



Characterization, luminescence and EPR investigations of Eu^{2+} activated strontium aluminate phosphor

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ABSTRACT

Strong blue-green light emitting Eu doped SrAl_2O_4 phosphor was synthesized by a low-temperature initiated, self-propagating and gas producing combustion process in a very short time (<5 min). The prepared powder was characterized by X-ray diffraction, Fourier-transform infrared spectrometry and scanning electron microscopy. The excitation spectrum shows a peak at 397 nm. Upon excitation at 397 nm, the emission spectrum exhibits a well defined broad band with maximum at 493 nm corresponding to $4f^65d \rightarrow 4f^7$ transition. Electron paramagnetic resonance (EPR) measurements at X-band showed low field signals due to Eu^{2+} ions in $\text{SrAl}_2\text{O}_4:\text{Eu}$.

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1. Introduction

Rare earth activated inorganic phosphors are widely used in a variety of applications, such as lamp industry, color display, radiation dosimetry and X-ray imaging. It is also known that the emission of Eu^{2+} ions varies from blue to red depending on the host lattice due to crystal-field effects [1]. The luminescent properties of Eu^{2+} -doped strontium aluminate phosphors have been studied extensively because they show a long anomalous phosphorescence and/or a short-time decay depending on the conditions of preparation used [2,3]. Polycrystalline $\text{SrAl}_{12}\text{O}_{19}:\text{Mn}$ is known as a green-emitting phosphor for plasma display panels [4] and Pr^{3+} , Nd^{3+} doped $\text{SrAl}_{12}\text{O}_{19}$ crystals show good laser properties [5]. Recently, luminescence of Eu^{2+} in some strontium aluminate hosts (e.g., SrAl_2O_4 , $\text{SrAl}_2\text{B}_2\text{O}_7$, SrAl_4O_7 , $\text{SrAl}_{12}\text{O}_{19}$, $\text{Sr}_3\text{Al}_2\text{O}_6$, and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$) co-doped with other rare-earth ions, have attracted much attention due to their special long afterglow phenomenon [6–8]. The aluminate of interest in the present study is SrAl_2O_4 . In the past, it has been reported that, to obtain strontium monoaluminate

(SrAl_2O_4) below 1200 °C is quite difficult and there is always possibility of other phases such as SrAl_4O_7 , $\text{SrAl}_{12}\text{O}_{19}$, $\text{Sr}_3\text{Al}_2\text{O}_6$, and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ [9,10].

The alkaline earth aluminates have been studied for more than three decades [11,12] for use as luminescent materials or in cements. These aluminates have been prepared traditionally by solid state reactions [13,14], which, in general, demand high annealing temperatures and long times of firing, ca. 1300–1600 °C and 5–10 h, respectively. In addition, products can be strongly sintered and the doping luminescent ions may not be homogeneously dispersed. Alternatively low-temperature methods, e.g. sol-gel [15–17], pechini [18], hydrothermal [19] and microwave [20] methods can be used instead of the direct solid state reaction due to economical interest and to enhance the properties of materials. However, combustion synthesis studies that compare the different methods are rare. Therefore, we have synthesized Eu doped SrAl_2O_4 material by a low-temperature initiated combustion process. The products were characterized using techniques such as powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectra, photoluminescence (PL) and electron paramagnetic resonance (EPR).

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2. Experimental

2.1. Sample preparation

Stoichiometric compositions of the metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing (O) and reducing (F) valencies of the components, which serve as the numerical coefficients for the stoichiometric balance so that the equivalence ratio ϕ_e , is unity (i.e. $O/F = 1$) and the energy released by the combustion is at a maximum [21].

Analytical grade corresponding metal nitrates (oxidizer), urea (fuel) and europium oxide (activator) were used as the starting materials. The above materials were mixed according to the chemical formula $Sr_{1-x}Eu_xAl_2O_4$, where $x = 0.01$. For this, we had taken 5 g $Al(NO_3)_3 \cdot 9H_2O$, 1.3962 g $Sr(NO_3)_2$, 2.6723 g CH_4N_2O and 0.0117 g Eu_2O_3 . These were mixed in an agate mortar and the resulting paste was transferred into a china crucible. The crucible containing the paste was introduced into a muffle furnace maintained at 500 °C. Initially, the paste melts and undergoes dehydration followed by decomposition with the evolution of large amounts of gases (oxides of nitrogen). The mixture then froths and swells forming foam, which ruptures with a flame and glows to incandescence. During incandescence the foam further swells to the capacity of the container. The entire combustion process is over in less than 5 min. The dish was then taken out and the foamy product is crushed into fine white powder and was used for characterization without any further heat-treatment.

2.2. Instruments

Powder samples were analyzed for XRD using a X'Pert PRO-MRD, made in Netherlands. It was used with Cu $K\alpha$ radiation at 40 kV and 40 mA and a scan rate of 0.02°/s in the 2θ range from 10° to 70°. The data were collected using the X'Pert Data Collector data acquisition software and analyzed by means of the X'Pert HighScore data analysis package. The morphology of the powders was obtained using a Hitachi S-4300 scanning electron microscope (SEM). FT-IR spectra were recorded using a Perkin-Elmer Rx1 instrument in the range 4000–400 cm^{-1} . Room temperature photoluminescence (PL) of the prepared phosphors was studied using a Hitachi F-4500 fluorescence spectrophotometer. Alternately, the PL and PL decay time measurements were carried out on an Edinburgh nF900 unit equipped with a Picoquant pulsed diode laser (PDL) as the excitation source. The laser provides a constant excitation wavelength of 375 nm. The frequency of the PDL during the decay time measurements was kept at 20 kHz with 5 V ampli-

tude. EPR measurements were carried out using a Bruker EMX 10/12 X-band ESR spectrometer.

3. Results and discussion

The formation of the crystalline phase of as-prepared products was confirmed by X-ray diffraction. Fig. 1 shows the X-ray patterns of $SrAl_2O_4:Eu$ powder. The X-ray pattern of combustion synthesized sample at furnace temperature 500 °C indicated a dominant phase of the standard $SrAl_2O_4$ (JCPDS, 74-0794). Beside of $SrAl_2O_4$ peaks there are some other peaks observed which might be corresponding to $SrO(Al_2O_3)_2$ [22,23] and $Sr_3Al_2O_6$ [24] phases. It has been reported in the literature that phase-pure $SrAl_2O_4$ could be achieved using conventional solid state process, the required temperature for synthesizing $SrAl_2O_4$ being 1400–1600 °C [25,26].

The FT-IR spectrum of $SrAl_2O_4:Eu$ powder is shown in Fig. 2. This spectrum exhibits broad band near 3433 cm^{-1} due to the OH^- stretching vibrations of free and hydrogen-bonded hydroxyl groups. However a weak absorption band at 1632 cm^{-1} appears from deformative vibration of water molecules, which is probably due to water absorption during the compaction of the powder specimens with KBr [27]. The appearance of a very weak band at 1382 cm^{-1} is due to the symmetric stretching vibrations of the N–O group, which might have resulted from the nitrate of the

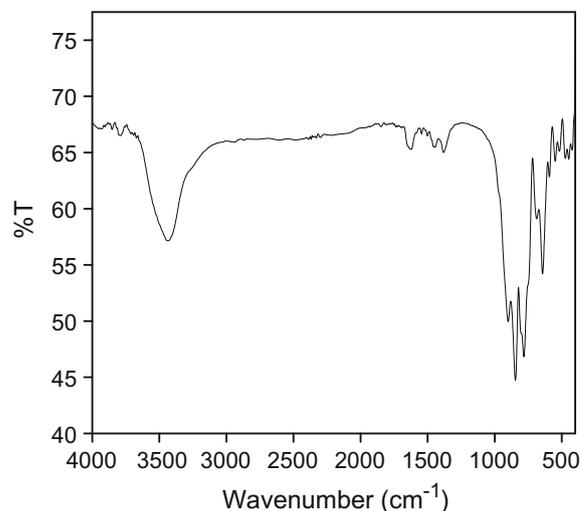


Fig. 2. FT-IR spectrum of $SrAl_2O_4:Eu$ phosphor at room temperature.

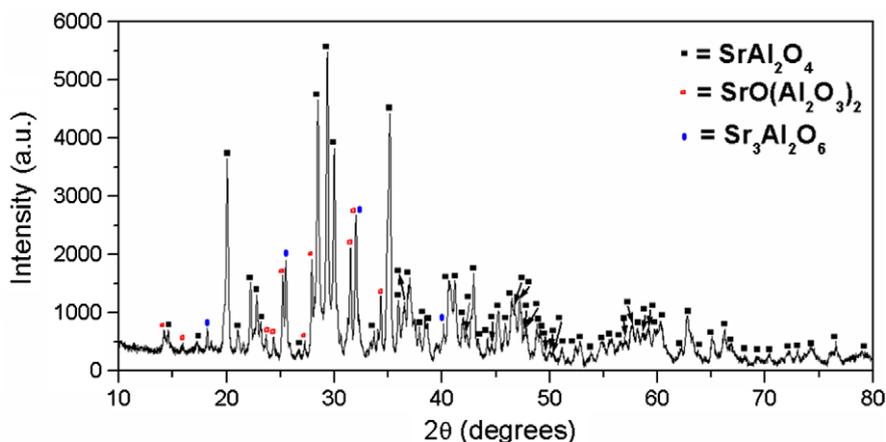


Fig. 1. XRD pattern of as-prepared $SrAl_2O_4:Eu$ phosphor.

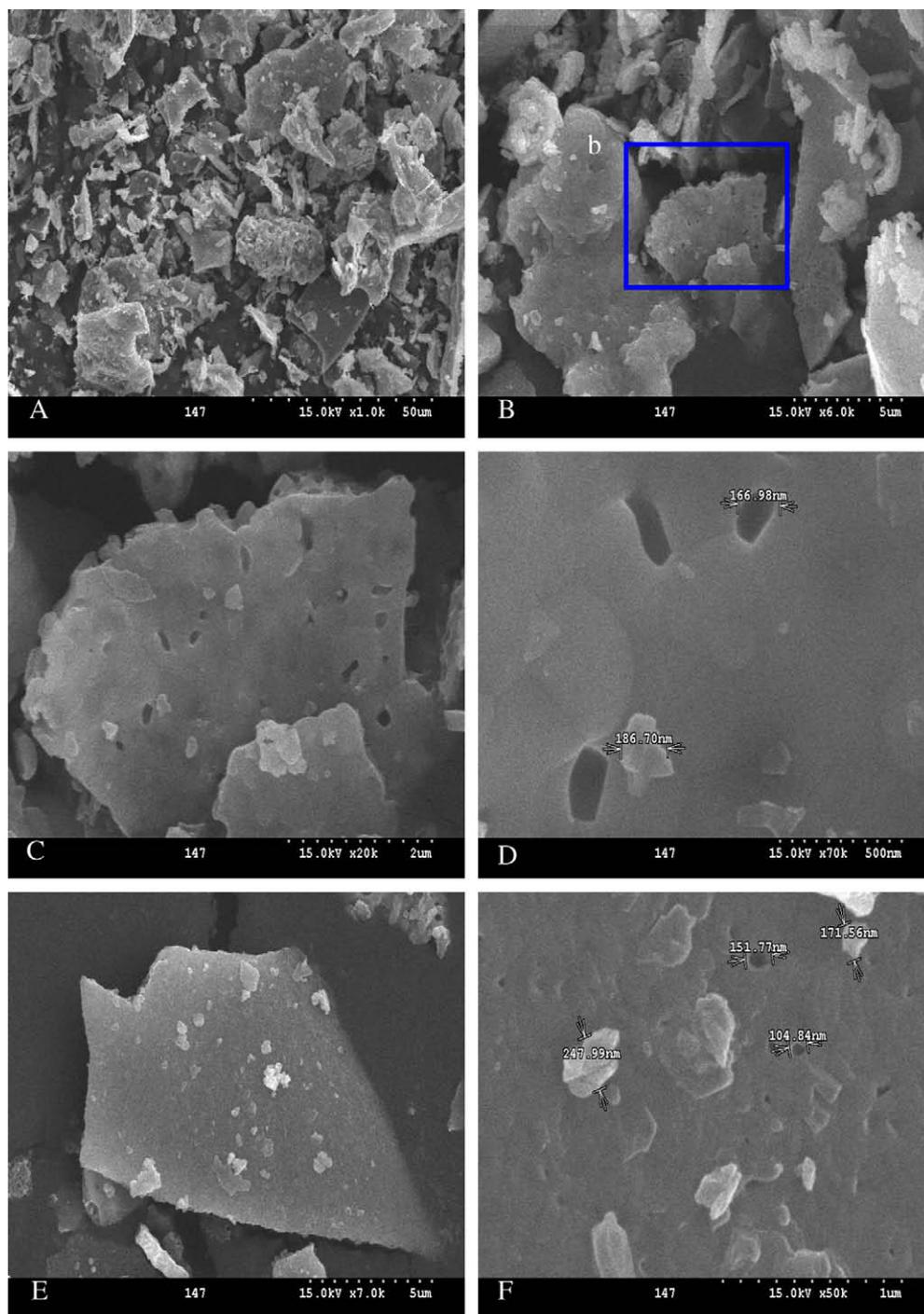


Fig. 3. SEM microphotographs of $\text{SrAl}_2\text{O}_4:\text{Eu}$.

starting material [28]. The metal–oxygen stretching frequencies in the range $400\text{--}1000\text{ cm}^{-1}$ are associated with the vibrations of Al–O, Sr–O and Sr–O–Al bonds [29]. The sample showed a strong peak at 846 cm^{-1} , assigned to the formation of SrAl_2O_4 [30].

Fig. 3 shows the SEM micrographs of $\text{SrAl}_2\text{O}_4:\text{Eu}$ at different magnifications. It can be seen from SEM micrograph at low magnification (Fig. 3(A)) that, shape and size of the crystals are dissimilar. Most of them are faceted crystals with varying sizes. This dissimilarity is caused due to the non-uniform distribution of temperature and mass flow during combustion. It can be observed that some of crystals have voids and pores while some do not (Fig. 3(B)). There is a crystal with pore (zone b) in Fig. 3(B). The pore morphology of

magnified zone b is shown in Fig. 3(C) and (D). It can be observed from Fig. 3(D), that the pore diameter is about 150 nm. These voids and pores might have been formed by the gases evolved during combustion. The morphology of magnified Fig. 3(E) is shown in Fig. 3(F). It can be seen from high magnification image that there are several small particles within a crystal and the surface also has some pores. The small particles are in the range of 150–250 nm. The pore diameter and pore size are comparable. The presence of several nanoparticles suggests that combustion synthesis has potential to produce nanoparticles.

The incorporation and stabilization of divalent Eu ions in SrAl_2O_4 sample were confirmed by the luminescence investigations.

It is well known that the emission of Eu^{2+} can be adjusted with the appropriate hosts, which can result in emission from UV to red light. Eu^{2+} emission in different host structures varies usually, leading to different emission peaks. For example, the emission peak of Eu^{2+} is at 463 nm in $\text{Sr}_{1.5}\text{Mg}_6\text{Al}_{55}\text{O}_{94}$ with magneto-plumbite structure [31], while it is observed at 490 nm in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ with orthorhombic structure structure [32], in $\text{Sr}_2\text{Al}_6\text{O}_{11}$ with orthorhombic structure (Pnmm), it is observed at 460 nm [32]. The photoluminescence spectra of the samples are shown in Fig. 4. The emission spectrum, corresponding to excitation at 397 nm, is depicted in Fig. 4a with one broad intense peak at 493 nm. The excitation spectrum corresponding to this peak is shown in Fig. 4b. The broad emission and excitation peaks suggest that they are associated with $4f \leftrightarrow 5d$ transitions of Eu^{2+} ions in the prepared samples. Photoluminescence on $\text{SrAl}_2\text{O}_4:\text{Eu}$ powder phosphor was also recorded with 375 nm laser excitation and is shown in Fig. 5. It also confirms the emission peak at 493 nm due to the transition of Eu^{2+} from the excited state of $4f^65d^1$ configuration to the ground state $4f^7$.

To probe further into the luminescence properties of the dopant ion, fluorescence decay time studies were done on the sample. The

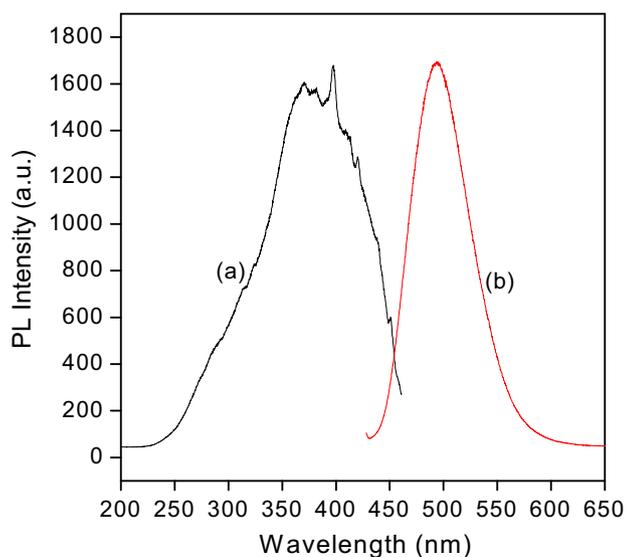


Fig. 4. Photoluminescence spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}$: (a) excitation spectrum ($\lambda_{\text{em}} = 493$ nm) and (b) emission spectrum ($\lambda_{\text{ex}} = 397$ nm).

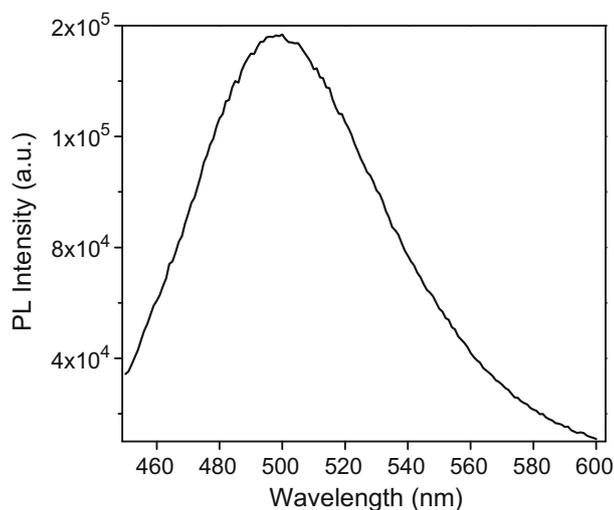


Fig. 5. Emission spectrum of $\text{SrAl}_2\text{O}_4:\text{Eu}$ (laser $\lambda_{\text{ex}} = 375$ nm).

inter electronic rearrangement taking place in the divalent europium ion is both laporte and spin allowed (being an f–d transition) and is expected to be very fast (of the order of nanosecond). In fact the divalent europium is reported to have decay time values in the range few hundreds of nanosecond to few microsecond. The lifetime for Eu^{2+} emission in SrAl_2O_4 single crystal has been reported with a decay time of 0.66 μs at room temperature [33]. Fig. 6 shows the luminescence decay curve for europium doped sample with $\lambda_{\text{ex}} = 375$ nm and $\lambda_{\text{em}} = 493$ nm. The lifetime data could be fitted into a bi-exponential decay fit via the following equation:

$$I(t) = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2),$$

where A and B_1 are scalar quantities, t is the time and τ_i are the decay time values. A best fit with $\chi^2 \sim 1.4$ was obtained for decay time values of 100 and 400 ns with relative percentages of 20 and 80, respectively. Undoubtedly the major fraction was due to Eu in $2+$ state, but the occurrence of the minor fraction with a life time of 100 ns was unexplained.

In order to unambiguously identify the two decay time components observed in the present case, a time resolved emission spectrometric (TRES) study was done on the sample. TRES study provides a powerful tool for identifying multiple species present in a system. By the virtue of triple resolution (excitation, emission and time resolution) systems having similar excitation and emission properties can also be differentiated. However, in the present case we could not see the presence of multiple species in the TRES spectrum. So the occurrence of a bi-exponential life time data is explained on the basis of the absence or presence of the metal ion in the vicinity of a number of defect centers. The presence of defect centers, in the vicinity of a luminescent ion, provides non-radiative path for the excited state population to decay and thus reduces the PL decay time.

The emission from SrAl_2O_4 was observed band at 493 nm, a shorter wavelength than the 512 nm observed by Ravichandran et al. [20], 518 nm observed by Song et al. [34] and 521 nm, observed by Palilla et al. [35]. Herein, they have also reported that the emission of Eu^{2+} in SrAl_2O_4 lattice, SrAl_2O_4 with stuffed tridymite structure to have two different low symmetric sites for Sr^{2+} ions with 9-fold co-ordination. In SrAl_2O_4 , Eu^{2+} could easily substitute for Sr^{2+} ions with comparable ionic radius and same charge. Our studies showed the emission peak position at 493 nm. This difference can be attributed to (i) our sample prepared by different synthesis method and (ii) the emission spectra of mixed phases,

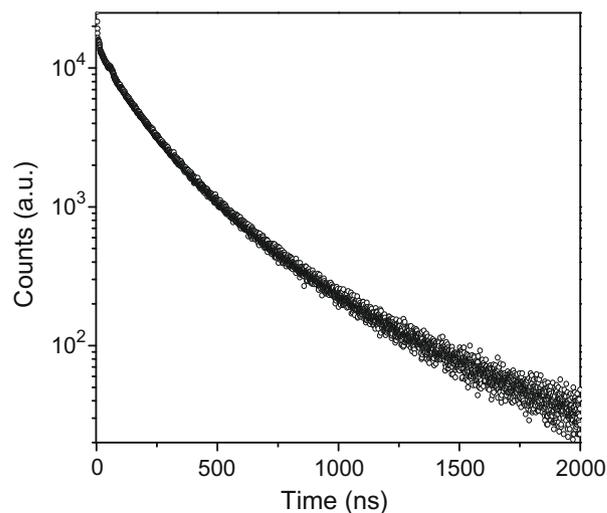


Fig. 6. Decay curve of $\text{SrAl}_2\text{O}_4:\text{Eu}$ under Picoquant pulsed diode laser (PDL) as the excitation source.

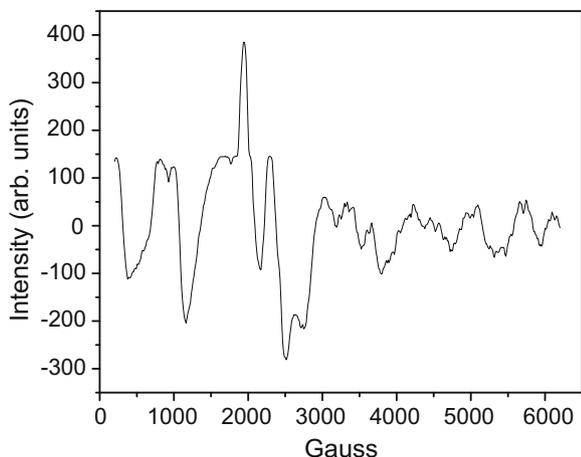


Fig. 7. EPR spectrum of SrAl₂O₄:Eu phosphor at room temperature.

which indicated that the existence of the impure phase in SrAl₂O₄:Eu greatly affected its luminescent property. Our sample does not have similar excitation and emission spectra reported by the previous workers. However, our sample shows strong photoluminescence, which may be due to the change in crystal field of Eu²⁺ ions in the mixed phase, which can lead to change in excitation and emission spectra. Moreover, the results indicate that the phosphor can be readily prepared by the combustion synthesis.

EPR spectrum of europium doped SrAl₂O₄, is shown in Fig. 7. The EPR signals consisted of a fine structure spreading over a wide field region. Eu²⁺ with 4f⁷ configuration has ⁸S_{7/2} as its electronic ground state. Unlike other rare earths, Eu²⁺ ion has long spin–lattice relaxation times so their EPR spectrum could be clearly identified. EPR of Eu²⁺ in the lower symmetries is known to give fine structure consisting of 7 lines resulting from the splitting $J = 7/2$ state into $2j + 1$ levels. The separations between these lines depend on the symmetry around Eu ion in the host. For cubic symmetry, all these lines coincide and only a single line around $g = 2$ will be observed. However, for symmetries other than cubic, fine structure lines with large zero field splittings, are prominently seen in the X-band EPR spectra [36]. Each of the fine structure is expected to show further splitting into 6-line structure (hfs) due to interaction of unpaired electron with Eu²⁺ ($I = 5/2$) nucleus. However, under the experimental conditions used in the present study, hfs could not be observed. In the present study, the EPR signals observed in the range 0–7 kG are due to large zero field splitting of Eu²⁺ ground state, which results from the mixing to the ground state with wave functions of higher energy states. The result of large zero field splitting of Eu²⁺ ground state, also reported earlier by Nakamura et al. [37]. The PL emission in the blue region had already indicated presence of Eu as Eu²⁺ ions in these phosphors. Their presence is further confirmed by EPR studies.

4. Conclusions

Our experiments reveal that in the prepared SrAl₂O₄ phosphor, Eu is stabilized in the divalent oxidation state. This phosphor could be prepared within several minutes, using the present combustion

method, leading to reduction in fast synthesis of aluminates. The SEM images showed that shape and size of crystalline particles were not uniform and there are several small particles present within grains. The vibrational stretching frequencies corresponding to the composites were confirmed by FT-IR spectroscopy. The results further suggest that Eu doped SrAl₂O₄ phosphor may be useful as blue-green-emitting phosphor. EPR spectra of SrAl₂O₄:Eu indicated the presence of Eu²⁺ at low symmetric lattice sites.

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