

Preparation, luminescence and defect studies of Eu^{2+} -activated strontium hexa-aluminate phosphor prepared via combustion method

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Abstract

Preparation of Eu^{2+} ions activated strontium hexa-aluminate phosphor using the combustion method is described. An efficient phosphor can be prepared by this method at reaction temperatures as low as 500 °C in a few minutes. Powder X-ray diffraction (XRD), transmission electron microscopy, scanning electron microscope analysis were used to characterize the as prepared product and the optical properties were studied by photoluminescence (PL) spectra. Thermally stimulated luminescence studies also have been carried out on $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}^{2+}$ phosphor. The TSL glow curve is broad and indicates two dominant peaks at 206 and 345 °C. Defect centres formed in irradiated phosphor have been studied using the technique of electron spin resonance. One of the centres is characterized by an isotropic g -value of 2.0055 and is assigned to a F^+ centre. The two annealing stages of F^+ centre in the region 125–230 and 340–390 °C appear to correlate with the release of carriers resulting in TSL peaks at 206 and 345 °C, respectively.

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1. Introduction

Phosphors containing rare-earth ions have received increasing attention in recent years due to their technological importance [1]. In particular, the luminescent properties of $\text{Eu}(\text{II})$ -doped strontium aluminate phosphors have been studied extensively because they show an anomalous long phosphorescence and a short-time decay depending on the conditions of preparation [2,3]. $\text{SrAl}_{12}\text{O}_{19}$ has the magnetoplumbite structure and belongs to the D_{6h}^4 space group [4]. Strontium aluminate ($\text{SrAl}_{12}\text{O}_{19}$) is a convenient host crystal for rare-earth and transition metal dopants. Polycrystalline $\text{SrAl}_{12}\text{O}_{19}:\text{Mn}$ is known as a green-emitting phosphor for plasma display panels [5], and Pr- or Nd-doped $\text{SrAl}_{12}\text{O}_{19}$ crystals show good laser properties [6]. Recently, luminescence of Eu^{2+} in a few strontium aluminates 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 [7–9].

The emission of Eu^{2+} ions varies from blue to red depending on the host lattice due to crystal-field effects [10]. In view of the general interest in the green and yellow emitting Eu^{2+} -activated compositions in recent years, calcium and strontium silicates and phosphates have been investigated in detail [11,12]. Recently, thermally stimulated luminescence (TSL) and electron paramagnetic resonance (EPR) studies on alkaline earth sulphates and mixed alkaline earth sulphates doped with actinides and lanthanides phosphors have shown that the defect centres are intimately related to the process of TSL in these phosphors. The release of holes/electrons from defect centres at the characteristic trap site initiates the luminescence process in these materials [13–17]. Eu^{2+} -activated phosphors $M\text{Al}_2\text{O}_4$ and $M\text{Al}_{12}\text{O}_{19}$ ($M = \text{Ba}, \text{Sr}, \text{Ca}, \text{Mg}$) are well known since the studies by Blasse and Brill [18] in the 1960s. Their investigations lead to the conclusion that

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these compounds were adequate phosphorescent materials because of their high quantum efficiency in the visible region.

In the present study, we have prepared $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ phosphor via low temperature initiated combustion process, and have investigated the phosphor using X-ray diffraction (XRD), transmission electron microscopy, scanning electron microscope, fluorescence, TSL and ESR techniques in order to understand the role of europium ions in fluorescence and TSL properties. In this paper, the evidence for the co-existence of Eu^{2+} and Eu^{3+} in the samples is presented. In addition, the gamma radiation induced defect centres formed in this lattice were identified and their role in the TSL glow peaks was examined.

2. Experiment

2.1. Sample preparation

Stoichiometric composition of the redox mixture for a solution combustion were calculated using the total oxidizing (O) and reduction (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. $\text{O}/\text{F} = 1$) and the energy released by the combustion is at a maximum [19].

Analytical grade aluminium nitrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], strontium nitrate [$\text{Sr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], europium oxide (Eu_2O_3) and urea ($\text{CH}_4\text{N}_2\text{O}$) were used as the starting materials. The above four materials were mixed according to the chemical formula $\text{Sr}_{0.92}\text{Eu}_{0.08}\text{Al}_{12}\text{O}_{19}$. The resulting paste was transferred into a china crucible and 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 and ammonia). The mixture then froths and swells forming a 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 was complete in less than 5 min. The synthesis of the phosphor by the combustion process is illustrated in the flowchart in Fig. 1.

2.2. Instruments

Powder XRD pattern was recorded on a Philips X'pert X-ray diffractometer with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$) and nickel filter at a scanning step of 0.03° , continue time 10 s, in the 2θ range from 10° to 80° . Scanning electron micrographs (SEM) were taken on a JEOL JSM-5610LV scanning electron microscopy. TEM images were recorded on a JEOL-JEM 200CX transmission electron microscope. The sample used for TEM observations were prepared by dispersing products in ethanol followed by ultrasonic vibration for 30 min, then placing a drop of the dispersion onto a copper

grid coated with a layer of amorphous carbon. Photoluminescence (PL) measurements were carried out on an AMINCO-Bowman Series 2 luminescence spectrometer at room temperature. TSL glow curves were recorded with the usual setup consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (931B), dc amplifier and a millivolt recorder. ESR measurements were carried out on a Varian E-112 E-line Century series X-band ESR spectrometer. TCNE ($g = 2.00277$) was used as a standard for g -factor measurements. Step heat treatments were performed to follow the decay and evolution of the defect centres. These were carried out *in situ* in the ESR cavity using the Varian variable temperature accessory.

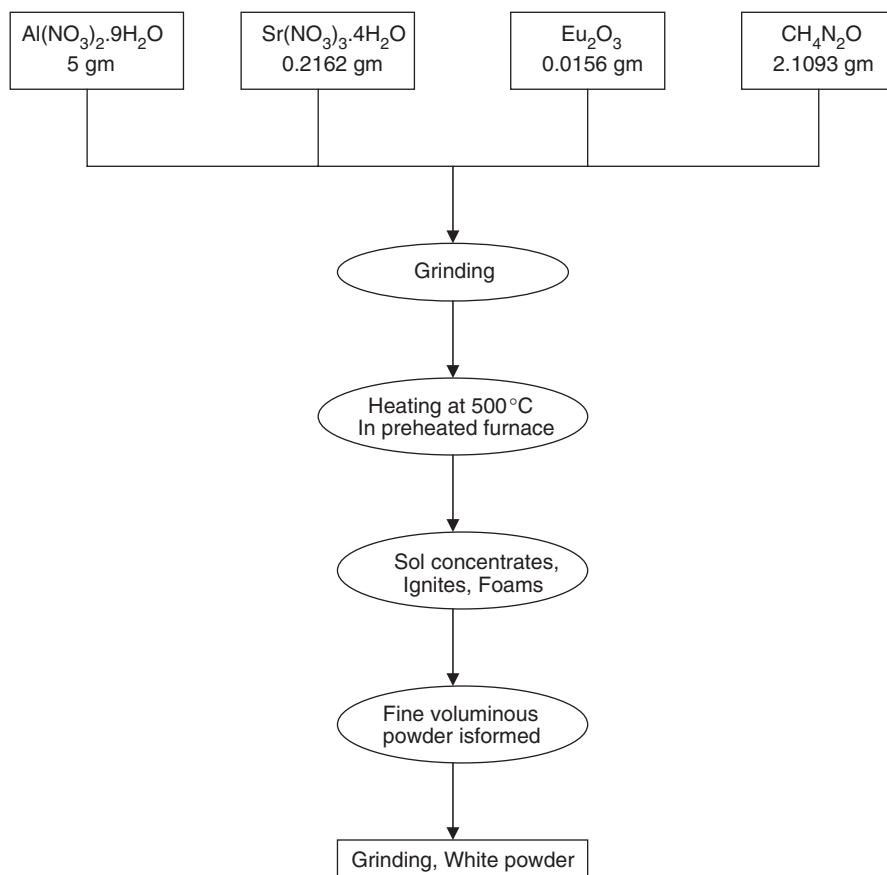
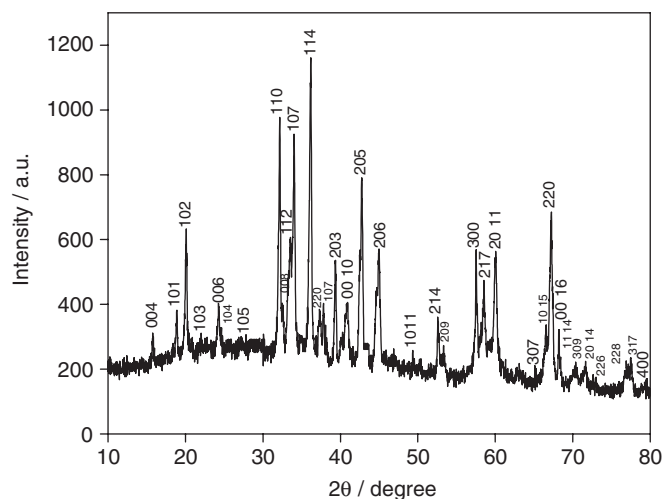
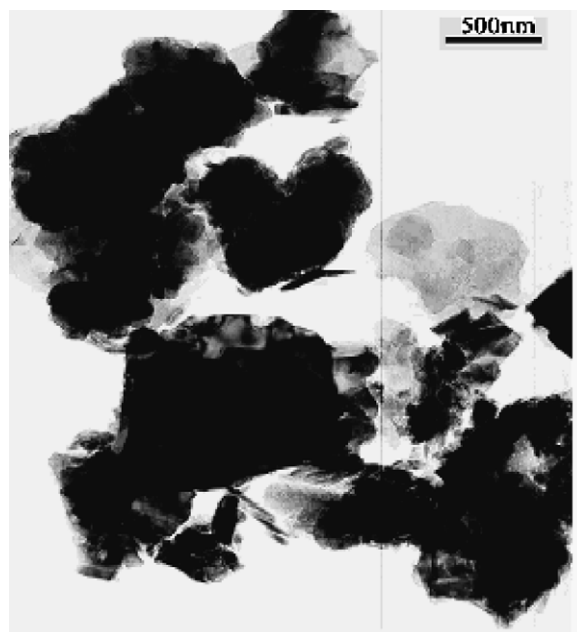
3. Results and discussion

3.1. XRD, TEM, SEM and PL studies

To study the crystalline structures of the products, XRD measurements were carried out at room temperature. Fig. 2 shows the XRD patterns of as prepared $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}^{2+}$. All the reflections can be indexed to the hexagonal $\text{SrAl}_{12}\text{O}_{19}$ phase. The XRD pattern matched perfectly with the JCPDS (80-1195). The TEM image of as prepared $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ and its agglomerate are shown in Fig. 3. It is clear from this TEM picture that the strontium hexaaluminate phosphor formed by the combustion process has nearly hexagonal platelet particles with sizes ranging from 0.4 to $1\ \mu\text{m}$ and the agglomerate sizes are less than $1.5\ \mu\text{m}$. The SEM micrograph Fig. 4 shows the macrostructure and the surface of the $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ foam. The foamy structure of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ reflects the inherent nature of the reaction. Reaction in the presence of urea allows the growth of faceted crystals. Most of the hexaaluminates took the form of hexagonal platelets with well-developed faces.

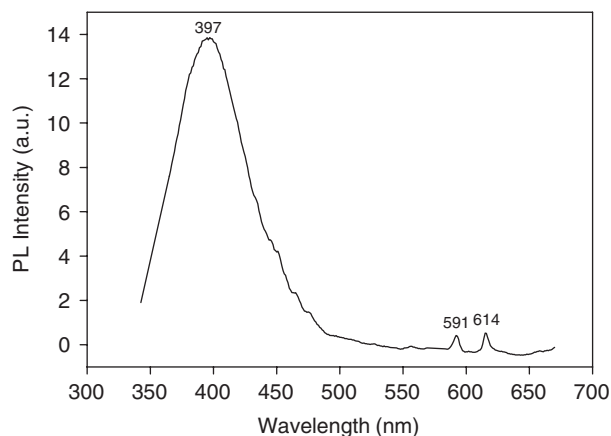
The hosts have different structures and Eu^{2+} emission in these hosts is located at characteristically different positions. For example, the emission maximum is located at 463 nm in $\text{Sr}_{5.5}\text{Mg}_6\text{Al}_{55}\text{O}_{94}$ [20], 520 nm in SrAl_2O_4 [20], 490 nm in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ and 460 nm in $\text{Sr}_2\text{Al}_6\text{O}_{11}$ [21]. The incorporation and stabilization of europium ions in the present phosphor were confirmed by luminescence investigations.

The emission spectrum corresponding to excitation at 341 nm is shown in Fig. 5. It is observed that there is a prominent band at 397 nm with two very weak bands at 594 and 615 nm. Emission spectra reveal the stabilization of europium ions in $\text{SrAl}_{12}\text{O}_{19}$ lattice in both divalent as well as trivalent oxidation states. Intense emission is observed at 397 nm. Verstegen and Stevels also reported similar appearance of emission peak at about 397 nm for Eu-doped $\text{SrAl}_{12}\text{O}_{19}$ phosphors [22]. However, they synthesized this phosphor using standard ceramic techniques with firing temperatures ranging from 1300 to 1600°C . The emission peak is observed at 397 nm and this peak is due to the transition of Eu^{2+} ion from excited state

Fig. 1. Flowchart for the synthesis of combustion derived SrAl₁₂O₁₉:Eu.Fig. 2. Powder XRD patterns of SrAl₁₂O₁₉:Eu.Fig. 3. TEM image of SrAl₁₂O₁₉:Eu.

of $4f^65d^1$ configuration to the ground state $^8S_{7/2}$ of $4f^7$ configuration. Further emission spectrum shows that Eu^{3+} ions with characteristic emission at 591 and 614 nm corresponding to $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively, are also formed during synthesis although intensity of these peaks is significantly much lower than that of 397 nm peak. The red emission of Eu^{3+} is due to

radiative transitions $^5D_0 \rightarrow ^7F_j$ [23]. The excitation spectra of Eu-doped SrAl₁₂O₁₉ phosphor is shown in Fig. 6. As in Eu-activated SrAl₁₂O₁₉ sample, intense excitation regions

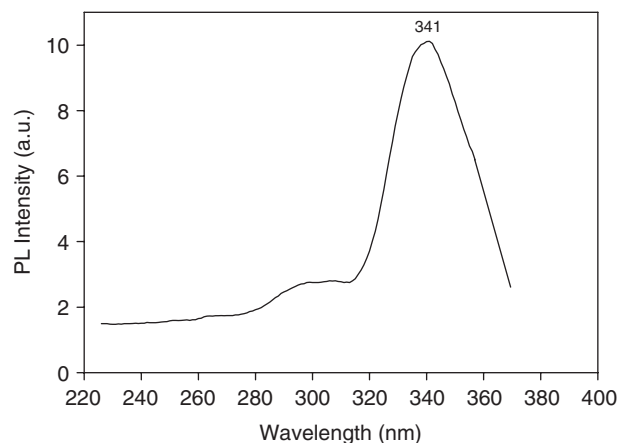
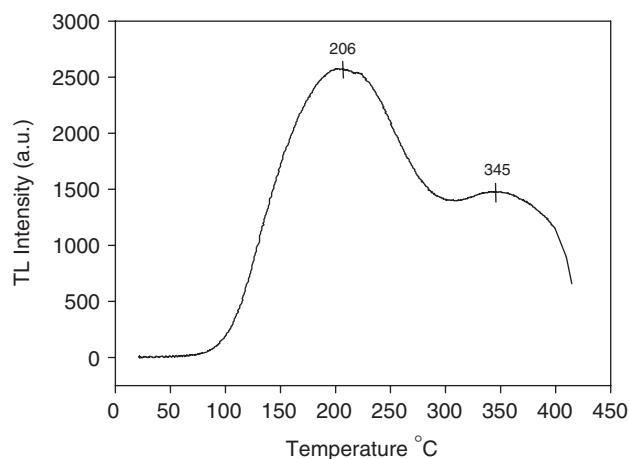
Fig. 4. SEM image of SrAl₁₂O₁₉:Eu.Fig. 5. Emission spectra of SrAl₁₂O₁₉:Eu ($\lambda_{\text{ex}} = 341$ nm).

are found almost in the UV spectra region, and are associated with $4f \rightarrow 5d$ electronic transitions. In this sample excitation is peaked around 302 nm and at 341 nm. These excitation peaks can be attributed to the $4f^7 (^8S_{7/2}) \rightarrow 4f^6 5d$ transitions. We observed that the more intense excitation peak occurs at 341 nm instead of 302 nm.

3.2. TSL and ESR studies

TSL studies on the freshly prepared SrAl₁₂O₁₉:Eu sample did not show any glow peak. However, gamma-irradiated (dose = 15 kGy) samples exhibited glow curve (Fig. 7) and the glow curve is broad and consists of a dominant peak at around 206 °C followed by another peak at 345 °C (heating rate = 3 °C/s). The TSL peak around 206 °C arises from shallow traps normally formed during gamma irradiation of the phosphor. The latter broad TSL peak around 345 °C is related to relatively deeper traps. From the continuity of the TSL emission from 100 to 400 °C, it appears that first-order kinetics are applicable.

Fig. 8(a) shows the room temperature powder ESR spectrum of the phosphor obtained after irradiation with

Fig. 6. Excitation spectra of SrAl₁₂O₁₉:Eu ($\lambda_{\text{em}} = 397$ nm).Fig. 7. Thermally stimulated luminescence glow curve of SrAl₁₂O₁₉:Eu.

⁶⁰Co gamma rays. It is seen that a few ESR lines are observed near the free electron resonance region. The ESR line labelled as I in Fig. 8(c) is due to a centre characterized by a single ESR line with an isotropic g -value 2.0055 and 1 G line width. Not many defect centres are expected to be formed in a system like SrAl₁₂O₁₉ and the most probable centre which can be observed is the F⁺ centre (an electron trapped at an anion vacancy). Hutchison [24] first observed such a centre in neutron irradiated LiF. In LiF, a single broad line (line width ~100 G) with a g -factor 2.008 was observed. X-ray or gamma irradiation also produces such a centre in other systems like alkali halides [25]. Such centres are characterized by (1) a small g -shift, which may be positive or negative, (2) a large line width and (3) saturation properties characteristic of an in homogeneously broadened ESR line. Unresolved hyperfine structure causes large line widths.

Irradiation leads to the removal of a negative ion from the lattice and an electron trapped at such an anionic vacancy is the basis for the formation of F⁺ centre. Hyperfine interaction with the nearest-neighbor cations is the major contribution to the line width. Defect centre I formed in the present system is characterized by a small g -

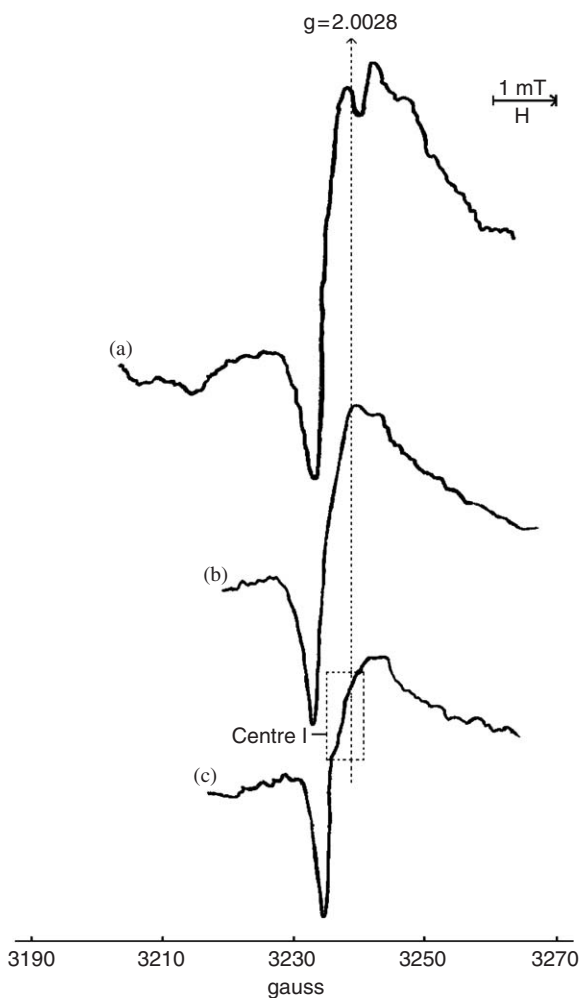


Fig. 8. (a) ESR spectrum of gamma irradiated $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ at room temperature. (b) and (c) refer to spectra from samples annealed at 200 and 250 °C, respectively.

shift and the line width, however, is relatively small. The centre also does not exhibit any resolved hyperfine structure. On the basis of these observations and considerations of the characteristic features of the defect centres likely to be formed in a system such as $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$, centre I is tentatively assigned to a F^+ centre.

The stability of centre I was measured using the step-annealing technique. The thermal annealing behaviour of centre I (Figs. 9 and 10) shows different temperature regions where there is a reduction in intensity of the corresponding ESR line. The approximate region from 125 °C to around 230 °C is likely to arise from recombination of charges, released from unknown traps, at F^+ centre sites. This region appears to correlate with the observed TSL peak at 206 °C. It should be mentioned that due to overlap of nearby ESR lines, it was difficult to measure precisely the intensity of centre I ESR line. The next annealing region from 340 to 390 °C is not well defined and is likely to correlate with the observed TSL peak at 345 °C.

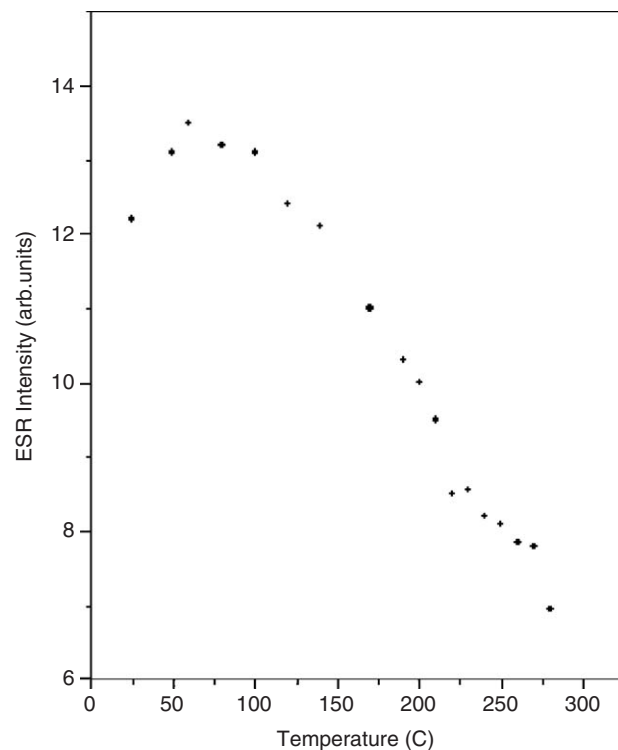


Fig. 9. Thermal annealing behaviour of F^+ centre in $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$.

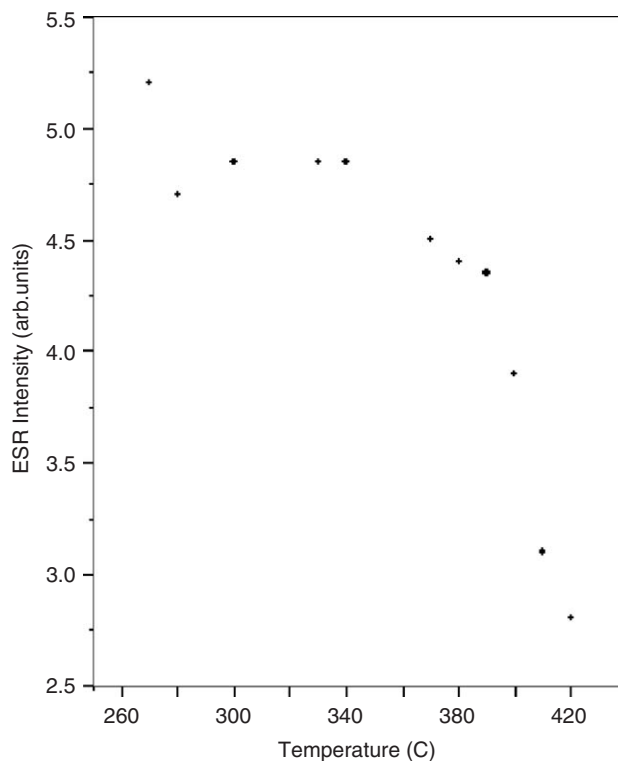


Fig. 10. Thermal annealing behaviour of F^+ centre in the high temperature range in $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$.

This region also appears to arise from recombination of charges, released from unknown traps, at F^+ centre. There is a considerable reduction in the intensity of ESR line of

F^+ centre above 390 °C and the centre is observed to decay at higher temperatures.

4. Conclusions

The present investigation on Eu-ion doped $SrAl_{12}O_{19}$ sample prepared via a combustion method indicates that europium ions were present both in divalent as well as trivalent oxidation states in the sample. We found that this phosphor is prepared within several minutes. The results in this case are encouraging because this method is not only time and energy saving but also found to be effective in lowering the cost of the phosphor. Two glow peaks were observed in gamma irradiated europium ion doped samples at 206 and 345 °C. Although the traps responsible for the TSL peaks at 206 and 345 °C could not be identified, their thermal decay was observed to correlate with two annealing stages of F^+ centre in the regions 125–230 and 340–390 °C, respectively. Eu^{2+} was observed as the dominant luminescent site.

Acknowledgments

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References

- [1] S.H. Poort, W.P. Blokpoel, G. Blasse, *Chem. Mater.* 7 (1995) 1547.
- [2] T. Matsuzawa, Y. Aoki, T. Takeuchi, Y. Murayama, *J. Electrochem. Soc.* 143 (1996) 2670.
- [3] M. Ashida, K. Okamoto, I. Ozaki, H. Fukuda, K. Ohmi, S. Tanaka, H. Kobayashi, M. Hayashi, M. Minamoto, in: *Proceedings of the International Display Workshop-98, Kobe, 1998*, p. 597.
- [4] A.J. Lindop, C. Matthews, D.W. Goodwin, *Acta Crystallogr. B* 31 (1975) 2940.
- [5] S. Shionoya, W.M. Yen (Eds.), *Phosphor Handbook*, Chemical Rubber Company Press, London, 1995 (Chapter 10).
- [6] L.D. Merkle, B. Zandi, R. Moncorge, Y. Guyot, H.R. Verdun, B. McIntosh, *J. Appl. Phys.* 79 (1996) 1849.
- [7] M. Akiyama, C. Xu, K. Nonaka, *Appl. Phys. Lett.* 73 (1998) 3046.
- [8] T. Katsumata, K. Sasajima, T. Nabaie, *J. Am. Chem. Soc.* 81 (1998) 413.
- [9] Tianyou Peng, Liu Huajun, Huanping Yang, Chunhua Yan, *Mater. Chem. Phys.* 85 (2004) 68.
- [10] S.H.M. Poort, W.P. Blokpoel, G. Blasse, *Chem. Mater.* 7 (1997) 1547.
- [11] S.H.M. Poort, W. Janssen, G. Blasse, *J. Alloys Compd.* 260 (1997) 93.
- [12] J.K. Park, M.A. Lim, C.H. Kim, H.D. Park, *Appl. Phys. Lett.* 82 (2003) 683.
- [13] S.J. Dhoble, S.V. Moharil, T.K. Gundu Rao, *J. Lumin.* 93 (2001) 43.
- [14] T.K. Seshagiri, A.G.I. Dalvi, M.D. Sastry, *Am. J. Phys. C* 21 (1988) 5891.
- [15] T.K. Seshagiri, V. Natarajan, M.D. Sastry, *Radiat. Meas.* 21 (1993) 271.
- [16] V. Natarajan, T.K. Seshagiri, R.M. Kadam, M.D. Sastry, *Radiat. Meas.* 35 (2002) 361.
- [17] V. Singh, T.K. Gundu Rao, Jian-Jun Miao, Jun-Jie Zhu, *Radiat. Effect Defects Solids* 160 (2005) 265.
- [18] G. Blasse, A. Brill, *Philips Res. Rep.* 23 (1968) 201.
- [19] S.R. Jain, K.C. Adiga, V.R. Pai Vernekar, *Combust. Flame* 40 (1981) 71.
- [20] J.M.P.J. Versteegen, *J. Electrochem. Soc.* 121 (1974) 1623.
- [21] B. Smets, J. Rutten, G. Hoeks, J. Verlijdsdonk, *J. Electrochem. Soc.* 136 (7) (1989) 2119.
- [22] J.M.P.J. Versteegen, A.L.N. Stevels, *J. Lumin.* 9 (1974) 406.
- [23] G. Blasse, A. Brill, W.C. Nieuwpoort, *J. Phys. Chem. Solids* 27 (1966) 1587.
- [24] C.A. Hutchison, *Phys. Rev.* 75 (1949) 1769.
- [25] W.C. Holton, H. Blum, *Phys. Rev.* 125 (1962) 89.