

# Preparation and Luminescence Characteristics of Eu<sup>2+</sup> Doped SrAl<sub>2</sub>B<sub>2</sub>O<sub>7</sub> Ceramic Phosphor

R. S. Palaspagar

Department of Physics, Shivramji Moghe College, Kelapur (Pandharkawada), Maharashtra, India

## ABSTRACT

Preparation of Eu<sup>2+</sup> ions activated strontium alumino-borate phosphor using the low cost and time saving combustion technique has been described. Powder X-ray diffraction (XRD) and field effect scanning electron microscope (FE-SEM) analysis were used to characterize the as prepared phosphor. The luminescence properties have been investigated by photoluminescence (PL) spectra. Sr<sub>x</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:xEu<sup>2+</sup> phosphor shows a stronger excitation band near 400 nm as well as enhanced blue emissions observed under 397 nm excitation wavelength. Optimum concentration and critical transfer distance of the synthesized phosphors were determined.

**Keywords:** Alumino-Borate, Combustion Synthesis, Photoluminescence.

## I. INTRODUCTION

Blue light emitting diodes (LEDs), phosphor-converted white LEDs (pc-WLEDs) have attracted extensive research and commercial interest due to their superior characteristics over traditional light emitting devices, such as high luminescence efficiency, long lifetime, energy-saving and environmental friendliness [1, 2]. White LEDs can be generated using two different methods, one of which is through the combination of a 450–470 nm blue InGaN chip and a yellowish phosphor coating [3]. However, the resulting white LEDs create problems, such as having a low color-rendering index (CRI), low luminous efficiency, and high color temperature [4,5]. Currently, the single-phase white light emitting phosphors pumped by UV chips present great potential with advantages of high color rendering indexes, low cost, and small color aberration [6]. Recently, alkaline earth metal (M) dialuminodiborates

(MAl<sub>2</sub>B<sub>2</sub>O<sub>7</sub>) have gained much attention as hosts for phosphor materials with better crystallinity, lower synthetic temperature and higher radiant efficiency, as compared to the corresponding other borates or aluminates host. In particular, Eu<sup>2+</sup> ion is unique as an activator since its broad band 4f<sup>6</sup>5d<sup>1</sup> → 4f<sup>7</sup> transition is parity-allowed and its radiative lifetime is relatively short and most interestingly, its emission is strongly dependent on the type of host, with possible emission wavelengths ( $\lambda_{em}$ ) ranging from ultraviolet to red spectral region [7]. However, the luminescent properties of Eu<sup>2+</sup> doped strontium aluminate phosphors have been studied extensively because they show anomalous long phosphorescence and short-time decay depending on the conditions of preparation [8, 9]. Lucus et. al. was firstly reported non-linear optical behavior of SrAl<sub>2</sub>B<sub>2</sub>O<sub>7</sub> material; also, the rhombohedra structure of SrAl<sub>2</sub>B<sub>2</sub>O<sub>7</sub> is described from the (BO<sub>3</sub>)<sub>∞</sub> planes perpendicular to the

original axis being linked alternatively by Al–O–Al bridges and Sr atoms [10,11].

Motivated by the investigations described above, we were encouraged to synthesis by solution combustion technique and study the effect of host compositions on the luminescent properties for  $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{2+}$  by systematically substituting  $\text{Sr}^{2+}$  in the host lattice.

## II. METHODS AND MATERIAL

The powder samples of  $\text{Sr}_{1-x}\text{Al}_2\text{B}_2\text{O}_7:x\text{Eu}^{2+}$  ( $x = 0.01, 0.03, 0.05, 0.06, 0.07$ ) were prepared by a solution combustion technique which is described earlier [12, 13]. The stoichiometric amounts of high purity starting materials,  $\text{Sr}(\text{NO}_3)_2$  (A.R.),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (A.R.),  $\text{Eu}_2\text{O}_3$  (high purity 99.9%),  $\text{H}_3\text{BO}_3$  (A.R.),  $\text{CO}(\text{NH}_2)_2$  (A.R.) have been used for phosphor preparation. The stoichiometric amounts of the ingredients were thoroughly mixed in an agate mortar, adding little amount of de-ionized water to obtain an aqueous homogeneous solution. The aqueous solution was then transferred into a china basin and slowly heated at lower temperature of  $70^\circ\text{C}$  in order to remove the excess water. The solution was then introduced into a preheated muffle furnace maintained at  $550^\circ\text{C}$ . The solution boils foams and ignites to burn with flame; a voluminous, foamy powder was obtained. The entire combustion process was over in about 5 min. Following the combustion, the resulting fine powders were annealed in a carbon reducing atmosphere at temperature  $850^\circ\text{C}$  for 90 min. and suddenly cooled to room temperature. The prepared materials were characterized by powder XRD and FE-SEM. Powder X-ray diffraction measurements were taken on Rigaku Miniflex II X-ray Diffractometer and compared with the ICDD files. Surface morphology of the calcined particles was observed by scanning electron microscopy (FE-SEM). PL & PLE measurements at room temperature were performed on Hitachi F-7000 spectrofluorometer with spectral resolution of 2.5 nm.

## III. RESULTS AND DISCUSSION

### 3.1 X-ray Diffraction Pattern

Fig. 1 shows the XRD pattern of  $\text{Sr}_{0.95}\text{Al}_2\text{B}_2\text{O}_7:0.05\text{Eu}^{2+}$  phosphor. All the peaks of the synthesized phosphors can be indexed and there were some high intensity peaks observed because of increased in the crystallinity of the sample. The  $\text{Sr}_{0.95}\text{Al}_2\text{B}_2\text{O}_7:0.05\text{Eu}^{2+}$  phosphor was consistent with the ICDD file [01-089-9063], which belongs to rhombohedral structure with space group of R32 (155). Due to the difference of the ion sizes and valence states between  $\text{Eu}^{2+}$  (0.125 nm),  $\text{Sr}^{2+}$  (0.126 nm) and  $\text{Al}^{3+}$  (0.054 nm),  $\text{Eu}^{2+}$  ions are expected to substitute for the place of  $\text{Sr}^{2+}$  in  $\text{SrAl}_2\text{B}_2\text{O}_7$  lattice [14].

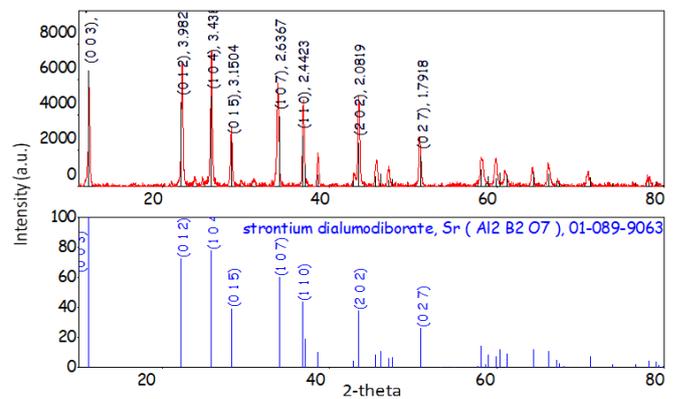


Fig. 1. X-ray diffraction patterns of the  $\text{Sr}_{0.95}\text{Al}_2\text{B}_2\text{O}_7:0.05\text{Eu}^{2+}$  phosphors.

### 3.2 FE-SEM micrographs of phosphor powders

The FE-SEM photographs of  $\text{Sr}_{0.95}\text{Al}_2\text{B}_2\text{O}_7:0.05\text{Eu}^{2+}$  powder prepared by solution combustion method are as shown in Fig. 2. The shape of the particles was observed to be rod like structure with agglomerate phenomenon for both the phosphors.

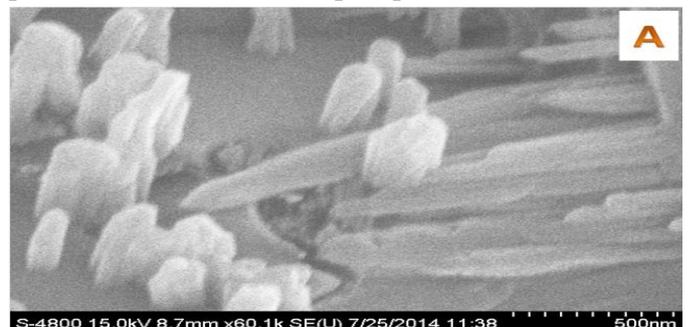
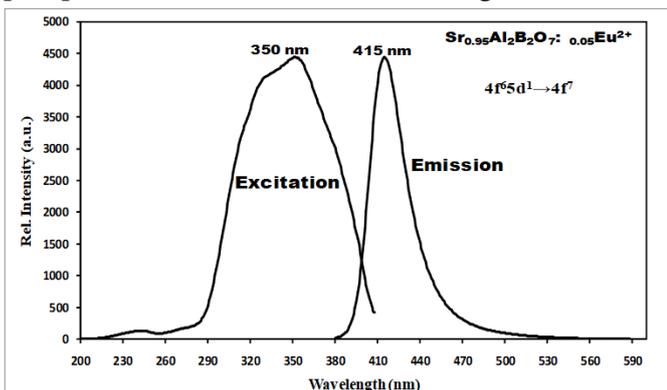


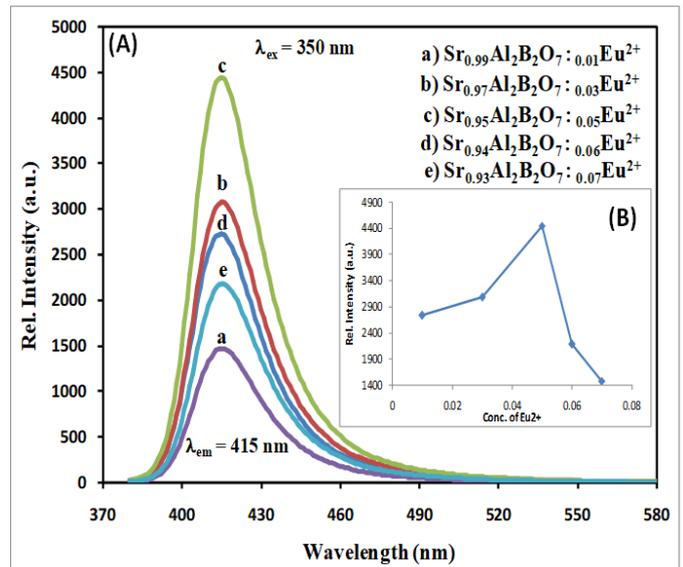
Fig. 2. FE-SEM image of  $\text{Sr}_{0.95}\text{Al}_2\text{B}_2\text{O}_7:0.05\text{Eu}^{2+}$

### 3.3 Photoluminescence analysis of SrAl<sub>2</sub>B<sub>2</sub>O<sub>7</sub>: Eu<sup>2+</sup>

Fig. 3 shows the excitation and emission spectra of Sr<sub>0.95</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>: 0.05Eu<sup>2+</sup> phosphor. When monitoring the emission wavelength at 415 nm, the excitation spectrum of the Sr<sub>0.95</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>: 0.05Eu<sup>2+</sup> phosphor exhibited a wide band in the UV region centered at 350 nm and originating from the 4f<sup>7</sup>→4f<sup>6</sup>5d<sup>1</sup> transition of the Eu<sup>2+</sup>. Thus, it is an efficient phosphor, which can be excited by UV InGaN chips (~400 nm). The emission spectra of Sr<sub>1-x</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:xEu<sup>2+</sup> phosphors with different Eu<sup>2+</sup> doping ratios are shown in Fig. 4. The luminescence intensities of the Sr<sub>1-x</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:xEu<sup>2+</sup> phosphors were enhanced with increasing Eu<sup>2+</sup> doping ratio and reached maximum at x = 5 mole %. When the Eu<sup>2+</sup> doping ratio was above optimum concentration, the phosphors luminescence intensity reduced continually, which can be ascribed to the concentration quenching of Eu<sup>2+</sup>. This quenching process often attributes to energy migration among Eu<sup>2+</sup> ions, because an over-doping concentration, the non-radiative relaxation between the neighboring Eu<sup>2+</sup> ions will enhance. The CIE color-coordinate parameters of Sr<sub>1-x</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:xEu<sup>2+</sup> phosphors are shown in Table 1, which shows that (x, y) coordinates vary from (0.164, 0.030) to (0.163, 0.031). The CIE results also indicate that the hues of the Sr<sub>0.99</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:0.01Eu<sup>2+</sup> phosphors are closer to that of white light.



**Fig. 3.** Excitation ( $\lambda_{em} = 415$  nm) and emission ( $\lambda_{ex} = 350$  nm) spectra of Sr<sub>0.95</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:0.05Eu<sup>2+</sup> phosphor.



**Fig. 4.** (A) Emission ( $\lambda_{ex} = 350$  nm) spectra of Sr<sub>1-x</sub>Al<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:xEu<sup>2+</sup> phosphors. (B) Inset: The dependence of emission intensity on Eu<sup>2+</sup> concentration.

The energy transfer from one activator to another generates the concentration quenching of luminescence. Blasse has pointed out that if the activator is introduced solely on Z ion sites,  $\chi_c$  is the critical concentration, N is the number of Z ions in the unit cell and V is the volume of the unit cell, then there is on the average one activator ion per  $V/\chi_c N$  [16]. The critical transfer distance ( $R_c$ ) is approximately equal to twice the radius of a sphere with this volume:

$$R_c = 2 \left[ \frac{3V}{4\pi\chi_c N} \right]^{1/3} \quad [1]$$

The critical transfer distance of the center Eu<sup>2+</sup> in SrAl<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup> phosphor by taking the appropriate values of V, N, and  $\chi_c$  (498.42 Å<sup>3</sup>, 4, and 0.05, respectively) is 18.51 Å.

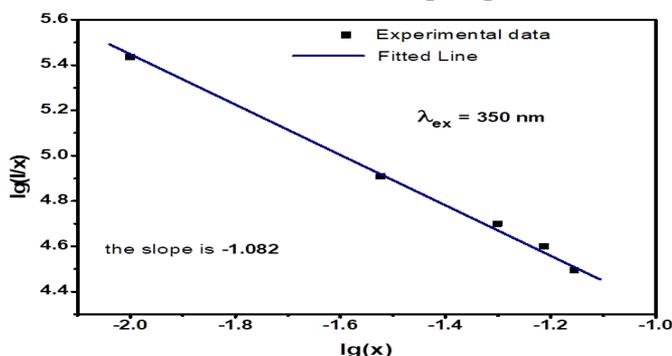
A non-radiative energy transfer from one Eu<sup>2+</sup> ion to another may occur by radiation re-absorption, exchange interaction, or multipole-multipole interaction [17]. The radiation re-absorption comes into effect only when there is a broad overlap of the fluorescence spectra of the sensitizer and activator in view of the emission and excitation spectra of the SrAl<sub>2</sub>B<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup> phosphor, this was unlikely to be occurring in this case. If the Eu<sup>2+</sup> – Eu<sup>2+</sup> distance is larger than 3 Å to 4 Å, the exchange interaction

becomes ineffective, and only a multipolar interaction is important. As the  $R_c$  for  $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{2+}$  phosphor is shorter than  $4\text{\AA}$ , the electric multipolar–multipolar interaction is the dominant mechanism of concentration quenching. When the electric multipolar interaction is involved in the energy transfer, there are several types of interactions, such as dipole–dipole (d–d), dipole–quadrupole (d–q), quadrupole–quadrupole (q–q) interactions, and so on. Thus, there is a need to clarify which type of interaction is involved in the energy transfer. To examine the type of non-radiative energy transfer, Dexter derived a formula of emission intensity (I) per activator ion [18] as follows:

$$I/x = K[1 + \beta(x)^Q/3]^{-1} \quad [2]$$

where  $x$  is the activator concentration;  $Q$  is a constant of multipolar interaction and equals 6, 8, or 10 for dipole–dipole; dipole–quadrupole or quadrupole–quadrupole interaction, respectively; and  $K$  and  $\beta$  are constants under the same excitation condition for the given host crystal.

The curve of  $\lg I/x$  vs.  $\lg x$  in  $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{2+}$  phosphor is shown in Fig. 9. The figure clearly shows that the relation between  $\lg I/x$  and  $\lg x$  is approximately linear and the slope is about  $-1.08$ . The  $Q$  value calculated based on the linear fitting using Eq. (2) is 5.55, which is close to 6. This finding indicates that the dipole–dipole interaction is the major mechanism for the concentration quenching of the fluorescence emission of  $\text{Eu}^{2+}$  ions in  $\text{SrAl}_2\text{B}_2\text{O}_7$  phosphor.



**Fig. 9.** Plot of  $\lg(I/x)$  as function of  $\lg(x)$  in  $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{2+}$ .

#### IV. CONCLUSION

In the present work,  $\text{Eu}^{2+}$  co-doped  $\text{SrAl}_2\text{B}_2\text{O}_7$  phosphors have been prepared by solution combustion technique. The  $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{2+}$  phosphor show blue-white emissions due to  $\text{Eu}^{2+}$  d→f transitions. The PL intensity increased and an apparent red shift in emission spectrum from 415 nm ( $x = 0.05$  mole) to 461 nm ( $x = 0.04$  mole) was observed. The optimum doping concentration of  $\text{Eu}^{2+}$  is 5 mol%, and the concentration quenching mechanism was determined to be electric dipole-dipole interaction. The  $\text{SrAl}_2\text{B}_2\text{O}_7:\text{Eu}^{2+}$  phosphors may be potential blue-emitting components for UV excited w-LEDs.

#### V. ACKNOWLEDGEMENT

Authors are thankful to the Chairman of FIST-DST project SGB Amravati University Amravati, for providing XRD facility to this work.

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