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# Doping optimization of Eu and Ho activator ions in polycrystalline $CaAl_2O_4$

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## ABSTRACT

Polycrystalline calcium aluminate, $CaAl_2O_4$ codoped with Eu and Ho was prepared by solid-state synthesis technique. The compositions prepared with 1 mol.% Eu (fixed) and 2–5 mol.% of Ho were investigated for photoluminescence characteristics. Phase, morphology and crystalline structure of prepared compositions were investigated by powder XRD, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. Intense UV excited luminescence was observed for $CaAl_2O_4$:$Eu^{2+}$, $Ho^{3+}$ in the blue region ($\lambda_{max}$ = 440 nm) due to transitions from $4f^6$ $5d^1$ to $4f^7$ transition of $Eu^{2+}$ ion. Deep traps are generated by $Ho^{3+}$ ion codoping results in long persistence in phosphorescence.

## 1. Introduction

The materials with general formula $MAl_2O_4$ ($M$: Ca, Sr, Ba) doped with $Eu^{2+}$ activator ion show strong photoluminescence in blue–green region [1,2]. These phosphors codoped with the second ion exhibit a rapid initial decay from the $Eu^{2+}$ ion followed by long persistence [3]. The persistence in decay has been attributed to the thermal activation of holes from traps followed by the emission of $Eu^{2+}$. These Ca, Sr and Ba aluminates possess safer, chemically stable, bright and long-lasting photoluminescence compared to the conventional sulfide based phosphors. This makes them useful in many applications, such as luminous paints in highway, airport, buildings and ceramics products, in textiles, dial plate of glow watch, warning signs and the escape routs. Valence state of the activator ion dictates the emission wavelength [4,5]. It has been reported that the trivalent $Eu^{3+}$ ions show red luminescence properties in highly stable lead based heavy metal oxide glasses [6,7]. The solid-state reaction process is quite simple and successfully used for the synthesis of polycrystalline phosphor materials [8,9]. Chemical synthesis techniques, such as co-precipitation, sol–gel, microwave, Pechini and combustion synthesis methods have also been reported to prepare rare earth ions activated alkaline earth aluminate phosphors [10,11]. The requirement of device quality phosphors in high-definition television and field-emission displays has triggered targeted studies to find new kinds of phosphors with desirable chemical and physical properties. Some emission studies on $BaAl_2O_4$:$Eu^{2+}$ [8,12] and $CaAl_2O_4$:$Eu^{2+}$, $Nd^{3+}$ [4] to develop intense and long lasting phosphorescence at room temperature have been performed previously.

We report the results on optimization of codoping of Eu and Ho in $CaAl_2O_4$:$Eu^{2+}$:$Ho^{3+}$. Powder XRD, SEM and TEM measurements were done to investigate the phase, morphology and crystalline structure of the synthesized material. Photoluminescence characteristics were studied by measuring excitation, emission and decay time with respect to $Ho^{3+}$ doping concentrations.

## 2. Experimental details

Phosphor material $CaAl_2O_4$:$Eu^{2+}$, $Ho^{3+}$ with varying concentrations of Ho were prepared by solid-state synthesis method. The Eu concentration was kept constant at 1 mol.% for all the prepared compositions. Varying concentrations of Ho were taken as 2 mol.%; 3 mol.%, 4 mol.% and 5 mol.%. High purity (Aldrich make, 99.99%) raw materials; $CaCO_3$, $Al_2O_3$, $Eu_2O_3$, $Ho_2O_3$ and $B_2O_3$ were used for preparing the charge. $B_2O_3$ (10–15 mol.%) was used as a flux. The desired composition for each material is weighted in stoichiometric ratios and mixed thoroughly with ethanol in an agate mortar. The resulting slurry was dried at 80 °C in a vacuum oven for 4 h. Mixed and grounded powders were sintered at 900 °C for 6 h in an air atmosphere. The sintered powders were annealed at 1300 °C for 2 h in a reducing atmosphere (5% $H_2$ and 95% $N_2$) to ensure the complete reduction of $Eu^{3+}$ to $Eu^{2+}$. The phase stability of the prepared polycrystalline compositions was investigated by powder XRD. Lattice parameters were calculated from the XRD results. The crystallite sizes and morphology was estimated by SEM technique. High-resolution transmission electron microscopy (HRTEM) was done to investigate the morphology and microstructure of the prepared compositions. HRTEM was carried out employing Philips Tecnai

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$G^2$-20 (FEI) electron microscope operating at 200 kV. Photoluminescence (PL) excitation and emission spectra were taken on Perkin-Elmer LS50B luminescence spectrometer. Each sample was loaded into a circular holder and excited with 254 nm radiation from a pulsed xenon lamp. The emission spectra were scanned in the range of wavelengths from 360 to 700 nm. To measure the excitation spectra, the analyzer monochromator was set to the maximum wavelength of the emission spectra and then an excitation monochromator was scanned in the range of 200–400 nm. The decay time was recorded using a pulsed Xenon lamp and oscilloscope.

## 3. Results and discussion

Calcium aluminate, $CaAl_2O_4$ co-doped with $Eu^{2+}$ and $Ho^{3+}$ (1 mol.% of $Eu_2O_3$ and 2–5 mol.% of $Ho_2O_3$) were prepared. The Ho codoping was optimized and its effect on crystalline structure and photoluminescence was investigated. The representative powder XRD patterns for the $CaAl_2O_4$:$Eu^{2+}$, $Ho^{3+}$ (1 mol.% $Eu_2O_3$ and 0–5 mol.% $Ho_2O_3$) are shown in Fig. 1. These XRD patterns clearly indicate that the pure monoclinic phase diffraction peaks of parent $CaAl_2O_4$ are dominant and matching well with the JCPDS data file (No. 23-1036). No other phase or unreacted residual starting material was observed. This confirms the synthesized phase is low-temperature monoclinic phase ($\alpha$-phase) of $CaAl_2O_4$. The calculated lattice parameters for monoclinic crystal system were $a = 8.705$ Å, $b = 8.110$ Å and $c = 15.223$ Å.

Scanning electron microscopy (SEM) was done to investigate the surface morphology and the crystallite sizes of the synthesized phosphor compositions. The powder samples reduced at optimized temperature of 1300 °C were used for these experiments. Fig. 2(a–c) shows the representative SEM micrographs taken for $CaAl_2O_4$:$Eu^{2+}$, $Ho^{3+}$ (for Ho concentrations of 2, 3 and 5 mol.%). The polycrystalline morphology is clearly observed in these micrographs. The crystallite sizes are varying from few microns to several tens of microns. High-resolution transmission electron microscopic (HRTEM) study is the best tool to know the local structure, structural transformation, particle size and microstructural morphology of the polycrystalline material. HRTEM studies were conducted to investigate the microstructure and the crystallinity of the synthesized material. Fig. 3(a–c) shows the representative HRTEM bright field micrographs for the samples having three different Ho concentrations. Corresponding selected area diffraction (SAD) patterns are inserted in the micrographs. The clarity of the HRTEM micrograph shows that the synthesized material crystallizes in single phase and no trace of secondary phases are observed. The difference in intensity is due to the thickness variation. The SAD patterns inserted in Fig. 3(a–c) are indicative of the crystalline particles having sufficient sizes to give the clear and strong diffraction spots. However, the streaks along the diffraction spots and faint diffuse scattering present in the SAD patterns is due to the point defects produced by doping of Eu and Ho active ions. Higher diffuse scattering and streaks can be seen for higher Ho concentration in Fig. 3(b and c).

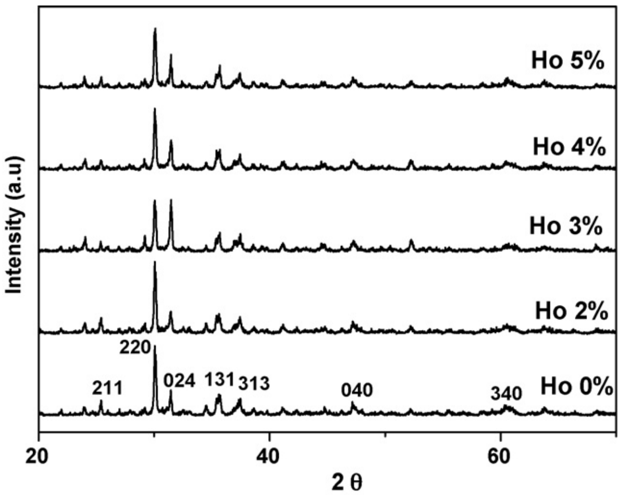

**Fig. 1.** Powder XRD patterns for $CaAl_2O_4$:$Eu^{2+}$, $Ho^{3+}$ (0, 2, 3, 4 and 5 mol.% Ho).

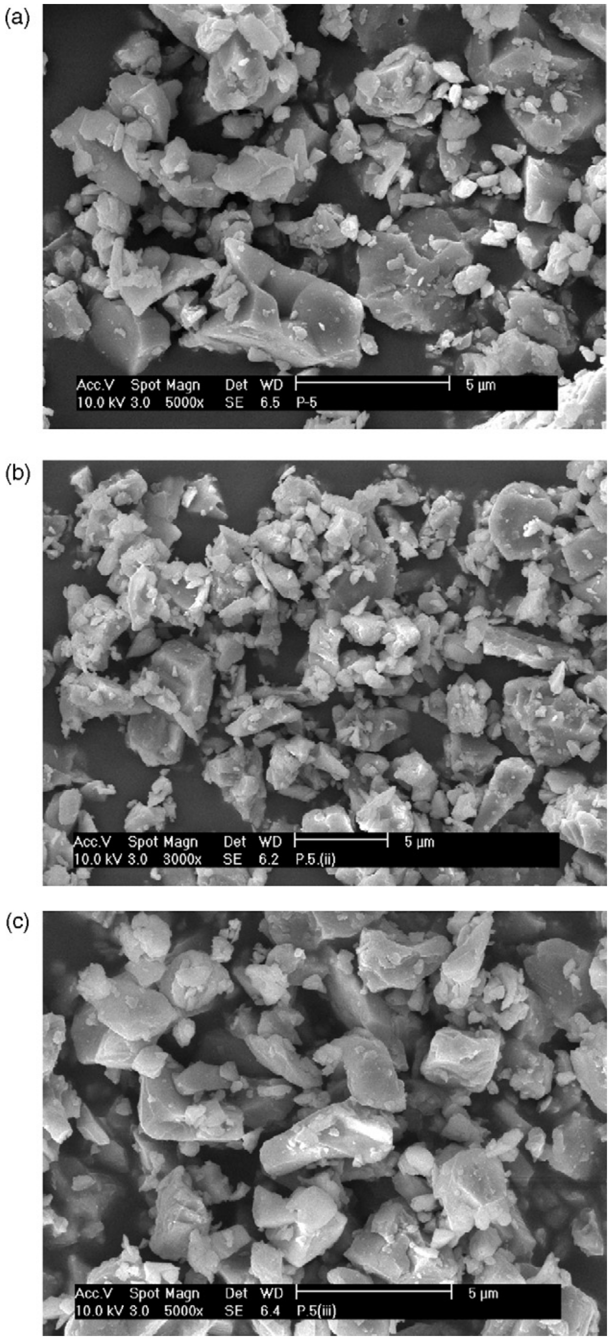

**Fig. 2.** Representative SEM micrographs for $CaAl_2O_4$:$Eu^{2+}$, $Ho^{3+}$ (2, 3 and 5 mol.% Ho).

The prepared polycrystalline compositions with varying Ho concentrations were investigated for photoluminescence. Strong and broad blue emission peak was observed for all the compositions. This is indicative of the monoclinic calcium aluminate as a host lattice. It further indicates that the Eu active ion is in divalent ($Eu^{2+}$, blue emission) rather than trivalent ($Eu^{3+}$, red emission) state. The excitation and emission spectra for $CaAl_2O_4$:$Eu^{2+}$ with various $Ho^{3+}$ concentrations are shown in Fig. 4(a and b). The excitation spectra of

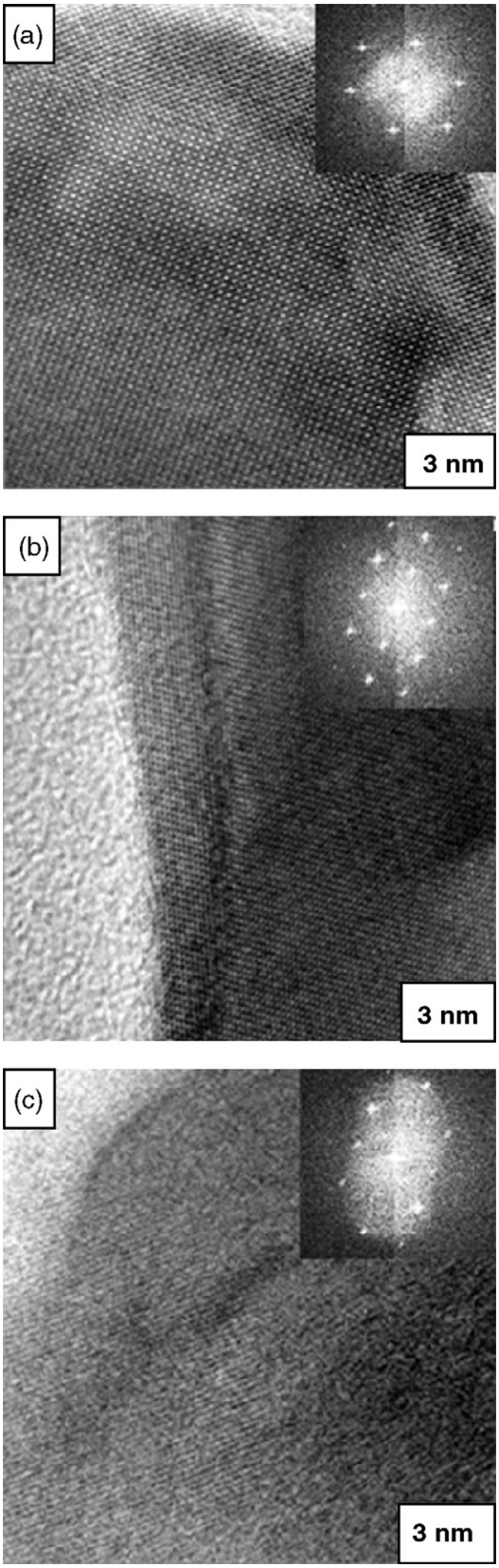

**Fig. 3.** Representative HRTEM micrographs for $CaAl_2O_4:Eu^{2+}$, $Ho^{3+}$ (2, 3 and 5 mol.% Ho). Corresponding SAD patterns are inserted into the micrograph.

the $CaAl_2O_4:Eu^{2+}$ codoped with $Ho^{3+}$ show two broad bands, one from 220 to 290 nm and other from 300 to 390 nm corresponds to the crystal field splitting of the $Eu^{2+}$ d-orbital. The emission is a symmetrical band at 440 nm which is attributed to typical $4f^6 5d^1$–$4f^7$ transition of $Eu^{2+}$ ion. These compositions of Eu and Ho codoped phosphors show higher emission compared to the parent phosphor. It was observed that when the phosphor material was doped with 1 mol.% $Eu^{2+}$ and 2 mol.% $Ho^{3+}$, the emission spectra have highest intensity. This combination of Eu and Ho concentration also shows longer decay time compared to other concentrations. The mechanism of the long persistence is due to the holes trapped-transported-detrap process [13–15].

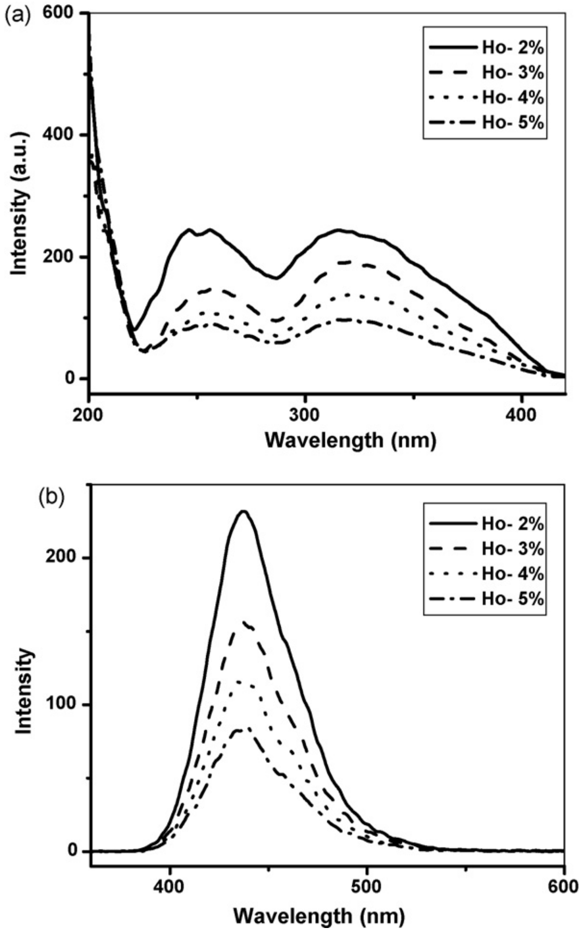

**Fig. 4.** Excitation (a) and emission (b) spectra for $CaAl_2O_4:Eu^{2+}$, $Ho^{3+}$ (2, 3, 4 and 5 mol.% Ho).

The $Ho^{3+}$ ion act as traps of holes and the trap levels lie in between the excited state and the ground state of $Eu^{2+}$ ion. When excited by the excitation light source, electron–hole pairs are produced in $Eu^{2+}$ ions, and the $Ho^{3+}$ traps capture some of the free holes moving in the valence band. When the excitation source is cut off, some holes captured by the $Ho^{3+}$ traps are thermally released slowly and relaxed to the excited state of $Eu^{2+}$, finally, returning to the ground state of $Eu^{2+}$ accompanied with emitting light. This is why this family of phosphor maintains a long persistent time after the excitation is cut off. Persistent luminescence curves for the $CaAl_2O_4:Eu^{2+}$, $Ho^{3+}$ phosphors are shown in Fig. 5. It can be seen from these curves that the samples show longer decay time compared to parent phosphor when the powder was efficiently activated by using a pulsed Xenon lamp for 15 min. It is known that the decay time for parent $CaAl_2O_4:Eu^{2+}$ is in microseconds. When the source lamp was switched off, the intensity of the persistence decreased rapidly and finally forms a stable long persistent emission for several minutes. It was found that when we increase the $Ho^{3+}$ concentration (above 2 mol.%) the emission intensity goes down. The reason seems to be that the concentration of $Ho^{3+}$ ions more than the optimum number produces more crystalline defects apart from the traps. These defects neutralize the

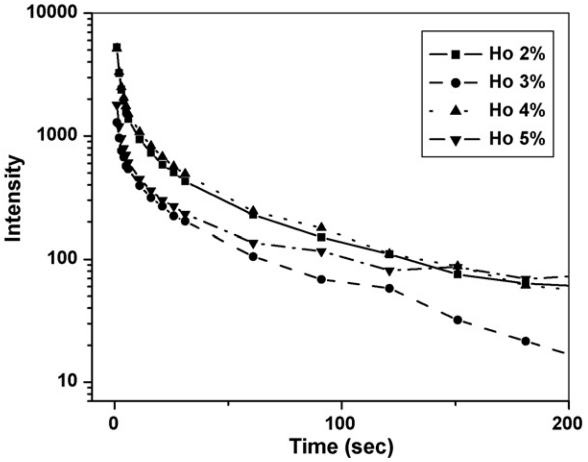

**Fig. 5.** Decay curves for $CaAl_2O_4$:$Eu^{2+}$, $Ho^{3+}$ (2, 3, 4 and 5 mol.% Ho).

electron–hole recombination process, therefore, reduce the emission intensity as well as traps responsible for the long persistence. Similar mechanism was found to be responsible for the $Eu^{2+}$ and $Nd^{2+}$ ion codoping in this aluminate phosphor which generates defect traps and results in slightly longer decay time [4]. The optimized concentration of the Eu (1 mol.%) and Ho (2 mol.%) is seems to be promising blue phosphor with longer persistent time.

## 4. Conclusions

$CaAl_2O_4$:$Eu^{2+}$ codoped with varying $Ho^{3+}$ were synthesized by solid state synthesis method. Powder XRD analysis shows that the prepared compositions retain the basic low-temperature monoclinic phase (α-phase). SEM and HRTEM investigations confirm the single-phase material with large size crystallites. The effect on PL intensity and decay time was investigated for varying $Ho^{3+}$ doping concentrations. It was optimized that the highest PL intensity is for the codoping combination of 1 mol.% Eu and 2 mol.% Ho. Decay time of the persistence for these codoped phosphors was found of several minutes.

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