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Synthesis, characterisation and luminescence investigations of Eu activated CaAl$_2$O$_4$ phosphor

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Abstract

Europium ion doped monoclinic CaAl$_2$O$_4$ phosphors were obtained at low temperatures (500 °C) by the combustion of corresponding metal nitrate–urea mixtures, over a time of 5 min. The product was investigated by X-ray powder diffraction, TEM and SEM. Photoluminescence spectra revealed that europium ions were present in divalent oxidation states. Electron paramagnetic resonance (EPR) measurements at X-band showed the presence of fine structure transitions from Eu^{2+} ions in CaAl$_2$O$_4$:Eu.
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1. Introduction

Rare earth and nonrare earth doped inorganic phosphors are widely used in a variety of applications, such as lamp industry, radiation dosimetry, X-ray imaging, and color 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 MAl$_{12}$O$_{19}$ (M = Sr, Ba, Ca, Mg) are well known since the studies by Blasse and Brill [4] in the 1960s. Their research led to the conclusion that these are phosphorescent materials with 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, MAl$_2$O$_4$:Eu^{2+} (M = Ca and Sr), has been developed with a view to replace ZnS:Cu [6]. At present, complex aluminates [7] as well as other materials [8] are

subject to investigation. All persistent luminescent aluminate phosphors show the strong, broad band blue/green emission characteristic of Eu^{2+} ion. The lifetime of luminescence for these phosphors is very long, up to 10 h, in contrast to materials doped with only Eu, with lifetimes of the order of a few hundreds of nanoseconds. Recently, Aitasalo et al. [9] have reported the sol–gel preparation, structure and luminescence of Eu^{2+} doped CaAl$_2$O$_4$ materials. They have observed the broad band UV excited luminescence of Eu^{2+} ions in hexagonal CaAl$_2$O$_4$:Eu at the blue region (λ_{max} = 448 nm) due to transitions from the 4f^{6}5d^1 to the 4f^7 configuration of the Eu^{2+} ion. The synthesis of metal aluminates usually involves the solid-state reaction of the corresponding metal carbonate with Al$_2$O$_3$ at high temperatures and for long time, e.g. CaCO$_3$–Al$_2$O$_3$ (1350 °C) [10], SrCO$_3$–Al$_2$O$_3$ (1450 °C) [11] and BaCO$_3$–Al$_2$O$_3$ (1150 °C) [12]. Although, fluorescence studies on MAl$_2$O$_4$ and MAl$_{12}$O$_{19}$ (M = Ba, Sr, Ca) have been reported long ago by Blasse and Brill [4], to our knowledge, there are very few reports on CaAl$_2$O$_4$:Eu phosphors synthesized via combustion method. The combustion process is an efficient technique for the preparation of phosphors due to the proper mixing of starting materials and

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relatively low reaction temperature resulting in more homogeneous products than those obtained by direct solid-state reaction. The direct solid-state preparation of monoclinic MAl_2O_4 is usually carried out at around 1300 °C, since impurities such as $M_3Al_2O_6$ are found at lower temperatures. On the other hand, a metastable orthorhombic form of $CaAl_2O_4$ has been prepared by sol–gel method [13,14]. In view of these, $CaAl_2O_4$:Eu phosphor was prepared in our study via low temperature initiated combustion process and was investigated using XRD, TEM, SEM, photoluminescence and EPR techniques in order to understand the role of europium ions in $CaAl_2O_4$ host. In this paper, the evidence for the existence of Eu^{2+} ions in the samples is presented.

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 $\emptyset e$, is unity (i.e. $O/F = 1$) and the energy released by the combustion is at a maximum [15].

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 $Al(NO_3)_2 \cdot 9H_2O$, 1.5580 g $Ca(NO_3)_2 \cdot 4H_2O$, 2.6640 g CH_4N_2O and 0.0117 g Eu_2O_3 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. 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 $CaAl_2O_4$ 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_α radiation ($\lambda = 0.15418$ nm) and nickel filter at a scanning step of 0.03°, counting 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 was prepared by dispersing products in ethanol followed by ultrasonic vibration for 30 min, then
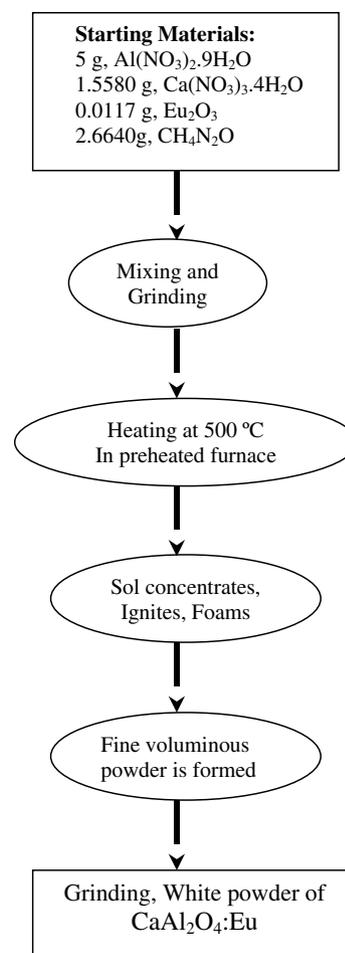

Fig. 1. Flowchart for the synthesis of combustion derived $CaAl_2O_4$:Eu.

placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. PL experiments were carried out on a Shimadzu RF-5301 PC spectrophotometer. EPR measurements were carried out on a Bruker EMX 10/12 X-band EPR spectrometer.

3. Results and discussion

The XRD patterns of prepared $CaAl_2O_4$:Eu^{2+} is shown in Fig. 2. The diffraction peaks correspond to the all planes, which can be indexed to the pure monoclinic phase for $CaAl_2O_4$. Calculated lattice parameters are as follows: $a = 8.702$, $b = 8.092$, $c = 15.18$ and $\beta = 90.18$. The XRD pattern matched perfectly with that reported for $CaAl_2O_4$ (JCPDS (70-0134)). No peak of any other phase was detected. The SEM micrograph of the as-prepared powder, shown in Fig. 3a, reflects the foamy and agglomerate particle nature of the powder. The foamy structure of monoclinic $CaAl_2O_4$:Eu reflects the inherent nature of the reaction. The surface of the powder (Fig. 3b and c) shows a lot of voids and pores, which may be formed by the evolved gases during combustion. The TEM microphotograph of $CaAl_2O_4$ shows their morphology (Fig. 4). The

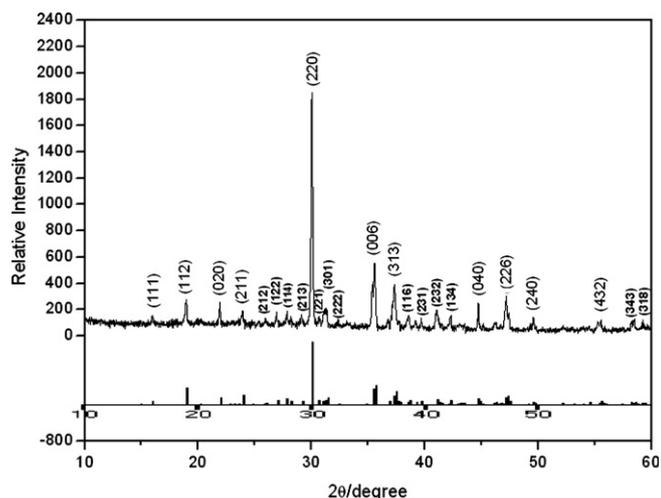Fig. 2. X-ray powder diffraction patterns of CaAl$_2$O$_4$:Eu.

Fig. 4. TEM image of CaAl$_2$O$_4$:Eu.

particle sizes of the CaAl$_2$O$_4$ calculated from the TEM observation are estimated as greater than 1 μm.

The incorporation and stabilization of Eu in the sample were confirmed by the luminescence investigations. The photoluminescence spectrum of the sample is shown in
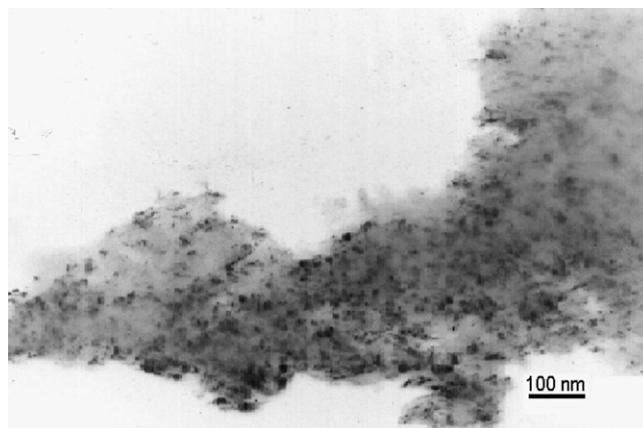
Fig. 5. The emission spectra, corresponding to excitation of Eu^{2+} at 330 nm as well as 255 nm, are depicted in Fig. 5 with one strong peak at 440 nm. Intense and broad excitation peaks of Eu^{2+} are found in the UV spectra region, and are associated with 4f → 5d electronic transitions. The emission peak observed at 440 nm, is due to the transition of Eu^{2+} from excited state of 4f^{6}5d^1 configuration to the
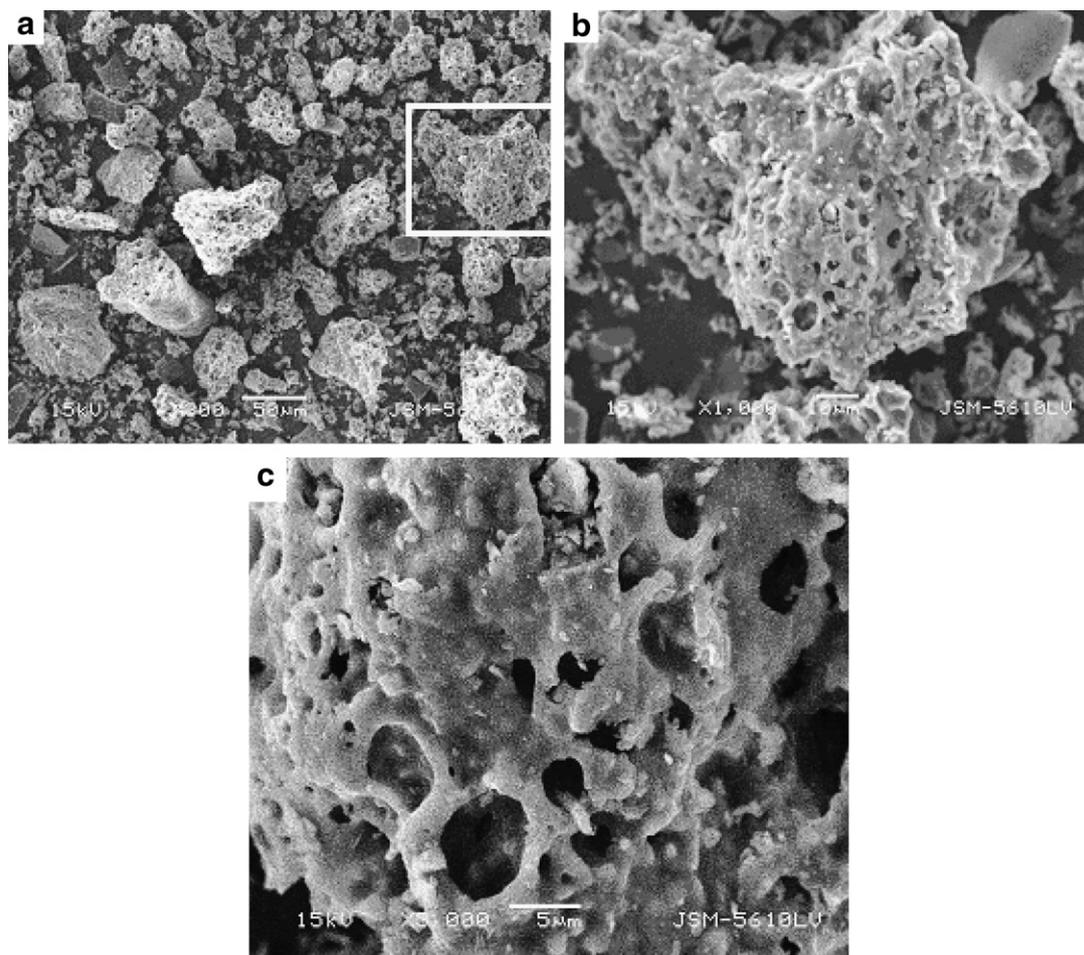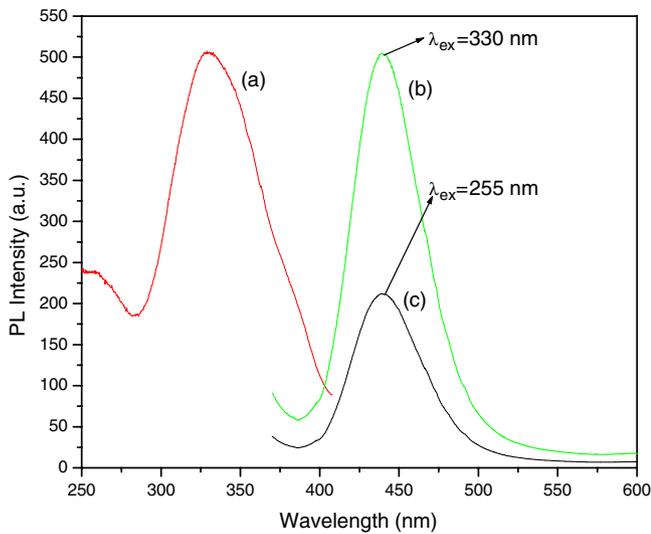

Fig. 3. SEM image of CaAl$_2$O$_4$:Eu.

Fig. 5. Photoluminescence spectra of Eu doped $CaAl_2O_4$: (a) excitation spectra of $CaAl_2O_4$ ($\lambda_{em} = 440$ nm), (b) emission spectra of $CaAl_2O_4$ ($\lambda_{ex} = 330$ nm) and (c) emission spectra of $CaAl_2O_4$ ($\lambda_{ex} = 255$ nm).

ground state $^8S_{7/2}$ of $4f^7$ configuration. Earlier Palilla et al. [16] have reported the similar peak at 440 nm for Eu doped monoclinic $CaAl_2O_4$. Recently, Aitasalo et al. [9] have reported an emission peak at 448 nm for hexagonal $CaAl_2O_4$:Eu^{2+}, synthesized using sol–gel technique. Herein the gel was first heated for 10 h at 180 °C to remove water and then 20 h at 850 °C in a N_2–12% H_2 gas sphere. The excitation peaks at 255 and 330 nm are due to transitions from $4f^7$ ground state to the crystal field split excited levels of $4f^6 5d^1$ state of Eu^{2+} ions ($4f^7 \rightarrow 4f^6 5d^1$). However in the emission spectra, we could not observe any narrow peaks in the 570–600 nm region, attributable to f–f transitions of Eu^{3+} ion (Fig. 5).

EPR spectra of Eu doped $CaAl_2O_4$, are shown in Fig. 6. Sharp features at 280, 1205, 2185, 3260, 3875, 5240 and 6540 G are present in the spectrum. Eu^{2+} with $4f^7$ configuration has $^8S_{7/2}$ as its electronic ground state. Unlike other rare earths, Eu^{2+} ion has long spin-lattice relaxation time leading to the observation of its EPR signals at room temperature. EPR of Eu^{2+} in the lower symmetries is known to give fine structure consisting of seven lines resulting from

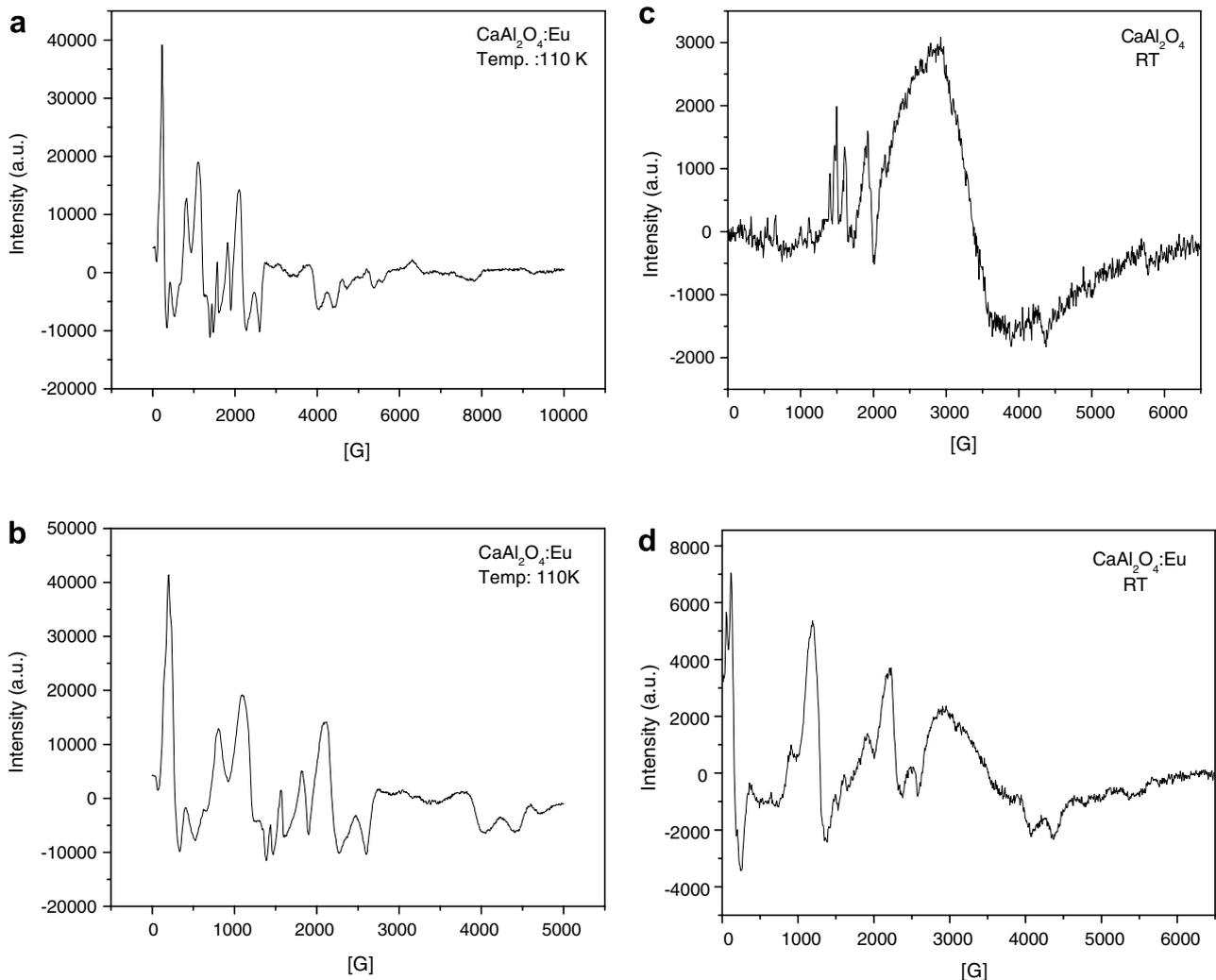Fig. 6. (a–d) EPR spectra of $CaAl_2O_4$:Eu.

the splitting $J = 7/2$ state into $2J + 1$ levels. The separation between these lines depends 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. Further the fine structure can show further splitting into six line structure (hfs) due to interaction of unpaired electron with Eu^{2+} ($I = 5/2$) nucleus. However, for symmetries other than this, usually broad fine structure lines are only seen in X-band frequency. With stuffed tridymite structure, $CaAl_2O_4$ is formed of a three dimensional net work of corner sharing AlO_4 tetrahedra. Each oxygen atom is shared by two aluminium atoms so that each AlO_4 group has one negative charge. The divalent calcium cations occupy interstitial sites within the tetrahedral frame work. In the stuffed tridymite structure, Ca ions are reported to occupy two sites, each surrounded by nine oxygen atoms [17]. Eu^{2+} ions (ionic radius -1.09 Å) are expected to substitute Ca^{2+} ions (ionic radius -0.94 Å). For such symmetries, the crystal field splitting is usually expected to be large and is of the order of zero field splitting [18]. In such a case, one is expected to observe the fine structure lines of Eu^{2+} ions. The EPR signals we have observed around 280, 1205, 2185, 3260, 3875, 5240 and 6540 G correspond to the fine structure lines of Eu^{2+} ions ($-7/2 \rightarrow -5/2$, $-5/2 \rightarrow -3/2$, $-3/2 \rightarrow -1/2$, $1/2 \rightarrow -1/2$, $1/2 \rightarrow 3/2$, $3/2 \rightarrow 5/2$, $5/2 \rightarrow 7/2$), similar to those observed by Nakamura et al. in $SrAl_2O_4:Eu^{2+}$ [18]. As reported by these authors and also by Kaiya et al. [19], high frequency EPR spectra of the sample will be required to calculate zero field splitting parameters. Therefore in our study, we are contented to state that these lines are due to low symmetry Eu^{2+} ions.

4. Conclusions

The present work on Eu doped monoclinic $CaAl_2O_4$ sample prepared via a combustion method indicates that Eu ions are present in divalent oxidation state as seen from its PL and EPR spectra. Further EPR results suggest that Eu^{2+} ions are present in low symmetry lattice sites. The synthesis method is time and energy saving and will be useful in lowering the cost of the phosphor. Combustion synthesis technique is faster than other methods of synthesis such as co-precipitated sulphates, oxalates, sol–gel, and spray decomposition processes.

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