Synthesis, photoluminescence, thermoluminescence and electron spin resonance investigations of CaAl$_{12}$O$_{19}$:Eu phosphor

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Abstract

The present paper describes the synthesis of europium-doped calcium aluminate phosphor using the combustion method. An efficient blue emission phosphor can be prepared at reaction temperatures as low as 500$^\circ$C in a few minutes by this method. Characterization of the powder was done by X-ray diffraction, transmission electron microscopy, scanning electron microscope analysis and the optical properties were studied by photoluminescence spectra. Thermoluminescence (TL) studies also have been carried out on CaAl$_{12}$O$_{19}$:Eu$^{2+}$ phosphor. The TL glow curve shows peaks at 174 and 240$^\circ$C. Defect centres formed in irradiated phosphor have been studied using the technique of electron spin resonance. Step annealing measurements indicate that one of the annealing stages of a defect centre appear to correlate with the release of carriers resulting in TL peak at 174$^\circ$C. The centre is characterized by an isotropic $g$-value of 2.0046 and is assigned to a $F^+$ centre.

Keywords: Phosphors; Doping; Luminescence; Defect centres

1. Introduction

Rare-earth and non-rare-earth-doped inorganic phosphors are widely used in a variety of applications, such as lamp industry, radiation dosimetry, X-ray imaging, and colour display [1]. In particular, the luminescent properties of europium-ion doped phosphors have been studied extensively for their applications in these areas [2,3]. Eu$^{2+}$ activated phosphors MAl$_2$O$_4$ and MAI$_{12}$O$_{19}$ (M = Sr, Ba, Ca, Mg) are well known since the studies by Blasse and Brill [4] in the 1960s. Their researches lead to the conclusion that these compounds were adequate phosphorescent materials because of their high quantum efficiency in the visible region. The emission of Eu$^{2+}$ ions varies from blue to red depending on the host lattice due to crystal-field effects [5]. A completely new generation of persistent luminescent phosphors, Eu$^{2+}$-doped alkaline-earth aluminates, MAI$_2$O$_4$:Eu$^{2+}$ (M = Ca, Sr), has been developed to replace ZnS:Cu [6]. At present, complex aluminates [7] as well as other materials [8] are subject to investigation. All persistent luminescent aluminates phosphors show the strong, broad band blue/green emission characteristic of the Eu$^{2+}$ ion. 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 [9,10]. Eu$^{2+}$-doped barium magnesium aluminate with the typical composition of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ is considered to be a potential candidate for use as a blue-emitting phosphor in high-resolution devices (e.g. high density TVs) and low voltage driving devices (e.g. field emission display (FED), cathode ray tube (CRT), and plasma display panel (PDP)) [11–13], because of its good quantum efficiency and light output of high absorption under vacuum ultraviolet excitation [12,14]. In fact, BaAl$_{12}$ O$_{19}$:Mn is known as a green-emitting phosphor for PDPs [15], and Pr- or Nd-doped SrAl$_{12}$O$_{19}$ crystals has been suggested as one of the potential material with good laser properties [16]. In recent years, a number of publications related to the thermoluminescence (TL) and electron spin
resonance (ESR) properties of Eu\(^{2+}\)-doped aluminates have appeared [17–21].

In this article, we report a low temperature initiated combustion method for the synthesis of Eu-doped CaAl\(_{12}\)O\(_{19}\) phosphors. The products were characterized by using techniques such as powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL), TL and ESR. It has been established on the basis of TL and ESR studies that, defect centres are related to the process of TL in phosphors. It has been observed that the release of holes/electrons from defect centres at characteristic traps initiate luminescence process in these materials. In the present investigation, the evidence for the co-existence of Eu\(^{2+}\) and Eu\(^{3+}\) in the samples is presented. In addition, we have studied the gamma radiation-induced defect centres formed in CaAl\(_{12}\)O\(_{19}\):Eu system using techniques such as ESR and TL.

2. Experimental

2.1. Synthesis

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 \(\phi_e\), is unity (i.e. O/F = 1) and the energy released by the combustion is at a maximum [22].

All the reagents were of analytical purity, and were used without further purification. For a quick material screening, material elaboration was done following the flow chart given in Fig. 1. In a typical procedure, 5 g Al(NO\(_3\))\(_2\)-9H\(_2\)O, 0.2413 g Ca(NO\(_3\))\(_3\)-4H\(_2\)O, 2.1093 g CH\(_4\)N\(_2\)O and 0.0156 g Eu\(_2\)O\(_3\) were mixed in an agate mortar and the resulting pest 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 underwent dehydration followed by decomposition with the evolution of large amounts of gases. 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 over in less than 5 min. In the present investigation, we have synthesized particle CaAl\(_{12}\)O\(_{19}\)-doped with Eu\(^{2+}\) ions through a low temperature initiated combustion process.

2.2. Instruments

Powder XRD pattern was performed on a Philips X’pert X-ray diffractometer with graphite monochromatized CuK\(_\alpha\) radiation (\(\lambda = 0.15418\) nm) and nickel filter at a scanning step of 0.03°, continuing time 10 s, in the 2\(\theta\) 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. The PL spectra were acquired with an AMINCO-Bowman Series 2
luminescence spectrometer at room temperature. TL 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. Samples were irradiated with gamma rays from a \(^{60}\)Co source (dose rate \(~12\) Gy/min). Reasonable ESR signal intensity of defect centres could be observed with a total gamma dose of about \(2000\) Gy.

3. Results and discussion

3.1. XRD, SEM and TEM studies

The XRD patterns of as-prepared \(\text{CaAl}_{12}\text{O}_{19}:\text{Eu}^{2+}\) is shown in Fig. 2. The diffraction peaks correspond to the all planes, which can be indexed to the pure hexagonal phase for \(\text{CaAl}_{12}\text{O}_{19}\). The XRD pattern matched perfectly with the JCPDS (07-0085). No peak of any other phase was detected. The SEM micrograph Fig. 3 shows the macro-structure and the surface of the \(\text{CaAl}_{12}\text{O}_{19}:\text{Eu}\) foam. The foamy structure of \(\text{CaAl}_{12}\text{O}_{19}:\text{Eu}\) 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 TEM image of as-prepared \(\text{CaAl}_{12}\text{O}_{19}:\text{Eu}\) and its agglomerate are shown in Fig. 4. It is clear from this TEM picture that the calcium hexaaluminate phosphor formed by the combustion process has nearly hexagonal platelet particles with sizes ranging from 0.4 to 1.5 \(\mu\)m and the agglomerate sizes are less than 2 \(\mu\)m.

3.2. PL study

Europium ions can be stabilized in host lattice in either divalent or trivalent oxidation state. The incorporation and stabilization of Eu ions in the sample were confirmed by the luminescence investigations. The PL spectrum of the sample for excitation at 344 nm is shown in Fig. 5. The emission spectrum reveals one strong band at 413 nm and two very weak bands at 591 and 614 nm. The intense excitation observed in the UV region are associated with \(4f\rightarrow5d\) electronic transitions. The excitation bands at 302 and 341 nm, are due to the \(4f^7\) \(^{8}S_{7/2}\) \(\rightarrow 4f^6 5d\) transitions. We observed that the excitation band at 341 nm is more intense than that at 302 nm. The emission band observed at 413 nm, is due to the transition of \(\text{Eu}^{2+}\) from excited state of \(4f^6 5d^1\) configuration to the ground state \(^{8}S_{7/2}\). Verstegen and Stevels have earlier reported the similar \(\text{Eu}^{2+}\) emission band about at 413 nm in \(\text{CaAl}_{12}\text{O}_{19}\) phosphor [23]. They
synthesized these phosphors using solid-state reaction firing temperature ranged between 1300 and 1600 °C. It is obvious from Fig. 5 that emission bands characteristic of Eu$^{3+}$ ions are also present in our samples. The emission bands at 591 and 614 nm are due to $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively.

3.3. TL and ESR studies

Fig. 6 shows the TL glow curve of CaAl$_{12}$O$_{19}$:Eu phosphor irradiated with gamma dose of 15 kGy. The heating rate used was 5 °C/s. A dominant TL peak is observed at 240 °C with an unresolved peak at 174 °C. The shape of the TL peaks is difficult to observe due to the overlapping. Since the main peak is not well resolved, the trapping parameters could not be calculated in the present form. Since the TL peaks arise from different trapped centres, ESR studies will be helpful to identify the trapping centres.

ESR spectrum of the phosphor taken in the powder form recorded at 25 °C after irradiation with $^{60}$Co gamma rays showed the presence of a few ESR lines in the vicinity of free electron resonance. Fig. 7(a) shows this spectrum observed immediately after irradiation. Careful examination showed that one of the centres [labeled as I in Fig. 7(b)] is characterized by a single ESR line with an isotropic $g$-value 2.0018 and 4G line width. A likely trapping centre which can be formed in a system like CaAl$_{12}$O$_{19}$ is the F$^+$ centre (an electron trapped at an anion vacancy). This centre was first observed by Hutchison [24] in neutron irradiated LiF. In LiF, a single broad line (line width~100 G) with a $g$-factor 2.008 was observed. A similar centre has been observed in other systems, notably in alkali halides after X-ray or gamma irradiation [25]. The main characteristic features of such centres are: (1) a small $g$-shift, which may be positive or negative, (2) a large line width and (3) saturation properties characteristic of an in homogenously broadened ESR line.

The large line width arises from an unresolved hyperfine structure. The F$^+$ centre consists of an electron occupying an anionic vacancy formed by the removal of a negative ion from the lattice. Hyperfine interactions with the nearest-neighbor cations account for most of the line width. Defect
centre I formed in the present system is characterized by a small $g$-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 CaAl$_2$O$_{19}$: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 is shown in Fig. 8 and it is seen that the centre decays in the temperature region 100–200 °C. No specific TL role could be assigned to this centre.

Thermal annealing experiments, particularly near 160 °C, revealed the presence of another centre (centre II). The ESR spectrum of this centre is shown in Fig. 7(c) and the species is characterized by a single ESR line with an isotropic $g$-value 2.0046 and 4 G line width. Centre II is also tentatively assigned to a F$^+$ centre. The thermal annealing behaviour of centre II (Fig. 9) shows different temperature regions where there is a reduction in intensity of the corresponding ESR line. The approximate region from 170 °C to around 220 °C is likely to arise from recombination of charges, released from unknown traps, at F$^+$ centre (centre II) sites. This region appears to correlate with the observed TL peak at 174 °C. There is a further reduction in the intensity of ESR line above 230 °C and the centre is observed to decay at higher temperatures.

After the decay of centre II, another ESR line could be observed clearly without any overlap from nearby lines and the ESR spectrum of this centre is shown in Fig. 7(e). This centre (III) is also characterized by a single line with an isotropic $g$-value 2.0040 and 6.5 G line width. The thermal annealing behaviour of centre III in the temperature region

![Fig. 8](image1.png)

**Fig. 8.** Thermal annealing behaviour of centre I (F$^+$ centre) in CaAl$_2$O$_{19}$:Eu system.

![Fig. 9](image2.png)

**Fig. 9.** Thermal annealing behaviour of centre II (F$^+$ centre) in CaAl$_2$O$_{19}$:Eu system.

![Fig. 10](image3.png)

**Fig. 10.** Thermal annealing behaviour of centre III in CaAl$_2$O$_{19}$:Eu system.
where the line could be clearly seen is shown in Fig. 10. No specific TL role could be assigned to this centre.

From the observed ESR and TL studies it appears that the TL peak at 174 °C arises from unknown traps releasing charge carriers which combine with electrons at F⁺ centre (centre II) sites.

4. Conclusions

Based on the results presented above, the following conclusions may be highlighted:

1. The present investigation on europium-doped CaA1₂O₁₉ phosphor prepared via a combustion method indicates that europium ions are present both in divalent as well as trivalent oxidation state in the sample. The major advantages of the combustion process are its simplicity, speed and cost.

2. The observed TL glow curve of CaAl₁₂O₁₉:Eu indicates a major TL peak at 240 °C and a smaller peak at 174 °C. Two of the defect centres formed in the crystal lattice due to gamma irradiation of the CaAl₁₂O₁₉:Eu system are tentatively assigned to F⁺ centres.

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References