Notably barium and strontium aluminates have been reported to be good host materials. Strontium aluminates doped with Eu have very high quantum efficiency, long persistency and better stability than the other alkaline earth aluminates. In the SrO –Al$_2$O$_3$ system, four well-known phosphor hosts exist, namely SrAl$_2$O$_4$, SrAl$_{12}$O$_{19}$, Sr$_2$Al$_2$O$_{11}$ and Sr$_4$Al$_4$O$_{35}$$^{5,4}$. The corresponding Eu$^{2+}$-doped phosphors give very low persistence, which lasts for nanoseconds to a few seconds. Green-emitting SrAl$_2$O$_4$ that has been co-doped with Dy$^{3+}$ and Eu$^{2+}$ ions and recrystallized with B$_2$O$_3$ flux has been regarded as a useful phosphor$^5$. It has very good brightness and long persisting phosphorescence and greater chemical stability than the traditional ZnS:Cu, Co phosphor. Because it is not radioactive, this material can be safely used as the phosphorescent pigment for luminous watches and clocks. This phosphor is also used for ‘cold lighting’ that emits no infrared radiation. The phosphorescence characteristics of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ were explained in terms of the trapping and thermal release of the charge carriers (hole) at room temperature where-in Eu$^{2+}$ is an activator and Dy$^{3+}$ served as a trapping center$^6$. Katsumata et al.$^7$ have reported that among the four strontium aluminates mentioned above, only the crystals of the first two compounds are found to exhibit phosphorescence when co-activated with Eu$^{2+}$ and Dy$^{3+}$, with emission peak around 520 and 400 nm, respectively. The emission studies on BaAl$_2$O$_4$:Eu$^{2+}$, CaAl$_2$O$_4$:Eu$^{2+}$, Nd$^{3+}$ and their solid solution in different Ba/Ca ratios is reported earlier$^8$.$^9$. It is well known that the trivalent Eu$^{3+}$ ions show red luminescence properties in highly stable lead based heavy metal oxide glasses$^{10}$. The solid solution of BaAl$_2$O$_4$:Eu$^{2+}$ and CaAl$_2$O$_4$:Eu$^{2+}$, Nd$^{3+}$ show tunability and long persistency.

We have prepared BaAl$_2$O$_4$ based materials with the substitution of Ba by Sr with 0, 50 and
100% and having Eu$^{2+}$ and Dy$^{3+}$ ions as activator and trapping center to achieve long afterglow. The emission and the single phase limit of Sr in BaAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphor was observed by using XRD, SEM and TEM measurements. The PL and decay time measurements were done to correlate the substitution effect on emission and persistence.

2. Experimental details

Solid solution in the series Sr$_{1-x}$Ba$_x$Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ (x = 1, 0.50 and 0) were prepared. Each composition was co-doped with 0.25 mol% Eu$^{2+}$ and 0.25 mol% Dy$^{3+}$. Mixed and grounded powders were sintered at 1200°C for 6 h in an air atmosphere. The resulting powders were 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 phase and crystallinity of the synthesized compositions were investigated by powder XRD using Rigaku D/MAX-2200V diffractometer with Cu K$_\alpha$ radiation. The SEM and TEM studies were done to investigate the crystallinity and surface morphology. Philips Tecnai G$^2$-20 (FEI) electron microscope operating at 200 kV was used for TEM experiments. The photoluminescence (PL) emission spectra were taken on Perkin-Elmer LS50B luminescence spectrometer. The emission spectra were scanned in the range of wavelengths 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 set to wavelengths 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 set to wavelengths from 360 to 700 nm.

3. Results and discussion

Concentrations of Eu$^{2+}$ and Dy$^{3+}$ in Sr/BaAl$_2$O$_4$ were optimized and both were kept 0.25 mol% in the present study. Fig. 1 shows the XRD patterns for the Sr$_{1-x}$Ba$_x$Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ compositions with varying Sr/Ba concentrations. The XRD patterns show the monoclinic phase diffraction peaks of parent SrAl$_2$O$_4$ and hexagonal phase for the BaAl$_2$O$_4$ for x = 0 and 1 respectively. Representative XRD pattern for x = 0.5 is also given for the comparison. Diffraction peaks for the solid solution for x = 0.5, show the mixed phase of both end members. The structural transformation from hexagonal BaAl$_2$O$_4$ to monoclinic SrAl$_2$O$_4$ can easily be seen from the XRD patterns.

Lattice parameters for the parent BaAl$_2$O$_4$ and SrAl$_2$O$_4$ were calculated from XRD data and are matching well with the JCPDS data file (PDF#17-0306 and PDF# 74-0794). The lattice parameter calculated were: for hexagonal BaAl$_2$O$_4$, a = 8.788 Å and c = 5.158 Å. Little amount of doped rare earth active ions Eu$^{2+}$ and Dy$^{3+}$ has almost no effect on the basic crystal structure of both the end members of the phosphor family.

Fig. 1 Powder XRD patterns for Sr$_{1-x}$Ba$_x$Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ (a) x = 0.5, (b) x = 0 and (c) x = 1.
ly the 10.0 zone axis SAD pattern is seen in inset of Fig. 3(c) for monoclinic SrAl$_2$O$_4$ phase. The crystal structure changes from hexagonal to monoclinic on decreasing the value of x from 1 to 0.

The emission spectra for Sr$_{1-x}$Ba$_x$Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ phosphors for different values of x (x=1, 0.5 and 0) are shown in Fig. 4. The emission band has a peak at 492 nm, 495 nm and 488 nm for the compositions for x=1, 0.5 and 0 respectively. These emissions are attributed to the typical 4f$^5$5d$^1$–4f$^7$ transition of Eu$^{2+}$ ion. The valence state of the activator ion dictates the emission wavelength$^{11,12}$. The blue shift was observed in the emission spectra when composition moves from BaAl$_2$O$_4$ (492 nm) to SrAl$_2$O$_4$ (488 nm). The emission intensity increases with increasing Sr compositions being highest for SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$.

Fig. 5 shows the decay time curves for Sr$_{1-x}$Ba$_x$Al$_2$O$_4$:Eu$^{2+}$, 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 persistent time for this doubly doped phosphor is found due to the doping of second sensitizer ion Dy$^{3+}$. The Dy$^{3+}$ ion incorporation creates deep traps in the energy band gap of the host material. These traps act as hole trapping levels near the conduction band$^{13}$. When the excitation source is switched off, the relaxation of these secondary ions from deep traps is very slow which leads to the long persistence.

4. Conclusions

Phosphor materials with varying Ba/Sr compositions in the series Sr$_{1-x}$Ba$_x$Al$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ were synthesized by solid state reaction method. Powder XRD was done to investigate the solid solution
for their phase and crystallinity. The structural change from hexagonal BaAl$_2$O$_4$ to monoclinic SrAl$_2$O$_4$ was observed. The blue shift was observed in the emission spectra when composition moves from BaAl$_2$O$_4$ to SrAl$_2$O$_4$. Higher emission intensity and longer decay time was found for Sr-rich compositions being highest for SrAl$_2$O$_4$. Long persistent time observed for doubly doped phosphor is because of the creation of the deep traps generated by the sensitizer ion Dy$^{3+}$.

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**References**