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Intense blue-emitting $Ca_5Al_8O_{14}$: Eu phosphor for mercury free lamp

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Abstract : The calcium aluminates doped with Eu ions, $Ca_5Al_8O_{14}$: Eu, phosphors are prepared by the combustion method. The formation of crystalline aluminates was confirmed by X-ray diffraction pattern. The prepared phosphors were characterized by SEM, TGA, DTA, particle size analyzer and Photoluminescence (PL) techniques. From the UV-excited luminescence spectra it was found that the Eu ions acts as a luminescent centre with luminescence at the blue (λ_{max} = 470 nm) region due to $4f^6 5d^1 \rightarrow 4f^7$ transition. The excitation spectra show the broad band at 355 nm wavelength (λ_{em} = 470 nm). The excitation 355 nm is a mercury free excitation and therefore $Ca_5Al_8O_{14}$: Eu may be useful for the solid state lighting phosphor in lamp industry.

Keywords : $Ca_5Al_8O_{14}$, PL, phosphor, noncentrosymmetric.

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1. Introduction

The fabrication of a blue-emitting GaN light emitting diode (LED) in 1993 [1] brought a significant revolution in lighting technology and then, the first commercial white emitting LED solid-state lighting was developed using this blue-emitting LED in 1997 [2]. It is the combination of a 460 nm blue GaN-LED and the yttrium aluminum garnet (YAG) : Ce^{3+} phosphor, which shows a bright yellow emission under excitation with blue radiation (460 nm) [3]. However, the spectral composition of the light produced by this approach is different from that of natural white light due to the poor colour rendering property caused by the lack of red component. Presently, the emission bands of LEDs are shifted to near UV range around 400 nm, which can offer a higher efficiency solid-state lighting [4]. Alternatively mixing of blue, green and red phosphors with one LED is explored [5]. The current phosphors for near UV GaN-based LEDs are

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$BaMgAl_{10}O_{17}$: Eu^{2+} for blue, ZnS : (Cu^{+}, Al^{3+}) for green and Y_2O_2S : Eu^{3+} for red [6]. However, the efficiency of the Y_2O_2S : Eu^{3+} red phosphor is about eight times less than that of the blue and green phosphors, the lifetime of Y_2O_2S : Eu^{3+} is inadequate under UV irradiation, and these sulfide-based phosphors are chemically unstable. The search for stable, inorganic rare-earth-based red phosphors with high absorption in the near UV/blue spectral region is therefore an attractive research task.

Noncentrosymmetric oxides represent an interesting class of materials owing to their technologically important properties; such as ferroelectricity a second order nonlinear optical (NLO) behaviour are the numerous applications [7]. Among them $Ca_5Al_8O_{14}$ is a noncentrosymmetric oxide with properties such as optical activity; pyroelectricity and piezoelectricity [7,8]. In this study, we concentrate on the polar crystal class of oxide $Ca_5Al_8O_{14}$ doped with Eu, is synthesized by combustion technique. The prepared phosphors are further characterized by X-ray diffraction pattern; thermogravimetric analysis, differential thermal analysis, Scanning electron microscopy (SEM) and photoluminescence techniques.

2. Experimental

The $Ca_5Al_8O_{14}$ phosphors were prepared by the combustion technique. All the reagents were of analytical purity and used without further purification. The starting materials were taken as aluminium nitrate [$Al(NO_3)_3.9H_2O$], calcium nitrate [$Ca(NO_3)_2.6H_2O$] with high purity [99.9%]. Europium oxide [Eu_2O_3] was used as europium nitrate by dissolving europium into nitric acid. The correct amount of excess urea [$CO(NH_2)_2$] was then injected into the precursor solution. Each precursor solution was vigorously stirred for 10 min until it became gelatinous. The precursor solution was then introduced into a muffle furnace maintained at 500°C. Initially, the solution underwent dehydration; then spontaneous ignition occurred followed by smoldering combustion with enormous swelling. This process produced foamy and voluminous products followed by large amount of gases.

The prepared phosphors were characterized by XRD, TG, DTA, SEM, particle size analyzer and photoluminescence techniques.

3. Results

In order to determine the crystal structure and establish chemical nature of the combustible product, XRD study was carried out. The small amount of doped rare earth ions has virtually no effect on phase structures. The result shown in Figure 1 indicates that the obtained products are of high purity and crystallinity when prepared by the combustion process.

Photoluminescence behaviour :

Eu^{2+} doped phosphors usually show intense broad band PL with a short decay time

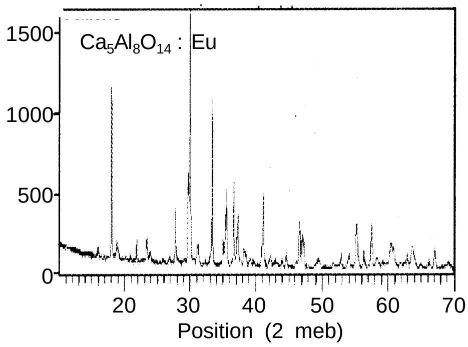

Figure 1. XRD analysis of $Ca_5Al_8O_{14}$.

of the order of nanoseconds. The emission of Eu^{2+} is very strongly dependent on the host lattice and can occur from the ultraviolet to red region of the electromagnetic spectrum. This is because the 5*d* → 4*f* transition is associated with the change in electric dipole and the 5*d* excited state is affected by crystal field effect. The Eu^{2+} emission from many phosphor hosts is intense enough to find important applications, *e.g.* in fluorescent lamps, LED and plasma display. An important class of phosphor is based on Eu^{2+} doped aluminate of alkaline earth metals.

The incorporation and stabilization of Eu ions in the sample were confirmed by luminescence investigations. The intense excitations observed in the UV region (254 nm and 355 nm) are associated with the 4*f* → 5*d* electronic transition. The broad band excitation at 355nm is due to the $4f^7(8S^{7/2}) \rightarrow 4f^6\ 5d$ transition as shown in Figure 2. It may be noted that the PL spectra of $Ca_5Al_8O_{14}$ shows intense broad Eu^{2+} emission bands peaking at 472 nm for the 355 nm excitation. This is as expected from the allowed nature of emission transition of Eu^{2+} ion between $4f^6\ 5d^1 \rightarrow 4f^7$ levels (Figure 3). The highest intensity for Eu^{2+} ion is observed for the 9-mol% concentration in $Ca_5Al_8O_{14}$ phosphor by 355 nm excitation. At 11-mol% concentration the PL intensity of phosphor is reduced due to the concentration quenching effect.

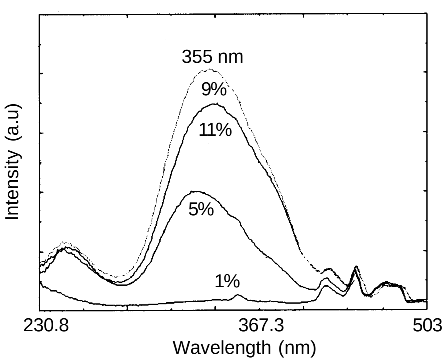

Figure 2. PL excitation spectra of $Ca_5Al_8O_{14}$: Eu.

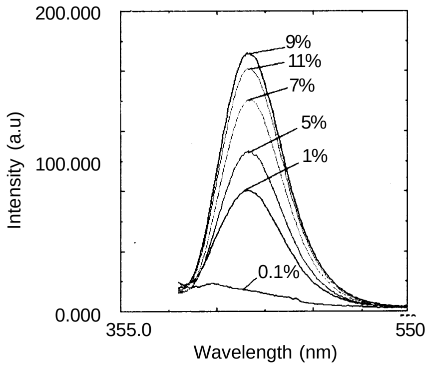

Figure 3. PL emission spectra of $Ca_5Al_8O_{14}$: Eu (λ_{ex} = 355 nm).

Scanning electron microscopy :

In order to study the morphology structure of phosphor prepared by combustion synthesis, scanning electron microscopy has been carried out. The SEM micrographs in Figure 4 shows the microstructure and the surface of the $Ca_5Al_8O_{14}$ foam. Irregularly

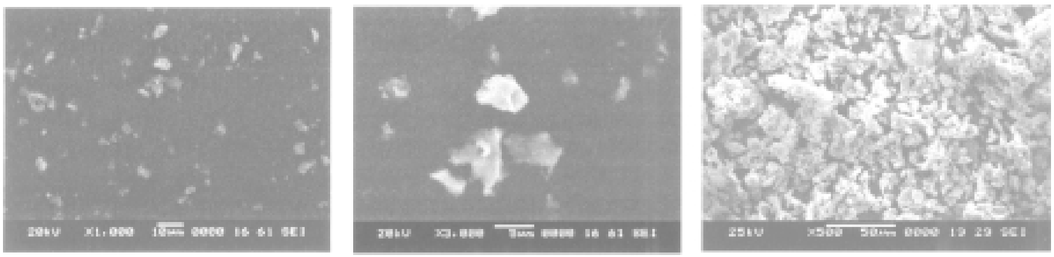

Figure 4. SEM study of $Ca_5Al_8O_{14}$: Eu.

shaped particles with sharp corners are seen in Figure 4. A wide range of distribution of particles ranging from 0.5 to 10 μm is observed. The foamy structure of phosphor reflects the inherent nature of the reaction. In case of combustion synthesis, instantaneous and *in situ* very high temperature combined with release of large volumes of volatiles from liquid mixture is likely to result in the production of particles in fluffy form. Reaction in the presence of urea allows the growth of faceted crystals. The energy-dispersive X-ray spectroscopy (EDS) of the micron phosphor shown in Figure 5 confirms that the nano-phosphors are composed of aluminium, calcium, oxygen, and europium elements (C came from the carbon tape used to support the sample), in which the platinum originates from the platinum sputtered sample for SEM measurement. Figure 6 gives the particle size distributions of sample $Ca_5Al_8O_{14}$. The average particle size observed by particle size analyzer is about 4.3 μm.

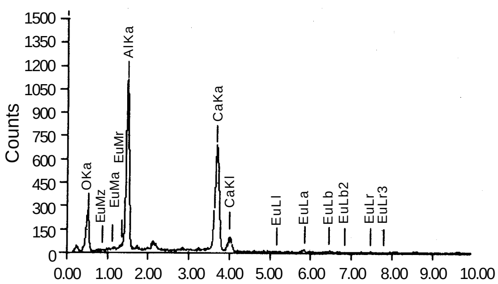

Figure 5. EDS spectrum of $Ca_5Al_8O_{14}$: Eu.

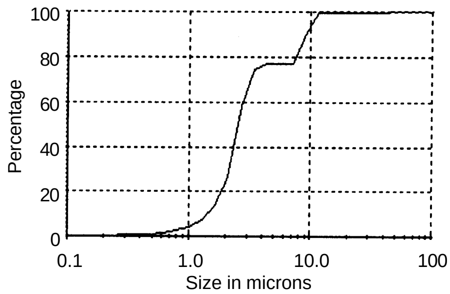

Figure 6. Particle size analysis.

Thermal analysis :

The TGA and DTA curves presented in Figure 7 indicate a significant weight loss up to 200°C, which is attributed to the moisture loss, absorbed after the thermal treatment of gel at 500°C. After 200°C the weight loss curve appears to be linear, which shows that the phosphor is stable and there is no weight loss up to 900°C. The heat flow curve shows that there is an endothermic and exothermic peak at 600°C and 800°C, which may be due to the increase in crystallinity of the sample and due to disappearance of impurity phases. According to TG curve, the total weight loss of the sample is nearly 5%, which is negligible. Hence it can be stated that the phosphor prepared by the combustion technique is thermally stable and does not decompose over a usable temperature range.

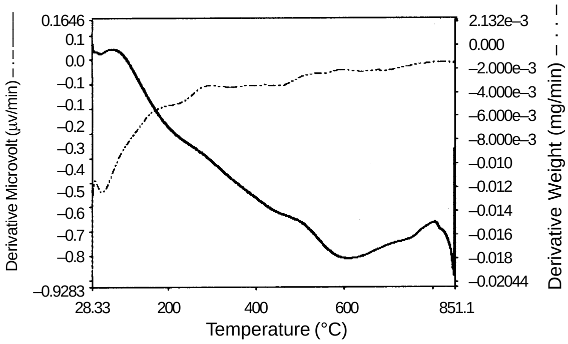

Figure 7. TGA/DTA analysis of $Ca_5Al_8O_{14}$ phosphor.

4. Conclusion

The $Ca_5Al_8O_{14}$: Eu, phosphors are prepared by the combustion method. The formation of crystalline aluminates is confirmed by X-ray diffraction pattern. The prepared phosphor is characterized by SEM, TGA, DTA and photoluminescence (PL) techniques. SEM micrograph shows the faceted 5–10 μm crystals. From the UV-excited luminescence spectra it is found that the Eu ions act as luminescent centres with luminescence at the blue (λ_{max} = 470 nm) region due to $4f^5 5d^1 \rightarrow 4f^7$ transition. The excitation spectra show a broad band at 355 nm wavelength (λ_{em} = 470 nm). The excitation at 355 nm is a mercury free excitation and therefore $Ca_5Al_8O_{14}$: Eu may be useful for mercury free lamp phosphor in lamp industry.

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