Research Letter Photoluminescent Spectra of Nd³⁺ Codoped CaAl₂O₄:Eu²⁺ Blue Phosphor

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Phosphor material CaAl₂O₄:Eu²⁺ codoped with varying concentrations of Nd³⁺ was prepared by solid-state reaction method. Prepared materials with 1 mol% Eu²⁺ and Nd³⁺ (0.5 to 5 mol%) show high brightness and long persistent luminescence. The phase and crystallinity of the synthesized materials were investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Photoluminescence excitation and emission spectra were taken to investigate the luminescence characteristics. Broadband UV excited luminescence of the CaAl₂O₄:Eu²⁺, Nd³⁺ was observed in the blue region ($\lambda_{max} = 440$ nm) due to transitions from 4f⁶ 5d¹ to the 4f⁷ configuration of the Eu²⁺ ion. The Nd³⁺ ion doping in the phosphor generates deep traps which result in long afterglow phosphorescence.

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1. INTRODUCTION

The growing demand for phosphor materials in highdefinition television screens and field-emission displays has triggered targeted studies to find new phosphors [1]. Alkaline earth aluminates MAl₂O₄:Eu²⁺ (M: Ca, Sr, Ba) phosphor doped with Eu²⁺ with strong photoluminescence at the blue-green visible region have been studied extensively. The afterglow lifetime and intensity can be enhanced by codoping with the second rare earth ion [2]. Those phosphors exhibit a rapid initial decay from the Eu²⁺ 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+} [3]. Compared with sulfide phosphorescent phosphors, Sr- and Ca-based aluminate phosphors possess safer, chemically stable, very bright, and long-lasting photoluminescence with no radiation. This opens 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 and escape routine, and so forth [4]. The solid-state reaction process has been used intensively for phosphor synthesis. Phosphors of small particles are generally obtained by grinding the larger phosphor particles. Those processes easily introduce additional defects and greatly reduce luminescence efficiency [5]. It is well known that the valence state of the activator dictates the emission wavelength [6, 7]. Similarly the trivalent Eu³⁺ ions show red luminescence properties in highly stable lead-based heavy metal oxide glasses [8]. The doping of Nd³⁺ is very crucial for the development of new nonlinear optical materials [9]. With the development of scientific technologies on materials, several chemical synthesis techniques, such as coprecipitation [10], sol-gel [11], microwave [12], Pechini [13], and combustion [14] 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 component 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 [15]. Some emission studies on BaAl₂O₄:Eu²⁺ [16] and CaAl₂O₄:Eu²⁺, Nd³⁺ [3] to develop intense and long lasting phosphorescence at room temperature have been performed previously.

We present the results on the effect of Nd codoping on crystalline structure and PL characteristics of CaAl₂O₄:Eu²⁺,



FIGURE 1: Representative powder XRD pattern of $CaAl_2O_4$:Eu²⁺, Nd³⁺ (for 2, 3, and 5 mol% Nd).

Nd³⁺ 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 material.

2. EXPERIMENTAL DETAILS

Phosphor material CaAl₂O₄:Eu²⁺, Nd³⁺ with Eu concentration keeping 1 mol% and varying concentrations of Nd (0.5, 1, 2, 3, and 5 mol%) were prepared by solid-state reaction method. High purity (Aldrich make, 99.99%) raw materials, CaCO₃, Al₂O₃, Eu₂O₃, Nd₂O₃, and B₂O₃, were used for preparation of the charge. The quantity of the flux B₂O₃ 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 hours. Well-mixed and grounded powders were sintered at 900°C for 6 hours in an air atmosphere. Finally the powders were annealed at 1300°C for 2 hours in a reducing atmosphere (5% H₂ and 95% Ar) to ensure the complete reduction of Eu³⁺ to Eu²⁺. Phase and crystallinity of the synthesized compositions were investigated by powder XRD using Rigaku D/MAX-2200V diffractometer with Cu K_{α} 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 G²-20 (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 to 400 nm. The decay time was recorded using a pulsed xenon lamp and oscilloscope.

3. RESULTS AND DISCUSSION

Calcium aluminate, CaAl₂O₄ codoped with Eu²⁺, and Nd³⁺ (with 0.5, 1, 2, 3, and 5 mol% of Nd₂O₃) were prepared and investigated. Figure 1 shows the representative powder XRD pattern for the CaAl₂O₄:Eu²⁺ for 2, 3, and 5 mol% Nd₂O₃. As can be seen, pure monoclinic phase diffraction peaks of parent CaAl₂O₄ 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 = 8.702 Å, b = 8.095 Å, and c = 15.213 Å. There is no visible difference in these XRD patterns except small variation in the intensity. Small amount of doped rare earth active ions Eu²⁺ and Nd³⁺ has almost no effect on CaAl₂O₄ 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. Figures 2(a), 2(b), and 2(c) show the representative SEM micrographs taken for CaAl₂O₄:Eu²⁺ for three different Nd composition (2, 3, and 5 mol%) samples. 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.

TEM studies were conducted to investigate the effect of doping on the microstructure and crystallinity of the synthesized material. Figures 3(a) and 3(b) show the representative bright field high-resolution (HREM) image for the 2 and 5 mol% Nd samples. 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 Figures 3(a) and 3(b) are indicative of the crystalline particles having 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 are due to the point defects produced by doping of Eu and Nd active ions. Higher diffuse scattering and streaks can be seen for higher Nd concentration in Figure 3(b).

The prepared phosphor compositions exhibit blue emission. This indicates that the matrix has the monoclinic calcium aluminate phase and the Eu ion is in divalent (Eu²⁺, blue emission) rather than trivalent (Eu³⁺, red emission) state. The excitation and emission spectra for CaAl₂O₄:Eu²⁺ with various Nd³⁺ concentrations are shown in Figures 4(a) and 4(b). The excitation spectra of the CaAl₂O₄:Eu²⁺ codoped with Nd³⁺ show two broadbands, one from 230 to 280 nm and other from 290 to 380 nm corresponds to the crystal field splitting of the Eu²⁺ d-orbital. The emission is a symmetrical band at 440 nm which is attributed to the typical 4f⁶ 5d¹-4f⁷ transition of Eu²⁺ ion. When



FIGURE 2: SEM micrographs of the sample CaAl₂O₄:Eu²⁺, Nd³⁺ (for 2, 3, and 5 mol% Nd).



FIGURE 3: Representative TEM micrograph and corresponding SAD patterns of $CaAl_2O_4$:Eu²⁺, Nd³⁺, (a) 2 mol% Nd and (b) 5 mol% Nd.

the phosphor materials were doped with 1 mol% Eu^{2+} and 2 mol% Nd^{3+} , the emission spectra have highest intensity. The mechanism of the long persistence is due to the holes trapped-transported-detrapped process [17]. The Nd^{3+} ion works as traps of holes, and the trap levels lie in between the excited state and the ground state of Eu^{2+} ion. The cross-section between the trap and rare earth levels is appropriate for obtaining the effective depopulation of the excited states. After being excited by the irritation lights, electron and hole pairs are produced in Eu^{2+} ions, and the Nd^{3+} traps capture some of the free holes moving in the valence band. When the



FIGURE 4: Excitation and emission spectra of $CaAl_2O_4$:Eu²⁺, Nd³⁺ (for 0.5, 1, 2, 3, and 5 mol% Nd).

excitation source is cut off, some holes captured by the Nd³⁺ traps are thermally released slowly and relaxed to the excited



FIGURE 5: Decay time of $CaAl_2O_4$:Eu²⁺, Nd³⁺ (for 0.5, 1, 2, 3, and 5 mol% Nd).

state of Eu²⁺, finally, returning to the ground state of Eu²⁺ accompanied with emitting light. This is why this family of phosphor maintains a long persistent period after the excitation is cut off. When we further increase the Nd³⁺ concentration (above 2 mol%), the emission intensity goes down. The reason seems to be that the concentration of Nd³⁺ ions more than the optimum number produces more crystalline defects apart from the traps. These defects neutralize the electronhole recombination processes, therefore, reduces the emission intensity as well as traps responsible for the long persistence. Persistent luminescence curves for the CaAl₂O₄:Eu²⁺ phosphors are shown in Figure 5. It can be seen from these curves that the samples show quite long decay time of when the powder was efficiently activated by using a pulsed xenon lamp for 15 minutes. When the source lamp was switched off, the intensity of the persistence decreased rapidly and finally formed a stable long persistent emission for several tens of minutes (about 30 minutes to 1 hour).

4. CONCLUSIONS

Phosphor compositions $CaAl_2O_4:Eu^{2+}$ codoped with varying Nd³⁺ were synthesized using solid-state reaction method. XRD analysis shows that the synthesized compositions retain the basic low-temperature monoclinic phase (α -phase). SEM and TEM investigations confirm the single-phase material with large size crystallites. The effect on PL intensity and decay time was investigated for varying Nd³⁺ doping concentrations. It was optimized that the highest PL intensity is for the codoping combination of 1 mol% Eu and 2 mol% Nd. The decay time of the persistence indicated that the persistent luminescence phosphor has bright phosphorescence and maintains duration of several minutes.

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