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Eu Doping Effect on $CaAl_2O_4:Eu^{2+}$ Phosphor Material

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ABSTRACT

High brightness and long persistent luminescence phosphor $CaAl_2O_4:Eu^{2+}$ was prepared with varying Eu^{2+} concentration by solid state reaction technique. Synthesized materials were investigated by powder X-ray diffractometer (XRD), SEM, TEM, photoluminescence excitation and emission spectra. Broad band UV excited luminescence of the $CaAl_2O_4:Eu^{2+}$ was observed in the blue region ($\lambda_{max} = 440$ nm) due to transitions from the $4f^65d^1$ to the $4f^7$ configuration of the Eu^{2+} ion. The decay time of the persistence indicated that the persistent luminescence phosphor has bright phosphorescence and maintains a long duration. These materials have great potential for outdoor night time displays.

Key Words : Phosphor, Solid state reaction, X-ray and electron diffraction, SEM, Luminescence

1. INTRODUCTION

Phosphors with long persistent time can emit light for a long time in the darkness after irradiation with sunlight or artificial light. Eu^{2+} doped alkaline earth aluminates $MAl_2O_4:Eu^{2+}$ (where, M:Ca, Sr, Ba) phosphors with strong photoluminescence at the blue-green visible region are well studied materials. The rare earth metal ions doped calcium aluminate, $CaAl_2O_4$, phosphors, because of their high efficiency, anomalous long phosphorescence and good stability, have been studied in depth and used widely. In particular, $CaAl_2O_4:Eu^{2+}$, 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. 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 [1]. With the development of scientific technologies on materials, several chemical synthesis techniques, such as co- precipitation [2], sol-gel [3-6], microwave [7], Pechini [8] and combustion [9] 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 combustion process to prepare the precursor powders, however, has been extensively applied to the preparation of various oxide materials. 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 [10]. Some emission studies on $BaAl_2O_4:Eu^{2+}$ [11] and $CaAl_2O_4:Eu^{2+}$, Nd^{3+} [12] to develop intense and long lasting phosphorescence at room temperature have been performed previously.

In the present paper we investigate the effect of Eu concentration variation on PL of $CaAl_2O_4:Eu^{2+}$ phosphor prepared by solid-state reaction method. Powder X-ray diffraction (XRD), SEM and TEM measurements were performed to investigate the phase and crystallinity of the material. Photoluminescence (PL) and decay time measurements were carried out and results are compared for different Eu doping concentrations.

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2. EXPERIMENTAL DETAILS

Phosphor composition $CaAl_2O_4:Eu^{2+}$ with varying concentration of Eu (0.5, 1.0, 2.0 mol %) was prepared by solid state reaction technique. High purity (99.99%) raw materials (Aldrich and High Purity Chemical Institute, Japan make) $CaCO_3$, Al_2O_3, Eu_2O_3 and B_2O_3 in appropriate quantities as per the stoichiometric composition were used for preparation of the charge. Composition for each material was weighted in proper stoichiometric ratios and mixed thoroughly with acetone in an agate mortar. The resulting slurry was dried at 80°C in a vacuum oven. Well mixed and grounded powders were sintered at 900°C for 6h in an air atmosphere. Finally the powders were annealed at 1300°C for 2h in a reducing atmosphere (5% H_2 and 95% Ar) to ensure complete reduction of Eu^{3+} to Eu^{2+}.

The phase and crystallinity of the synthesized compositions were investigated by powder XRD using Rigaku D/MAX-2200V diffractometer with Cu K_a radiation. The SEM and TEM studies were done to investigate the crystallinity and surface morphology of the final powder. Philips Tecnai G2-20 (FEI) electron microscope operating at 200 kV was used for TEM experiments. The sample for TEM observation was prepared by suspending the particles in methanol by ultrasonification and drying a drop of the suspension on a carbon coated copper grid.

The photoluminescence (PL) 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 taken in the range of wavelengths from 360-700 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 also recorded using a pulsed Xenon lamp and oscilloscope.

3. RESULTS AND DISCUSSION

Calcium aluminate, $CaAl_2O_4:Eu^{2+}$ was synthesized by solid state reaction method. The Eu^{2+} concentration in $CaAl_2O_4:Eu^{2+}$ was optimized. Figure 1 shows the representative XRD pattern for the $CaAl_2O_4:Eu^{2+}$ (Eu composition 0.5 mol %). The XRD pattern shows clear monoclinic phase diffraction peaks of parent $CaAl_2O_4$ and are matched well with JCPDS data file No. 23-1036. The lattice parameters calculated from XRD data are matching well with the literature values [13]. The calculated lattice parameters for monoclinic crystal system were a=8.702 Å, b=8.095 Å and c=15.213 Å. Furthermore, a little amount of doped rare earth active ions Eu^{2+} has almost no effect on $CaAl_2O_4$ basic crystal structure.

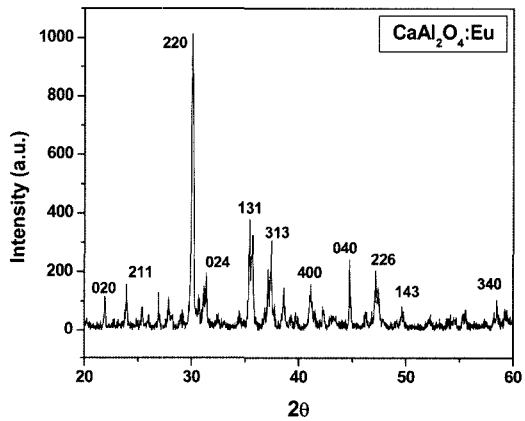
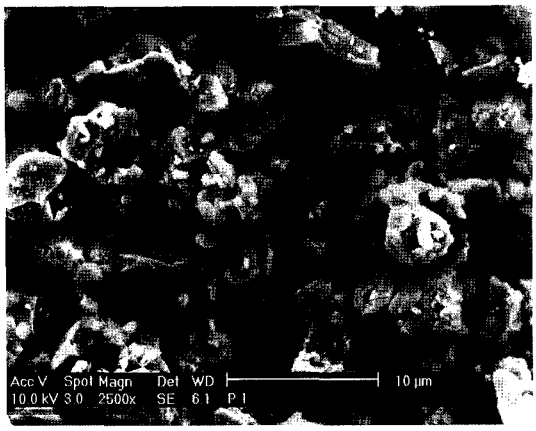


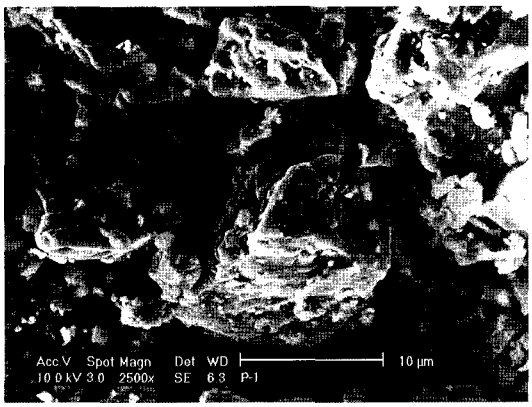
Fig. 1. Powder XRD pattern for $CaAl_2O_4:Eu^{2+}$.

Scanning electron microscopy (SEM) study was carried out to investigate the surface morphology and the crystallite sizes of the synthesized phosphor powder. The powder samples reduced at temperature 1300°C and 1325°C were taken for these experiments. Fig. 2 (a, b) shows the representative SEM micrographs taken for $CaAl_2O_4:Eu^{2+}$ for two samples reduced at two different temperatures. The crystallite size increases when the annealing temperature increases, however, there was no change in structure or optical properties of the samples. It is clearly seen from these micrographs that the crystallites sizes are varying from few microns to several tens of microns. The crystallites are having sharp surface morphology like single crystalline grains.

TEM studies were conducted to investigate the



(a)



(b)

Fig. 2. SEM micrographs for the sample $CaAl_2O_4:Eu^{2+}$, (a) at 1300°C and (b) 1325°C.

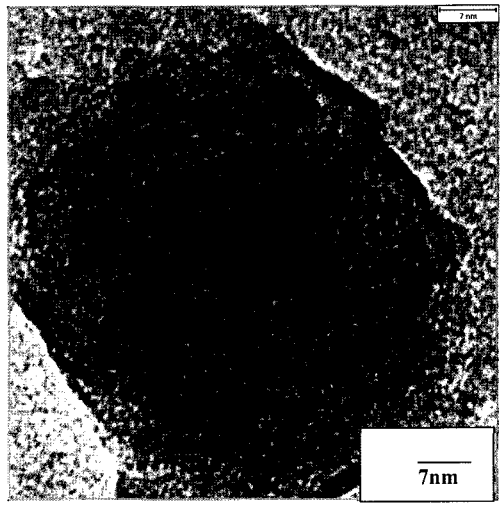


Fig. 3. TEM micrographs for the sample $CaAl_2O_4:Eu^{2+}$.

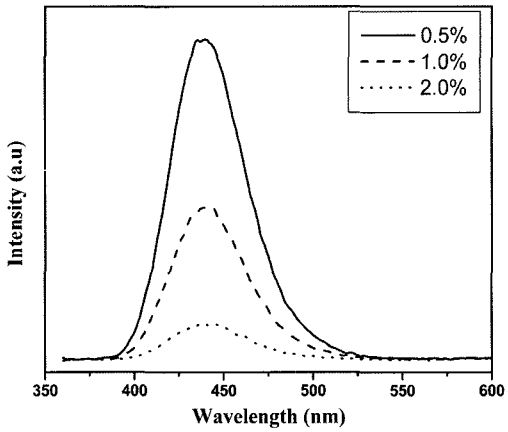


Fig. 4. Emission spectra or $CaAl_2O_4:Eu^{2+}$.

morphology and the crystallinity of the synthesized material. Fig. 3 shows the representative bright field micrograph for the sample. The micrograph shows that the micron size crystallites are formed with agglomeration. Like the scanning electron micrographs these crystallites have sharp crystalline faces. These crystalline particles have sufficient size to give the clear and strong single crystal diffraction pattern.

The prepared phosphor compositions exhibit blue emission. This indicates that the matrix already has the monoclinic calcium aluminate phase and that the Eu ion is in divalent (Eu^{2+}, blue emission) rather than trivalent (Eu^{3+}, red emission) state. The emission spectra for $CaAl_2O_4:Eu^{2+}$ phosphor (Eu concentration 1.0 and 2.0 mol %) are shown in Fig. 4. The excitation spectra of the $CaAl_2O_4:Eu^{2+}$ phosphor shows a broad band at 250 to 320 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 the typical $4f^65d^1 - 4f^7$ transition of Eu^{2+} ion. The highest emission was observed for Eu, 0.5 mol%. Higher the Eu concentration the lower the emission intensity due to creation of crystal defects in the lattice.

Persistent luminescence curves of the $CaAl_2O_4:Eu^{2+}$ phosphor (Eu concentration 0.5 mol %) is shown in Fig. 5. It is clearly seen from the decay curve that the sample shows quite long decay time when the powder was efficiently activated by using a pulsed

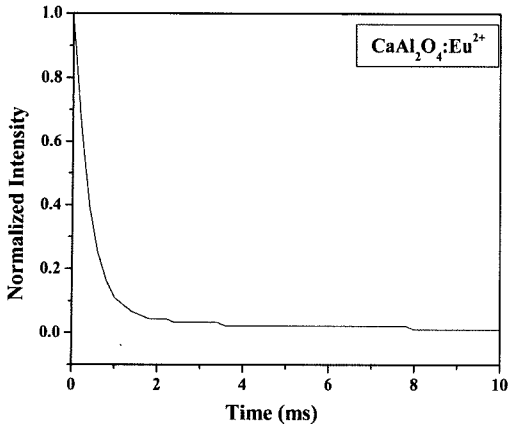


Fig. 5. Decay time for $CaAl_2O_4:Eu^{2+}$.

Xenon lamp for 15 min. When the source lamp was switched off, the intensity of the persistence decreased rapidly and finally formed a stable long persistent emission for several milliseconds.

4. CONCLUSIONS

The phosphor compositions $CaAl_2O_4:Eu^{2+}$ with varying Eu^{2+} were synthesized successfully using solid state reaction method. XRD analysis was done to investigate the solid solution for their phase and crystallinity. SEM and TEM investigations indicate the formation of single phase material with large size crystallites. The effect on PL was investigated with varying Eu^{2+} concentration. It was observed that the PL was highest for 0.5 mol % Eu concentration. The higher Eu concentration act as the crystalline defects which decreases the emission intensity. The decay time of the persistence indicated that the persistent luminescence phosphor has bright phosphorescence and maintains duration of several tens of milliseconds.

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