Research Article

Investigation of Annealing and Crystallite Size on the Photoluminescence Properties of Ca$_2$Al$_2$SiO$_7$: Eu Phosphors Prepared by Spray Pyrolysis

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Crystalline gehlenite (Ca$_2$Al$_2$SiO$_7$) phosphor, doped with Eu ions, was successfully synthesized by the spray pyrolysis method followed by annealing temperature. The crystallite size and photoluminescence characterization were investigated as function of the annealing temperature. The X-ray diffraction pattern indicates that all peaks could be ascribed to the tetragonal Ca$_2$Al$_2$SiO$_7$ phase in which the dopant could not affect the crystal structures. All annealed powders emitted red luminescence at 613 nm under excitation of 394 nm. However, at 1300 °C annealing temperature for Ca$_2$Al$_2$SiO$_7$ doped with Eu ions, the maximum photo luminescent intensity has been obtained.

1. Introduction

Recently, white light-emitting diodes (WLEDs) have received considerable attention owing in the fields of signage, displays, television (HDTV), communication, cathode ray tube (CRT), and field emission displays (FED) [1–5]. Due to its promising properties such as high luminous efficiency, energy saves, long lifetimes, and applicability for the development of smart lighting devices, it is a candidate for new lighting systems in the future [6–11]. Basically, there are two fundamental ways to produces white light by using a LED phosphor system. The first way is to combine blue InGaN with yellow emitting Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (YAG:Ce$^{3+}$) phosphors. However, this type of WLEDs shows a higher correlated color temperature (CCT) and a lower color rendering index (RI) which is due to the lack of red color component. The second way is by combining tricolor phosphor (i.e, red, green, and blue) coexisted by a near-UV. This type of combination can yield high color reproducibility and high color rendering index. However, Y$_2$O$_2$:Eu$^{3+}$ red-emitting phosphor faces some drawbacks under near UV including lower efficiency and instability compared to the BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ blue- and Ba$_2$LiSi$_7$AlN$_{12}$:Eu$^{2+}$ green-emitting phosphors due to the release of sulfide gas [12, 13].

Recently, alkaline Earth aluminosilicates have attracted much attention and become an interesting in the field of luminescent materials because of their high chemical and thermal stability, excellent hardness and water-resistant property, comparing with sulfide phosphors [14, 15]. Among, the aluminosilicate group gehlenite materials
present superior photoluminescence properties when doped with rare Earth metal ions. Rare Earth ions-doped gehlenite (Ca$_2$Al$_2$SiO$_7$) have been extensively investigated over the last few decades. For example, Er$^{3+}$ and Nd$^{3+}$ ions-doped Ca$_2$Al$_2$SiO$_7$ have broad absorption bands facilitating to make laser pumped materials. Whereas Eu$^{3+}$ ion-doped Ca$_2$Al$_2$SiO$_7$ have effectively been excited by a near-UV light due to $^5D_0 \rightarrow ^7D_4$ transition of Eu$^{3+}$ ion and emit red light as a result of $^7D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$, have been reported as a potential red phosphor used in WLEDs [16–18].

In the previous work, there are few reports on gehlenite (Ca$_2$Al$_2$SiO$_7$) doped Eu phosphors using spray pyrolysis method [19]. The obtained result was amorphous phase and the result showed that red mission was obtained. Hence, YAG: Europium phosphors by spray pyrolysis using a filter expansion aerosol generator have been reported that the intensity of photoluminescence (PL) of the amorphous phase was low due to short residence time. Postannealing was required to develop the crystallinity of the particles and to activate the dopants [20].

In this paper, we report a novel systematic experimental study on the photo luminescent properties and the red emission enhancement of Ca$_2$Al$_2$SiO$_7$: Eu phosphors were investigated as a function of annealing temperature. At last, the correlation of crystallite size and luminescence properties of phosphors was discussed.

2. Methods and Materials

2.1. Sample Preparations. Ca$_2$Al$_2$SiO$_7$:xEu$^{3+}$ sample was prepared from (Ca(NO$_3$)$_2$.4H$_2$O, 99%, Alfa Aesar, Heysham, UK), (Al(NO$_3$)$_3$.9H$_2$O, 99%, Alfa Aesar), (C$_8$H$_2$O$_4$Si, 98%, Acros, Pittsburgh, PA), and 0.14M (Eu$_2$O$_3$, 99%, Alfa Aesar), all of analytical grade (A.R.) were employed in this experiment. Diluted hydrochloric acid solution of 0.5 M was added as flux. Initially, the raw materials were weighed according to the nominal compositions of Ca$_2$Al$_2$SiO$_7$: Eu phosphor. Then, the raw materials were mixed and stirred thoroughly until the transparent precursor solutions were obtained. The transparent precursor solutions were gone through the ultrasonic atomizer system (KT-100A, King Ultrasonic, and New Taipei, Taiwan) with the frequency of 1.65 MHz. The precursor droplets were produced and passed through the furnace with three heating zones. These three heating zones provide the evaporating, calcining, and cooling functions at 250, 1000, and 350°C, respectively. The phosphor particles were collected by a charged of cylindrical stainless steel at the end of quartz tube. Finally, the collected powders were annealed at different temperatures from 1100°C to 1500°C in air for 1h.

2.2. Characterization. The phase compositions of the prepared Ca$_2$Al$_2$SiO$_7$: Eu phosphors were identified by powder X-ray diffraction analysis. XRD pattern has been obtained from Bruker D8 advanced X-ray powder. Field emission scanning electron microscope (JSM 6500F, JEOL, Tokyo, Japan) was used to observe surface morphology of phosphor particles. The PL measurements of excitation and emission spectra were recorded on a spectrofluorometer (FP8500, Jasco, Tokyo, Japan) fitted with a sensitive photomultiplier tube. This spectrofluorophotometer provides corrected excitation and emission spectra in the 200 to 600 and 550 to 750 nm ranges, respectively. All measurements were carried out at the room temperature.

3. Results and Discussion

Figure 1 shows the crystal structure of the prepared Ca$_2$Al$_2$SiO$_7$: Eu phosphors characterized by powder XRD analysis. All the diffraction peaks of the annealed Ca$_2$Al$_2$SiO$_7$: Eu phosphor were in good agreement with standard JCPDS file 35 0755.

From the diffraction peaks the crystal structure was attributed to the tetragonal Ca$_2$Al$_2$SiO$_7$ phase. This indicates that no impurity phase was found; i.e., small amount of doped europium ions does not change the gehlenite (Ca$_2$Al$_2$SiO$_7$) crystal structure. All results of XRD diagrams show that the materials have Ca$_2$Al$_2$SiO$_7$ single-phased structure with pure tetragonal phase.

As shown from Figure 2, the FE-SEM measurements reveal that the surface morphologies of Ca$_2$Al$_2$SiO$_7$: Eu phosphor powders annealed at various temperature. In Figure 2(a), the micrographs powders show that the particles were sphere particles. In Figure 2(b), the particles were almost spheroidal and have some extent of agglomeration. In Figures 2(b) and 2(c), the particles were aggregate and irregular. Furthermore, Figures 2(d)–2(e) shows that as annealing temperature increases the particles are more aggregated and agglomerated. In general, the morphological images of the prepared Ca$_2$Al$_2$SiO$_7$: Eu phosphor shows that particles were aggregated tightly due to the high temperature treatment.

At about 260 nm, in the U region, the excitation spectrum of Ca$_2$Al$_2$SiO$_7$: Eu phosphor shows a broad band...
and several sharp lines were appeared between 320 and 600 nm. As shown from Figure 3, the excitation spectrum is predominantly composed of two main parts: (1) the broad band occurs between 230 and 300 nm, in this region, the charge transfer state (CTS) band due to the europium-oxygen interactions happen, due to an electron transfer from 2p an (oxygen) orbital to an empty 4f shell of europium. (2) A different sharp line was found between 320 and 600 nm due to the f–f transition of Eu$^{3+}$ ions. At 394 nm excitations, the intense sharp peak was observed which consistent to $7F_0 \rightarrow ^5D_0$ transition of Eu$^{3+}$ ions. Different weak excitation peaks are located at 320, 382, 400, 414, 465, and 532 nm and are related to the same transition state or intraconfigurational 4f–4f transitions of Eu$^{3+}$ ions in the host matrix lattices, which can be assigned to $7F_0 \rightarrow ^5H_{6j}$, $7F_0 \rightarrow ^5D_0$, $7F_0 \rightarrow ^5G_{4j}$, $7F_0 \rightarrow ^5D_3$, and $7F_0 \rightarrow ^5D_2$ transitions, respectively. Then, the prepared Ca$_2$Al$_2$SiO$_7$: Eu phosphor can be successfully excited by near-UV (NUV) at about 394 nm effectively. Due to the effective excitations, matching with UV and NUV-LED, so the prepared phosphor greatly promises for potential practical applications of WLED.

As shown from Figure 4, the emissions were measured, in which the excitation wavelength was monitored at 394 nm. The emission spectrum was composed of a series of sharp emission lines, corresponding to transitions from the excited states $^5D_0$ to the ground state $^7F_j$ ($j = 0, 1, 2, 3, 4$). At about 588 nm, the emission of orange color was observed which belongs to the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition of Eu$^{3+}$, and the transition hardly varies with the crystal field strength. $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$, which is very sensitive to the local environment around Eu$^{3+}$ ions, which belongs to the electric dipole effects in which the red emissions were observed at 613 nm. In spite of this, it depends on the symmetry of the crystal field. Two strong peaks which were found at 588 and 613 nm emissions peaks indicate that there are two Ca$^{2+}$ positions in the

![Figure 2: SEM images of Ca$_2$Al$_2$SiO$_7$: Eu phosphor annealed at various temperatures in air.](image)

![Figure 3: Excitation spectra of ($\lambda_{em} = 613$ nm) of Ca$_2$Al$_2$SiO$_7$: Eu phosphor annealed at various temperatures in air.](image)

![Figure 4: Photoluminescence (PL) spectra of ($\lambda_{ex} = 394$ nm) of Ca$_2$Al$_2$SiO$_7$: Eu phosphor annealed at various temperatures in air.](image)
Ca$_2$Al$_2$SiO$_7$ lattice. One position, Ca (I), is inversion symmetry and the other side, Ca (II), is noninversion symmetry. Other two emission peaks located at 580 and 655 nm are relatively weak, which is corresponding to the $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_3$ typical transitions of Eu$^{3+}$ ions, respectively.

Based on the emission of Ca$_2$Al$_2$SiO$_7$ phosphors-doped Eu$^{3+}$ ions, photoluminescence intensity was measured at various annealing temperatures. The emission intensity increases with annealing temperature increases from 1100°C to 1300°C. However, above the annealing temperature of 1300°C, the emission intensity becomes decreases, which may be ascribed due to one of the following possible reasons. First, the luminescence efficiency formed from the O–Eu–O group is well known to be efficient. However, as the annealing temperature is higher than 1300°C, there is a decrease in luminescence efficiency due to the competitive relationship existing between O–Eu–O and O–Eu–Si groups, that is, decreasing the content of O–Eu–O groups decreases the efficiency of luminescence. Secondly, due to high annealing temperature by itself, this is unfavorable for high luminescence intensity [21]. From emission spectra the effect of annealing temperature does not change the position of the photoluminescence peak, as the annealing temperatures rises from 1100°C to 1500°C. As shown from Figure 5, the crystallite size was estimated by using Scherer equation (Scherer size) from XRD patterns and the relationship of crystallite size and photoluminescence are shown in Figure 5 inset. As annealing temperature increases from 1100°C to 1300°C, the crystallite size increases in which the photoluminescence intensity also increases, which shows there is the enhancement of grain growth, which results in better crystallinity of Ca$_2$Al$_2$SiO$_7$:Eu and similar result was observed in the Y$_2$MoO$_{12}$ system [22].

However, beyond 1300°C, the crystallite size of the Ca$_2$Al$_2$SiO$_7$: Eu phosphor decreased. The reason is the enlarged nanoparticles size and increased defects could cause a higher probability of nonradiative transitions [23]. At higher temperature, there is a crystal growth and agglomeration of particles; as a result, there will be a decrease in PL intensity due to the light scattering. Luminescence properties of Ca$_2$Al$_2$SiO$_7$:Eu under annealing temperature demonstrated that it can be efficiently excited under UV light. Consequently, it can be applied as a promising candidate in phosphor-converted WLEDs.

As shown from Table 1, the $x$ and $y$ coordinates of the Ca$_{2-x}$Al$_2$SiO$_7$:xEu phosphors lie in the range of (0.635–0.637) and (0.362–0.365), respectively. The obtained CIE coordinates indicate the red-light emission. As seen from Figure 6, the CIE chromaticity diagram indicates the color purity of Ca$_2$Al$_2$SiO$_7$: Eu phosphors are very close to those corresponding dominant wavelength points, and pure red color purity phosphors have been obtained.

![Figure 5: Correlations of crystallite size and annealing temperature (inset: PL spectra vs. annealing temperature) of Ca$_2$Al$_2$SiO$_7$: Eu phosphor at ($\lambda$exc $=$ 394 nm).](image)

![Figure 6: CIE chromaticity diagram of Ca$_2$Al$_2$SiO$_7$: Eu phosphors annealed at various temperatures in air.](image)

| Temperature (°C) | $x$    | $y$    |
|------------------|--------|--------|
| 1100             | 0.636  | 0.363  |
| 1200             | 0.636  | 0.364  |
| 1300             | 0.637  | 0.362  |
| 1400             | 0.636  | 0.364  |
| 1500             | 0.367  | 0.362  |

Table 1: CIE chromaticity coordinates of Ca$_2$Al$_2$SiO$_7$: Eu phosphors as a function of temperature difference ($\lambda$exc $=$ 394 nm).
4. Conclusions

The effects of annealing temperature on the photoluminescence of Ca2Al2SiO7: Eu phosphor particles were successfully studied. Doping of europium with gehlenite phosphors does not affect the crystal structures rather enhancement of photoluminescence intensity occurs. Pure Ca2Al2SiO7: Eu phase and good crystallite were successfully prepared. The strongest emission peak at 613 nm attributed to $^5D_0$ $\rightarrow$ $^7F_2$ transition of Eu$^{2+}$ ions. The emission intensity was greatly dependent on annealing temperature, and the highest luminescence intensity was obtained at annealing temperature of 1300°C. The results indicated that the Ca2Al2SiO7 phosphor with a higher crystallite size had the strongest PL emission. In summary, a correlation can be established based on the relationship of annealing temperature and PL properties. As a result, crystalline Ca2Al2SiO7: Eu luminescence properties demonstrated that it can be efficiently excited under UV light and therefore, it can be applied as a promising phosphor candidate in phosphor-WLEDs.

Data Availability

The data used to support the findings of this study are included in the article.

Conflicts of Interest

No potential conflicts of interest were reported by the authors.

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