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Cr^{3+} doping optimization in $CaAl_2O_4:Eu^{2+}$ blue phosphor

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Abstract

A new composition of phosphor material $CaAl_2O_4:Eu^{2+}$ co-doped with Cr^{3+} was investigated. Various compositions with Eu^{2+} (1 and 2 mol%) and Cr^{3+} (0.05–0.1 mol%) were prepared by solid-state reaction method. These compositions show high brightness and longer persistent luminescence. Phase and crystallinity were investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Excitation and emission spectra were taken to investigate the luminescence characteristics. Broad band UV excited luminescence of the $CaAl_2O_4:Eu^{2+}$, Cr^{3+} was observed in the blue region ($\lambda_{max} = 440$ nm) due to transitions from $4f^6 5d^1$ to the $4f^7$ configuration of the Eu^{2+} ion. Cr^{3+} ion co-doping generates deep traps which results in longer afterglow phosphorescence compared to parent phosphor.

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Keywords: Blue phosphor; Solid-state reaction; XRD; SEM; TEM; Luminescence

1. Introduction

Phosphor materials having bright luminescence at low accelerating voltage are much in demand for various applications. The phosphor materials based on alkaline earth aluminates with the general formula, $MAl_2O_4:Eu^{2+}$ (M: Ca, Sr, Ba) doped with Eu^{2+} activator ion with strong photoluminescence at the blue–green visible region have been studied extensively [1–4]. It was found that the afterglow lifetime and luminescence intensity can be enhanced by co-doping with the second rare earth ion [5]. These doubly doped phosphors exhibit a rapid initial decay from the Eu^{2+} ion followed by a long persistence. This effect has been ascribed to the thermal activation of holes from traps followed by the emission of Eu^{2+} [6]. Compared to sulfide-based phosphors, Sr- and Ca-based aluminate phosphors possesses safer, chemically stable, very bright and long-lasting photoluminescence with no radiation. This open up an unexpectedly large field of applications, such as luminous paints in highway, airport, buildings and ceramics products, as well as in textile, the dial plate of glow watch, warning signs, escape routs, etc. [7].

Eu^{2+} doped phosphors usually show intense broad band photoluminescence (PL) with a short decay time of the order of tens of nanoseconds. The emission of Eu^{2+} is very strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electro-magnetic spectrum. This is because the $5d \leftrightarrow 4f$ transition is associated with the change in electric dipole and the 5d excited state is affected by crystal field effects. It is well known that the valence state of the activator dictates the emission wavelength [8]. Similarly the trivalent Eu^{3+} ions show red luminescence properties in highly stable lead-based heavy metal oxide glasses [9,10]. Notably barium and strontium aluminates have been reported to be good host material. Strontium aluminates doped with Eu have very high quantum efficiency, long persistence and better stability than the other alkaline earth aluminates. Solid-state reaction process is used intensively for the synthesis of polycrystalline phosphors materials. Phosphors of small particles are generally obtained by grinding the larger phosphor particles. Those processes easily introduce additional defects and greatly reduce luminescence efficiency [11]. With the development of scientific technologies on materials, several chemical synthesis techniques, such as co-precipitation [12], sol–gel [13], microwave [14], Pechini [15] and combustion [16] synthesis methods have been applied to prepare rare earth ions activation alkaline earth aluminate and/or its phosphors. All of these methods were conducted in liquid phases so that each com-

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ponent can be accurately controlled and uniformly mixed. The demand for phosphors in high-definition television and field-emission displays has triggered numerous studies to find new kinds of phosphors with strong chemical bonding [17]. Some emission studies on $BaAl_2O_4$:Eu^{2+} [18] and $CaAl_2O_4$:Eu^{2+}, Nd^{3+} [6] to develop intense and long-lasting phosphorescence at room temperature have been performed previously.

In this paper we present the results on the effect of Cr co-doping on crystalline structure and luminescence characteristics of $CaAl_2O_4$:Eu^{2+}, Cr^{3+} phosphor prepared by solid-state reaction method. Photoluminescence (PL) and decay time measurements were carried out. Powder XRD, SEM and TEM measurements were performed to investigate the phase and crystallinity of the synthesized material.

2. Experimental details

New blue phosphor material composition of $CaAl_2O_4$:Eu^{2+}, Cr^{3+} with the varying combinations of Eu and Cr were prepared by solid-state reaction method. Eu concentration was taken as 1 and 2 mol% and Cr concentrations was taken as 0.05 and 0.1 mol%. The combinations prepared were G.1(iii)—$CaAl_2O_4$:Eu^{2+} (1 mol%), Cr^{3+} (0.1 mol%), G.1(iv)—$CaAl_2O_4$:Eu^{2+} (1 mol%), Cr^{3+} (0.05 mol%) and G.1(v)—$CaAl_2O_4$:Eu^{2+} (2 mol%), Cr^{3+} (0.1 mol%). High purity (Aldrich make, 99.99%) raw materials; $CaCO_3$, Al_2O_3, Eu_2O_3, Cr_2O_3 and B_2O_3 were used for preparation of the charge. The quantity of the flux B_2O_3 is very crucial and dictates the calcination and reduction temperatures. 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. Well mixed and grounded powders were sintered at 900 °C for 6 h in an air atmosphere. Finally the powders were annealed at 1300 °C for 2 h in a reducing atmosphere (5% H_2 and 95% Ar) to ensure the complete reduction of Eu^{3+} to Eu^{2+}. Phase and crystallinity of the synthesized compositions were investigated by powder XRD using Rigaku D/MAX-2200V diffractometer with Cu Kα radiation. The SEM and TEM studies were done to investigate the crystallinity and surface morphology. Samples for TEM were prepared by suspending the particles in ethanol by ultrasonification and drying a drop of the suspension on a carbon coated copper grid. TEM was carried out employing Philips Tecnai G^2-20 (FEI) machine operating at 200 kV. The 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

Blue phosphor calcium aluminate, $CaAl_2O_4$ co-doped with Eu^{2+} and Cr^{3+} (1 and 2 mol% of Eu_2O_3 and 0.05 and 0.1 mol% of Cr_2O_3) were prepared and investigated. Fig. 1 shows the representative powder XRD pattern for the $CaAl_2O_4$:Eu^{2+} (1 mol%), 0.1 mol% Cr_2O_3. As can be seen, pure monoclinic phase diffraction peaks of parent $CaAl_2O_4$ are dominant in the XRD patterns, and are matching with the JCPDS data file (no. 23-1036). No other phase or unreacted starting material was observed. This confirms the synthesized phase is low-temperature monoclinic phase (α-phase). The calculated lattice parameters for monoclinic crystal system were $a = 8.703$ Å, $b = 8.097$ Å and $c = 15.216$ Å. Small amount of doped rare earth active ions

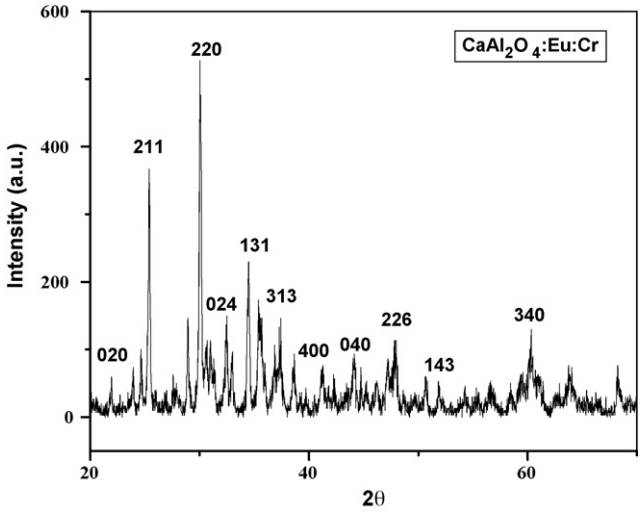

Fig. 1. Representative XRD pattern for $CaAl_2O_4$:Eu^{2+} (1 mol%), Cr^{3+} (0.1 mol%).

Eu^{2+} and Cr^{3+} has almost no effect on $CaAl_2O_4$ basic crystal structure. Scanning electron microscopy (SEM) study was carried out to investigate the surface morphology and crystallite sizes of the synthesized phosphor powder. The powder samples reduced at temperature 1300 °C were taken for these experiments. Fig. 2a–c shows the representative SEM micrographs taken for $CaAl_2O_4$:Eu^{2+}:Cr^{3+} for three different Eu and Cr combinations. It is clearly seen from these micrographs that the crystallites sizes are varying from few microns to several tens of microns. However, the crystallites are having sharp surface morphology of single crystalline grains.

The TEM study is the best tool to know about the local structure, structural transformation, particle size and morphology of the material. TEM studies were conducted to investigate the morphology and the crystallinity of the synthesized material. Fig. 3a–c shows the representative high resolution (HREM) bright field micrographs for the sample with three different Eu and Cr combinations. The corresponding selected area diffraction (SAD) patterns are inserted in the micrograph. The clarity of the HREM 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 pattern inserted in Fig. 3a–c are indicative of the crystalline particles have sufficient size to give the clear and strong diffraction spots. However, the streaks along the diffraction spots and diffuse scattering present in the SAD pattern is due to the point defects produced by doping of Eu and Cr active ions. Higher diffuse scattering and streaks can be seen for higher Eu/Cr concentration in Fig. 3c.

The prepared phosphor with new compositions exhibit blue emission. This indicates that the matrix has the monoclinic calcium aluminate phase and the Eu 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 Cr^{3+} concentrations are shown in Fig. 4a and b. The excitation spectra of the $CaAl_2O_4$:Eu^{2+} co-doped with Cr^{3+} show two broad bands, one from 230 to 290 nm and other from 300 to