

# Steady State and Time Resolved Spectroscopic Study of $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ phosphor for Light Emitting Diode Applications

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**Abstract**—Red light emitting  $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$  phosphors were synthesized by a customized sol-gel route. The as-synthesized samples were characterized by X-ray diffraction (XRD) and Fourier Transformed Infrared Spectroscopy (FTIR) to confirm the phase purity and the presence of aluminates groups in the phosphors, respectively. The steady state photoluminescence (PL) characteristics of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$  phosphors were investigated by PL excitation and emission spectra. The synthesized samples show red emission peaking at 616 nm upon 254 nm excitation. The colour quality of the emitted red light was also verified by CIE chromaticity diagram. Time resolved PL spectra showed the lifetime of the radiative emission in the microsecond scale. The present investigation recommends that this phosphor could be used as advanced luminescent materials for light emitting diode applications.

## 1. INTRODUCTION

White light emitting diodes (LEDs) have been gained tremendous interest as next generation solid state lighting devices due to their long life time, high luminous efficiency and environment friendly characteristics[1-2]. Rare earth doped phosphors are the essential part of WLED due to its characteristics intra 4f shell transition which is independent of both host material and temperature. Among the various phosphor materials, rare earth doped  $\text{SrAl}_2\text{O}_4$  (SRA) has got raring attention as luminescence materials in the literature due to their various practical applications such as traffic signs, emergency signs, advertising and safety cloth etc [2-3]. Several methods have already been employed to synthesize the rare earth doped  $\text{SrAl}_2\text{O}_4$  phosphor. Santos Jr et al. synthesized the  $\text{Eu}^{3+}$  doped  $\text{SrAl}_2\text{O}_4$  via sol-gel methodology and studied the optical property by computational and experimental method [4]. The  $\text{Eu}^{2+}$  doped  $\text{SrAl}_2\text{O}_4$  phosphors showed the good electroluminescence properties and the phosphors were synthesized by sol-gel process [5]. Yang et al. [6] prepared the  $\text{Cu}^{2+}$  co doped  $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$  phosphor by solid state reaction in a weakly oxidizing atmosphere. Qiang et al. [7] also prepared  $\text{Li}^+$  co-doped  $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$  phosphor powders through solid state reaction.  $\text{Li}^+$  co-doped

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  long after glow phosphors were synthesized by combustion method [8].

In the present work we have synthesized the  $\text{Eu}^{3+}$  doped  $\text{SrAl}_2\text{O}_4$  phosphor through customized Sol-gel route which can be easily scale up in a large quantity. The colour quality of the emitted light was also verified by CIE chromaticity diagram. The time resolved spectroscopy characterizations was also carried out and it was found that the lifetime of the radiative emission was in the microsecond range.

## 2. EXPERIMENTAL PROCESS

**Synthesis of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$  phosphor:**  $\text{Eu}^{3+}$  doped  $\text{SrAl}_2\text{O}_4$  phosphor powders were synthesized by citrate-nitrate sol-gel route. Analytical reagent grade  $\text{Sr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck, 99.9%),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck, 99.9%),  $\text{Eu}(\text{NO}_3)_3$  (prepared by dissolving  $\text{Eu}_2\text{O}_3$ , Sigma Aldrich 99.99% in  $\text{HNO}_3$  solution), citric acid (Merck, 99.9%) and ethylene-di-amine (Merck, 99.9%) were used as raw materials. For  $\text{Eu}_x:\text{Sr}_{(1-x)}\text{Al}_2\text{O}_4$  samples, the concentration of Eu were varied from 0 to 2% ( $x=0, 0.01, 0.02$ ). In a typical reaction stoichiometric amounts of strontium nitrate, aluminium nitrate, europium nitrate were dissolved in 40 ml deionized water (DI) and stirred for 30 minutes. Then citric acid aqueous solution was added in the precursor solution and the solution was stirred in a magnetic stirrer for another 30 minutes, resulting in a homogeneous transparent solution. Ethylenediamine was then added into the solution and the solution pH was adjusted to 5. Afterwards the solution mixtures were heated at  $80^\circ\text{C}$  to form highly viscous colloidal gel and the dried gel was heated at  $480^\circ\text{C}$  to remove the organic compounds. Finally, the obtained powders were ground in a mortar and heat treated at  $1000^\circ\text{C}$  for 4 h in a box furnace to obtain ultrafine pure and  $\text{Eu}^{3+}$  doped strontium aluminate powders.

### Characterizations

The as-prepared phosphors were characterized through X-ray diffraction (XRD) for purity and phase identification, using a Bruker D8 ADVANCE ECOX-ray powder diffractometer with monochromatic CuK $\alpha$  radiation, ( $\lambda = 1.5404 \text{ \AA}$ ). The FTIR spectra were taken in the mid IR region, (i.e. 400–4000 cm<sup>-1</sup>) by using a Shimadzu IR Affinity-1 spectrometer. The steady state photoluminescence spectra were taken on Shimadzu RF 5301 spectrofluorometer whereas the time-resolved photoluminescence was measured by using an Edinburgh luminescence spectrometer (Model No. FLSP-980) equipped with microsecond xenon flash lamp as the source of excitation.

### 3. RESULT AND DISCUSSION

The X-ray diffraction pattern of pure SrAl<sub>2</sub>O<sub>4</sub> and Eu<sup>3+</sup> doped SrAl<sub>2</sub>O<sub>4</sub> are shown in the Fig. 1. All the diffraction peaks can be readily indexed with the standard JCPDS card no. 74-0794 which clearly indicates the pure phase formation of monoclinic SrAl<sub>2</sub>O<sub>4</sub> crystals [9].

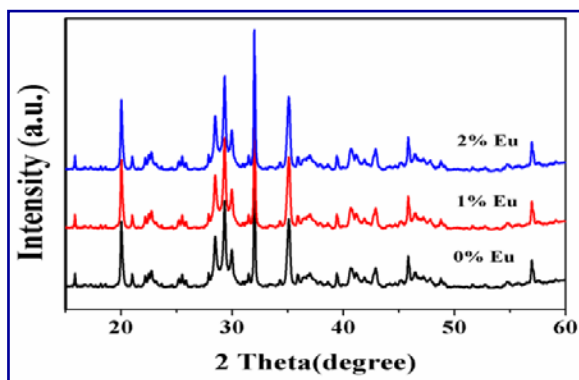


Fig. 1: XRD pattern of pure and Eu<sup>3+</sup> doped SrAl<sub>2</sub>O<sub>4</sub> phosphors.

Furthermore FTIR analysis was done to confirm the pure phase formation of SrAl<sub>2</sub>O<sub>4</sub> and Eu<sup>3+</sup> doped SrAl<sub>2</sub>O<sub>4</sub> phosphor. The peaks at 454 and 421 cm<sup>-1</sup> is found due to the symmetric bonding of O–Al–O group.

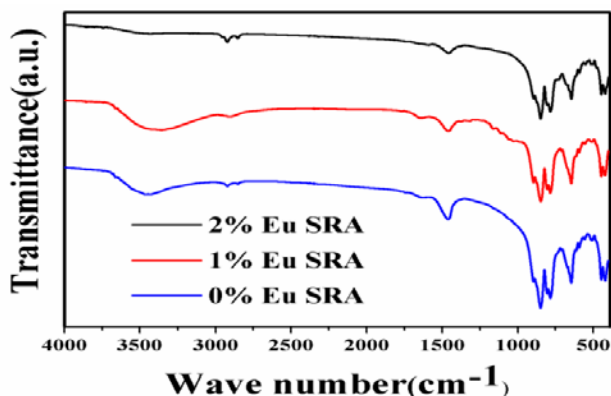


Fig. 2: FTIR spectra of pure, 1% Eu<sup>3+</sup> and 2% Eu<sup>3+</sup> doped SrAl<sub>2</sub>O<sub>4</sub> phosphor

The antisymmetric stretching bands are noticed in the range of 590–640 cm<sup>-1</sup> which can be attributed to the Sr–O vibrations. The bands positioned at 785 and 849 cm<sup>-1</sup> is attributed to the aluminate groups. The broad peak in the range of 3200–3700 cm<sup>-1</sup> is observed due to the vibration of OH groups [10].

The photoluminescence (PL) characteristics of the 1% Eu<sup>3+</sup>, 2% Eu<sup>3+</sup> doped SrAl<sub>2</sub>O<sub>4</sub> phosphors were investigated by PL excitation and emission spectra. In this experiment same amount of samples were taken each time during measurement. Fig. 3 shows the PL excitation spectra of 1% Eu<sup>3+</sup> doped SRA and 2% Eu<sup>3+</sup> doped SRA phosphors which were taken by monitoring the emission of Eu<sup>3+</sup> at 616 nm. The observed PL excitation spectra can be classified into two categories. Firstly the broad peak at 254 is attributed to charge transfer band (CTB) causing due to the transfer of electrons from fully filled 2p-orbitals of O<sup>2-</sup> to partially filled 4f levels of Eu<sup>3+</sup> [1].

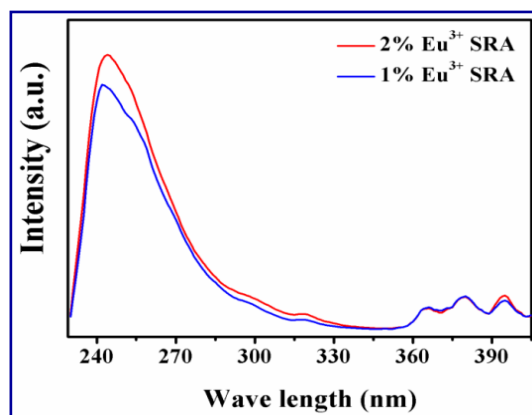


Fig. 3: Excitation spectra of 1% Eu<sup>3+</sup> doped and 2% Eu<sup>3+</sup> doped SrAl<sub>2</sub>O<sub>4</sub> phosphors monitored at 616 nm emission.

Secondly, in the longer wavelength region between 350 to 480 nm the peaks are found due to intra-configuration f-f transitions of Eu<sup>3+</sup> ions in the host lattice. These peaks are associated with Eu<sup>3+</sup> ground state to the higher levels in the 4f<sup>6</sup> configuration.

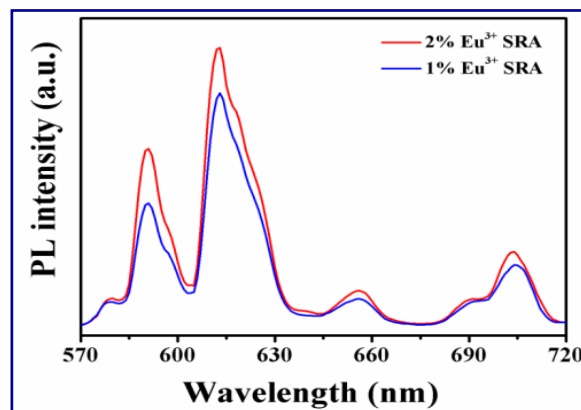


Fig. 4: PL emission spectra of 1% Eu<sup>3+</sup> doped and 2% Eu<sup>3+</sup> doped SrAl<sub>2</sub>O<sub>4</sub> phosphors recorded at 254 nm excitation

The observed peaks can be assigned as  ${}^7F_0 \rightarrow {}^5D_4$  (364nm),  ${}^7F_0 \rightarrow {}^5L_7$  (382 nm),  ${}^7F_0 \rightarrow {}^5L_6$  (394 nm) transitions respectively. The room temperature PL emission spectrum, excited by 254 nm, is shown in the Fig. 4. The four main peaks observed at 593, 616, 652 and 700 nm are assigned due to the  ${}^5D_0 \rightarrow {}^7F_{j(1-4)}$  transitions of  $\text{Eu}^{3+}$  ions respectively. It is well known that  ${}^5D_0 \rightarrow {}^7F_1$  lines originate from magnetic dipole transition, while the  ${}^5D_0 \rightarrow {}^7F_2$  lines originate from electric dipole transition [1].

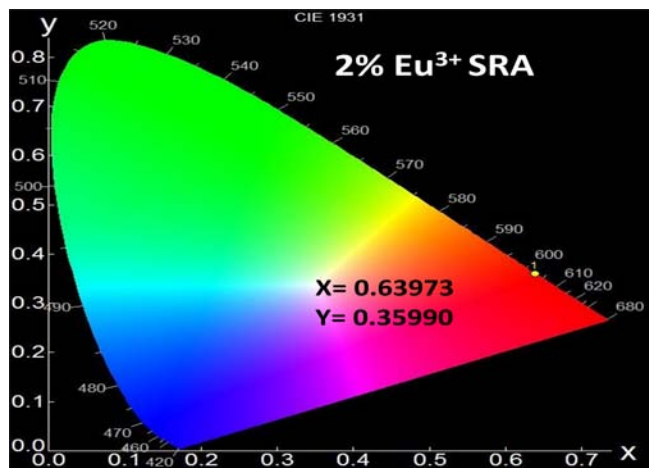


Fig. 5: Color co-ordinate of the 2%  $\text{Eu}^{3+}$  doped SRA phosphor

The CIE chromaticity coordinate (shown in Fig. 5) calculated from the PL spectrum is ( $x=0.63973$ ,  $y=0.35990$ ) which means that  $\text{Eu}^{3+}$  doped  $\text{SrAl}_2\text{O}_4$  phosphor could be used as a red light emitting material in solid state lighting applications.

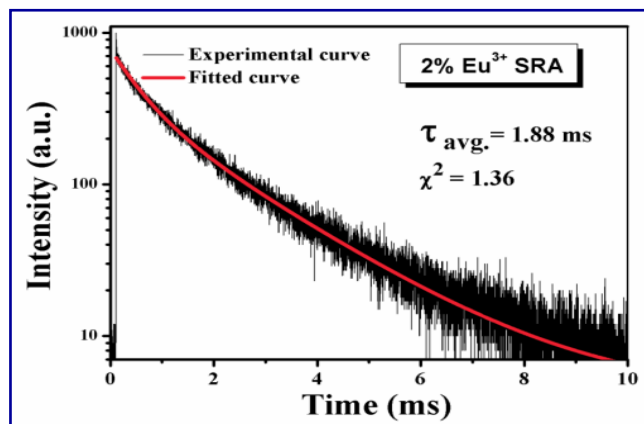


Fig. 6: Photoluminescence decay curve of 2%  $\text{Eu}^{3+}$  doped SRA phosphor

The time resolved spectroscopic technique was employed to determine the lifetime of the synthesized phosphors by keeping the emission at 616 nm. The decay curve was well fitted into a double-exponential decay equation as  $I(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$ . Where parameters  $A_1$  and  $A_2$  are the fitting constants and  $\tau_1$  and  $\tau_2$  are the decay

components. The average life time ( $\tau_{av}$ ) for double exponential decay is calculated by the following equation.

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

The average lifetime ( $\tau_{av}$ ) of 2%  $\text{Eu}^{3+}$  doped SRA is found to be 1.88 ms.

#### 4. CONCLUSION

We have successfully synthesized the pure and doped  $\text{SrAl}_2\text{O}_4$  phosphors by customized sol gel route. The samples were well characterized by XRD and FTIR. The resulting phosphors show the red emission at 616 nm upon 254 nm excitation. The steady state and time decay photoluminescence experiment clearly confirms that the synthesized phosphors could be used as highly luminescence materials for light emitting diode applications.

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