Luminescence Properties of Calcium Aluminate Phosphors

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Abstract

Luminescence properties of $CaAl_2O_4$ were studied. Rare earth Eu^{2+} doped alkaline earth aluminate $CaAl_2O_4$ phosphor was prepared by combustion synthesis using urea as a fuel at 600 °C. It was found that firstly the TL intensity increases with increase in UV irradiation time and it attains a maximum value for 15 minute irradiation time. TL intensity decreases with further increase in irradiation time. In photoluminescence (PL) spectrum, a broad emission peak of Eu^{2+} ion was observed in blue region at 441 nm, under 363 nm excitation due to transition from the $4f^65d^1$ to the $4f^7$ configuration of the Eu^{2+} ion. Optimum intensity of photoluminescence (PL) was found to be 0.05 mol% concentration of Eu^{2+}.

Keywords: Thermoluminescence (TL), Photoluminescence (PL), Aluminate phosphors

1.0 INTRODUCTION

Alkali halides have been a subject of study for the past six decades. They have lent a helping hand in understanding the physics of the solid state. The alkaline earth aluminates MAl_2O_4 are an important class of phosphorescence materials because of their high quantum efficiency in visible region [1], long persistence of phosphorescence, good stability, color purity and good chemical, thermal and radiation resistance [2-3]. Rare earth and non-rare earth inorganic phosphors are widely used in a variety of applications, such as light industry, radiation measurement, X-ray imaging technique and colour display [4]. Several aluminates are used as hosts for doping rare earth ions in luminescent applications. The luminescence in the visible region of Eu^{2+} doped alkaline earth aluminates $MAl_2O_4:Eu^{2+}$ (M = Ca, Ba, Sr) phosphor is of special interest in recent years due to these compounds, which are chemically stable and safe with very bright photoluminescence properties. Several scholars have made extensive investigations concerning the next generation of displays and lighting devices [5–7]. The rare earth metal ion-doped calcium aluminate phosphors, because of their high quantum efficiency, anomalous long phosphorescence and good stability, have been studied in depth and used widely. In particular $BaAl_2O_4:Eu^{2+}$, Nd^{3+} has been considered as a useful violet phosphor in the application of luminous clocks and watches as well as potential outdoor night time displays [8]. Aluminates of Ca, Ba and Sr doped with Eu^{2+} activator ion possess safe, chemically stable and intense photoluminescence in visible light [9, 10] compared with the conventional sulfide-based phosphors. These properties make them useful in many applications, such as luminous paints in highway, airport, buildings and ceramic products, in textile, dial plate of glow watch, warning signs and the escape routes [11].

Recently many studies on phosphors with calcium aluminate as host based on their persistent luminescence and photoconductivity spectrum have been reported [12]. Many phosphors such as $CaAl_2O_4:Eu^{2+}$, Dy^{3+} [13] and $CaAl_2O_4$: Ce^{3+} [14] were developed for their photoluminescence and high chemical stability.

Thermoluminescent materials are used as passive dosimeters in a wide range of radiological applications. Alkaline earth aluminate ceramics are important host materials that have been prepared and studied by several researchers for luminescence applications. Several reports dealing with the luminescence studies of $SrAl_2O_4$, $BaAl_2O_4$ and $MgAl_2O_4$ are available in the literature. However, there are very few researchers who reported $CaAl_2O_4$ as a TL material. In the present work, we report the thermoluminescence (TL) and photoluminescence (PL) properties of UV irradiated ($CaAl_2O_4:Eu^{2+}$) phosphor to find out its suitability in dosimetry applications. A facile combustion process was chosen to prepare Eu^{2+}-doped $CaAl_2O_4$ phosphor. Thermoluminescence (TL) and photoluminescence (PL) properties of Eu^{2+}-doped $CaAl_2O_4$ phosphor have been investigated.

2.0 EXPERIMENTAL

The flow chart for a quick material screening and material elaboration shown in fig. 1.

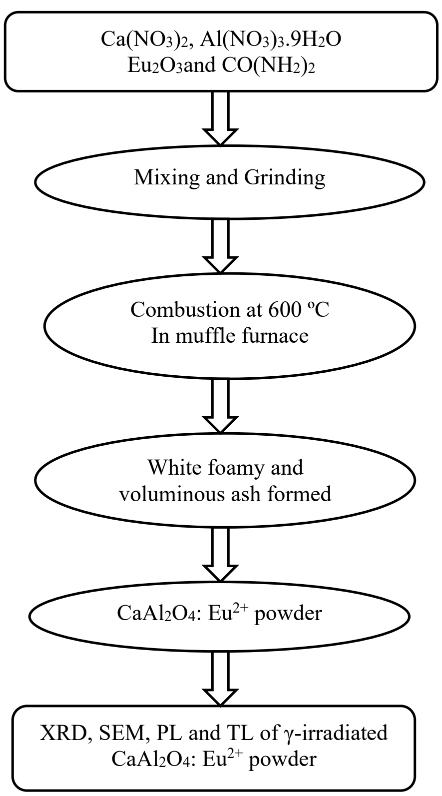

Fig. 1: Flowchart for the preparation and characterization

Analytical grade calcium nitrate $Ca(NO_3)_2$, aluminum nitrate $Al(NO_3)_3.9H_2O$, Europium oxide (Eu_2O_3) and urea ($CO (NH_2)_2$) were used as the staring materials. The starting materials were weighed according to the stoichiometry. First of all Eu_2O_3 was converted into $Eu (NO_3)_3$ by mixing Eu_2O_3 into 2 ml of dil. HNO_3. Then weighed quantities of each nitrate and urea were mixed together and crushed into mortar for 1 hour to form a thick paste. The resulting paste was transferred to crucible and introduced into a vertical cylindrical muffle furnace maintained at 600ºC initiating temperature. Initially the mixture boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases (oxides of carbon, nitrogen and ammonia). The process being highly exothermic continues and the spontaneous ignition occurs. The solution underwent smoldering combustion with enormous swelling, producing white foamy and voluminous ash. The flame temperature, as high as 1400 - 1600 ºC, converts the vapor phase oxides into mixed aluminates. The foamy product can easily be milled to obtain the precursor powder.

The crystalline structure and particle morphology of the resulting samples were investigated by X-ray diffraction analysis (XRD model D8 Advance Bruker AXS) using Cu/Kα radiation (λ = 1.54060Å). Data have been collected by step scanning 2θ from 10° to 80° and 9.6 s swept time at each step at room temperature. In order to study the surface morphology of phosphor scanning electron micrograph (SEM) were taken on a JOEL-JSM-6390A analytical scanning electron microscopy. PL was recorded using fluorescence spectrophotometer (Shimadzu RF-5301 XPC). For thermoluminescence measurement, sample was irradiated with UV light. A routine TL setup (Nucleonix TL 1009I) was used for recording TL glow.

3.0 RESULTS AND DISCUSSIONS

3.1 X-ray diffraction analysis

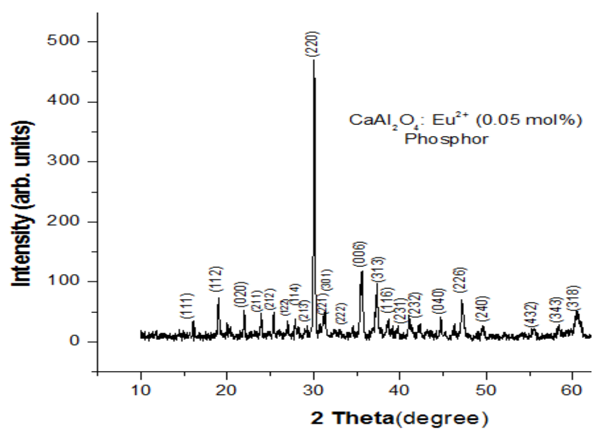

Fig. 2: X-ray diffraction (XRD) pattern of $CaAl_2O_4$:Eu (0.05) phosphor.

In Fig. 2. theXRD pattern of the prepared $CaAl_2O_4:Eu^{2+}$ is shown. 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 = 8.700, b = 8.0920, c = 15.19100 and β = 90.170. The XRD pattern matched well with that reported for $CaAl_2O_4$ (JCPDS No. 00-70-0134). The small amount of doped rare earth ions had virtually no effect on phase structure.

3.2 Surface morphology

Fig. 3. shows the SEM micrograph of the sample, revealing 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 shows a lot of voids and pores, which may have been formed by the evolved gases during combustion. The non-uniform and irregular shapes of the particle can be attributed to the non-uniform distribution of temperature and mass flow in the combustion flame.

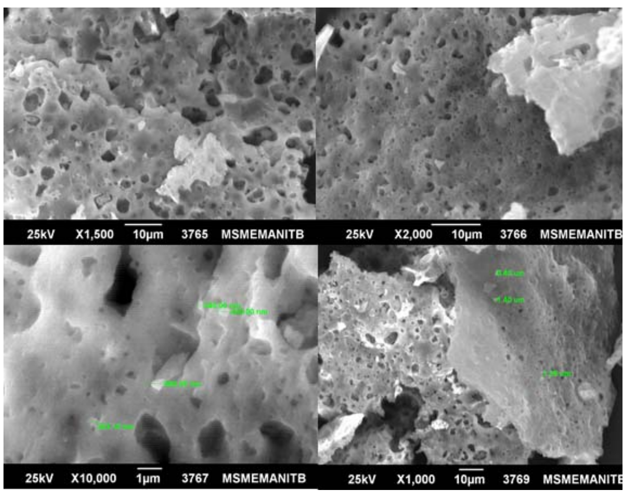

Fig. 3: SEM photograph of $CaAl_2O_4$:Eu (0.05) phosphor.

3.3 Photoluminescence

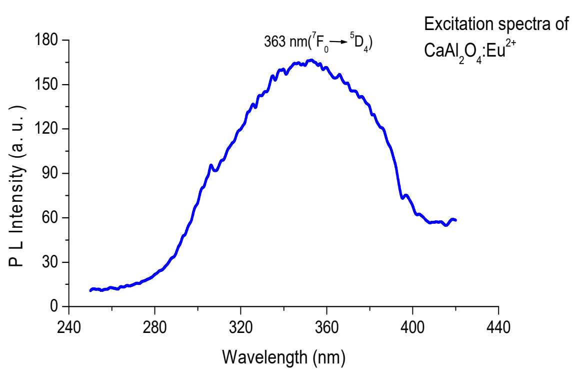

Fig. 4(a): Excitation spectra of $CaAl_2O_4:Eu^{2+}$ phosphor

Fig. 4(a) shows the excitation spectra of $CaAl_2O_4$: Eu^{2+} phosphor. In excitation spectra a broad peak centered at 363 nm is observed. This is attributed to transition between $4f^7$ ground state and $4f^6\,5d^1$ level of Eu^{2+} ions.The Photoluminescence emission spectra of $CaAl_2O_4$: Eu^{2+} (0.01, 0.02, 0.05, 0.1and 0.2 mol %) phosphors are shown in fig. 4(b). The PL emission spectra of phosphors were recorded at the excitation wavelength λex = 363 nm. Usually, the access concentration of dopant (RE elements) quenches the Photoluminescence, so it is necessary to experimentally find the critical concentration of Eu^{2+} to optimize the luminescence efficiency of $CaAl_2O_4$: Eu^{2+} under UV excitation. The emission spectra of $CaAl_2O_4$: Eu^{2+} phosphor showed one strong peak at 441 nm under 363 nm excitation. The observed emission peak at 441 nm is due to the transition of Eu^{2+} from excited state of $4f^65d^1$ configuration to the ground state $^8S_{7/2}$ of $4f^7$configuration. The optimized PL intensity is found for 0.05mol % concentration of Eu in $CaAl_2O_4$ host.

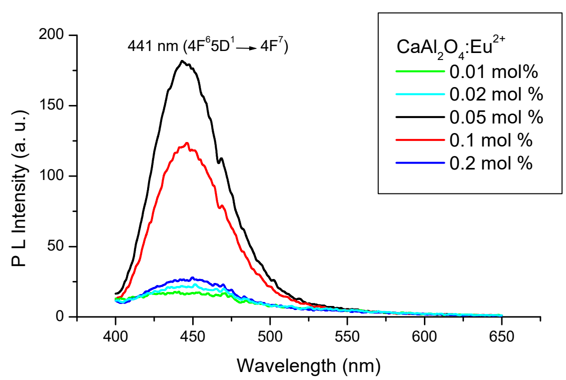

Fig. 4(b): Emission spectra of $CaAl_2O_4:Eu^{2+}$ phosphor for different doping concentrations

3.4 Thermoluminescence

Fig. 5(a) shows the TL response curve of Eu^{2+} (0.05mol %) doped $CaAl_2O_4$ phosphor for different UV exposure time. It is seen that the TL glow curve have principal glow peak at 120.8°C. It is seen that the TL intensity increases with increasing UV- dose and attains a maximum for 15 minute irradiation time (Fig.5 (b)) and it seems to be saturated for higher irradiation time. Upon further increase in UV dose, intensity decreases.

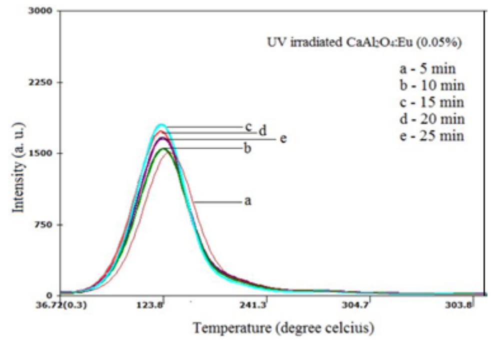

Fig. 5(a): TL glow curve of $CaAl_2O_4:Eu^{2+}$ (0.5 mol %) phosphor for different UV-irradiation time.

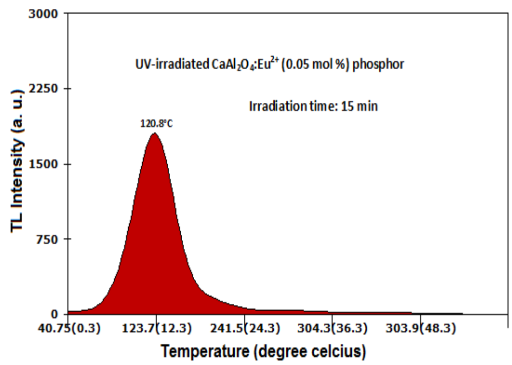

Fig. 5(b): TL glow curve of $CaAl_2O_4:Eu^{2+}$ (0.05 mol %) phosphor for 15 min of exposure time

Fig. 5(c) shows the TL emission spectra of $CaAl_2O_4:Eu^{2+}$ (0.05 mol %) phosphor. TL emission spectra show two peaks around 441 nm and 540 nm corresponding to blue color in the visible region, which is attributed to the transition $4f^65d^1 \rightarrow 4f^7$ ($^8S_{7/2}$) of Eu^{2+} ions. This is similar to the PL spectra. The similarity in TL and PL spectra exhibits that the same luminescence centre may be responsible for both.

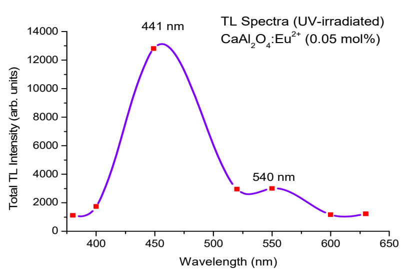

Fig. 5(c): TL spectra of $CaAl_2O_4:Eu^{2+}$ (0.05 mol %) phosphor

4.0 CONCLUSION

The TL intensity of $CaAl_2O_4$ was recorded after irradiation with UV light for different interval of time which has one peak at 120.8° C suggesting existence for trapping level. TL intensity increases with increase in UV exposure time and it is maximum for irradiation time 20 min. With further increase in exposure time, TL intensity decreases. It seems to be saturated for higher irradiation time(dose) and then the intensity decreases. TL emission spectrum shows two peaks around 441 nm and 540 nm, which can be attributed to Eu^{2+} emission and is similar to the PL spectra. This suggests that the same luminescence centre is responsible for both.

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