Luminescent Characteristics of Blue Phosphor $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ in White LED Applications by Solid State Method

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Abstract. Using the solid state reaction method, we synthesize the $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor powders at different sintering temperatures ranging from 1100 to 1500 °C. From X-Ray diffraction patterns, we confirmed that all the samples acquired mixed $\text{CaAl}_2\text{Si}_2\text{O}_8$ (triclinic), CaAlO_4 (Monoclinic) and SiO_2 (Hexagonal) phases. For the $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphors, the excitation spectra exhibited an unresolved broad band in the range from 200 to 420 nm and maximum intensity at 350 nm. The emission spectra of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ show broad band ranging from 400 to 560 nm and maximum wavelength is found to be at around 440nm, which can be ascribed to the electric-dipole-allowed $4f^65d^1 - {}^8\text{S}_{7/2}(4f^7)$ transition of the Eu^{2+} ions. The Commission International De L'Eclairage 1931 (CIE 1931) chromaticity coordinates for $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphors are calculated and represented at (0.168, 0.144).

1 Introduction

Light emitting diodes (LED) are the promising candidates for next generation solid lighting material owing to their lower energy consumption, high brightness, environmentally-friendliness, fast switching, small in size, longer lifetime and high efficiency, which starts to approach the theoretical limits[1-2]. White light emitting diodes (WLEDs) are usually fabricated with blue InGaN LED chips and yellow phosphors such as Ce^{3+} doped yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$), Eu^{2+} doped oxynitrides, and $\text{Eu}^{2+}/\text{Ce}^{3+}$ doped silicate based materials[3-6].

Eu^{2+} have been widely used for activators in phosphor materials [7-8]. Much attention has been paid towards the luminescent properties of Eu^{2+} ions activated compounds and the reduction processes of Eu^{3+} to Eu^{2+} in phosphor preparations. The Eu^{2+} ion shows broad emission bands excited by ultra-violet (UV) light (320 - 400 nm), arising from interconfigurational $4f^65d^1$ (excitation state) – $4f^7$ (ground state) allowed transition [9-10]. This transition is strongly dependent on the crystal fields of the host lattices since 5d orbitals are more sensitive to the ligand field. Accordingly, the Eu^{2+} becomes a very useful activator in phosphors for applications in displays, lamps and luminescent paintings [11]. In general, the reduction of ionic state from Eu^{3+} to Eu^{2+} needs sintering process in reduce atmosphere

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such as H_2/N_2 or carbon. If the reduction of Eu^{3+} to Eu^{2+} can be realized in air condition, it would highly reduce the cost and increase the safety in preparing the Eu^{2+} -activated phosphor materials [12-14].

Aluminum silicate is well known as a long-persistent phosphor host with high chemical stability and water resistance. The alkaline-earth materials of $\text{MAl}_2\text{Si}_2\text{O}_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) have drawn much attention for their good luminescence properties [15-17]. These compounds exhibit strong $4f^65d^1 - 4f^7$ luminescence on doping Eu^{2+} . A series of solid solutions containing isostructural members with slightly different size cations as hosts, such as $\text{MAl}_2\text{Si}_2\text{O}_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) would be an ideal system to study the effect of crystal chemical variation on the luminescence of Eu^{2+} ions, and may offer possibilities for commercial application [18, 19].

In this paper, study of the solid state reaction, sintering temperature dependent photoluminescence characteristics of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$, is reported. Also, lifetime and CIE chromaticity coordinates of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ have been discussed with PL spectra behaviour.

2 Experiment and measurement

The powder of the $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor was synthesized using a solid state reaction method. At first, $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ precursor powder was prepared by taking stoichiometric molar ratio of calcium carbonate (CaCO_3 , 99.95%, Aldrich), silicon dioxide (SiO_2 , 99.5 %, Aldrich), aluminium oxide (Al_2O_3 , 99.9%, Aldrich), europium oxide (Eu_2O_3 , 99.99 %, Aldrich). All reagents were taken without any further purification and mixture, then powders were grinded and mixed by the planetary ball-milling method. Powders have been sintered at 1100 - 1500 °C. Here we have increase temperature from room temperature to given sintered temperature with 4 °C per a minute, then all samples are keep in sintered temperature for 4 hour in carbon atmosphere, respectively.

The sintered phosphors were ground using an alumina mortar. The thermal properties of the precursors were examined by a thermogravimetric-differential thermal analysis (TG-DTA) at a heating rate of 4 °C/min. And the crystal structure of the phosphor was obtained by X-Ray diffractometer (PHILIPS X'Pert-MPD) with $\text{CuK}\alpha = 1.546 \text{ \AA}$ radiation at 40 kV and 30 mA. The X-ray diffraction patterns show the intensities of the diffraction peaks as a function of the detecting angle 2θ . The interplaner spacing (d), matching peaks our samples and reference for JCDPS data, is calculated using the software X'pert High Score Plus. Miller indices were then assigned to the reflection peaks in the diffraction patterns by comparing the data obtained from the samples. Both the photoluminescence and lifetime measurements of emission bands of the phosphors were recorded on the luminescence spectrophotometer (Photon Technology International (PTI)) with a Xe-arc lamp (60 W) as an excitation source.

3 Results and discussions

Figure 1. Thermogravimetric-differential thermal analysis curves of $\text{CaAl}_2\text{Si}_2\text{O}_8$ precursor in air

Figure 1 shows the TG-DTA measurements of $\text{CaAl}_2\text{Si}_2\text{O}_8$ precursor, which were carried out to monitor the decomposition process in the host lattice. The endothermic peaks and weight loss were observed until 161 °C. The weight loss is originated from the evaporation of water molecules in the precursor samples. In the heat absorbing section between 161 and 640 °C, one can see the weight loss again. It means that the absorbing section arise from the weight loss due to the decomposition of the remaining evaporation of water molecules and organic material. After 660 °C, endothermic behaviour without weight loss is confirmed and it means that remaining materials participate in the synthesis.

Figure 3. XRD patterns of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{3+}_{0.12}$ phosphors at different sintering temperatures

The XRD pattern of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor synthesized at 1100 - 1500 °C for 4hour under reduce atmosphere are shown in Figure 2. The main peaks of phosphors from XRD pattern corresponding to $\text{CaAl}_2\text{Si}_2\text{O}_8$ (JCDPS 41-1486, triclinic), CaAl_2O_4 (JCDPS 34-0440, Monoclinic) and SiO_2 (JCDPS 33-1161, Hexagonal) phase. Samples were crystallized into a triclinic phase with a space group of P-1. The calculated lattice constants sintered at 1300 °C were $a = 8.1430 \text{ \AA}$, $b = 12.8789 \text{ \AA}$, and $c = 14.1828 \text{ \AA}$, which are very close to the corresponding values ($a = 8.1756 \text{ \AA}$, $b = 12.8720 \text{ \AA}$, $c = 14.1827 \text{ \AA}$) in the standard JCPDS 41-1486. We have observed the increasing the intensity of the CaAlO_4 until 1300 °C, then the intensity gradually decreasing, and opt-out silicone oxide in the reaction is confirmed by increasing intensity of SiO_2 marked as triangle body in Fig 2.

Figure 2. XRD patterns of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{3+}_{0.12}$ phosphors as a function of sintering temeprature

FE-SEM images in Figure 3(a) - (e) of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor represent the particle shape and surface at each sintering temperature. The particles shows increasing irregular shape with increasing the sintering temperature. Also, the average particle and the crystallite sizes are increases depending on sintering temperature. The average crystallite sizes are displayed in Fig 5. Interestingly, we have observed the significantly increased average crystallite sizes until 1300 °C. After 1300 °C, the average crystallite size is almost independent on sintering temperature. Note that the particle size is increased with temperature. This can be explained by the Ostwald ripening process [20]. As shown in Figure 3(f), EDS was used to examine the elemental composition of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{3+}_{0.12}$ powder sintered at 1300 °C. The EDS spectrum of the $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{3+}_{0.12}$ powder shows the presence of Calcium (Ca), Aluminum (Al), Silicone (Si) and Europium (Eu), but other components are not detected.

Figure 4. (a) PLE and (b) PL spectra of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphors as a function of sintering temperature

Figure 4 shows the measured photoluminescence (a) excitation (PLE) and (b) emission (PL) spectra of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ at different sintering temperatures. The PLE spectrum monitored by the emission at 440nm exhibited a broad band within the range from 200 to 420 nm, which can be assigned to the transitions from the ground state $^8\text{S}_{7/2}(4f^7)$ to the crystal-field-split components of the $4f^65d^1$ configuration. The excitation band represent a triple overlapping peaks cantered at 320, 350 and 380 nm. The 320 nm (t_{2g}) and 380 nm (e_g) are due to the result of 5d orbital separation caused by crystal field splitting peaks, and 350nm is excitation by CaAl_2O_4 [21-22]. The $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor displayed blue luminescence excited by near-UV light. The emission spectrum of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ have a broad band from 400 to 670 nm with a maximum wavelength of about 450 nm, which can be ascribed to the electric dipole-allowed $4f^65d^1-8\text{S}_{7/2}(4f^7)$ transition of the Eu^{2+} ions. PL spectra indicate wide emission region extending to green region. It is obtained triple multi emission band consisted with wave length of 440, 460, and 505 nm by Gaussian-fitting method as shown in figure 4(b). The transition from $5D^1$ to be ground states can be split by crystal field. Actually, the emission bands are possible due to the allowed character of the $5d \rightarrow 4f$ transitions, and also to the existence of 460 nm of alkaline earth sites available for the activator. Although Eu^{2+} can occupy into the interstitial site in SiO_2 crystal [23]. Therefore, the overlapped 460nm and 505nm are due to different Eu^{2+} site in $\text{CaAl}_2\text{Si}_2\text{O}_8$ and this make different environment to Eu^{2+} . Also, the other emission peak (440 nm) is caused by CaAl_2O_4 [24]. From the inset of Figure 4(b), one can see the strongest peak in the blue region described by the coupling of 440 nm and 460 nm. In the emission spectrum, a third contribution in the yellow range around 560 nm is clearly visible. Phosphor converted LEDs (pc-LEDs), based on a blue $\text{In}_{1-x}\text{Ga}_x\text{N}$ diode and a yellow phosphor which is kind of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ [3-6], suffered from a low color rendering due to the lack of green and red light in the spectrum and of inherently high correlated color temperatures (CCT). To solve this problem consists by using a cyan phosphor with a small Stokes shift and uses a violet or near UV excited diode in

combination with an additional blue phosphor. Therefore, it is completely explained that $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphors have good color rendering.

Figure 5. Comparison of PL, PLE intensity and average crystallite size of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphors at the sintering temperatures ranging from 1100 - 1500 °C

Figure 5 shows comparison of PL, PLE intensity and average crystallite size of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphors at different sintering temperatures from 1100 - 1500 °C. We have calculated average crystallite size using the Scherrer equation expressed as $D = k\lambda/\beta\cos\theta$, where D is the average grain size, k (0.9) is a shape factor, λ is the Cu-K α wavelength (1.5406 Å) of X-ray, β is the full width at half maximum (FWHM) and θ is the diffraction angle of an observed peak, respectively. PLE and PL intensity is well matched with the average crystallite size. PLE and PL intensity is to reduce, and average crystallite size is increased above 1400 °C. PL and PLE intensity are affected by $\text{CaAl}_2\text{Si}_2\text{O}_8$ and CaAl_2O_4 . PL and PLE spectra of $\text{CaAl}_2\text{Si}_2\text{O}_8$ and CaAl_2O_4 have a similar region. This result is in good agreement with XRD patterns. Therefore, the maximum PL and PLE intensity was confirmed at 1300 °C for both $\text{CaAl}_2\text{Si}_2\text{O}_8$ and CaAl_2O_4 .

Figure 6. Luminescence decay curves at room temperature of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{3+}_{0.12}$ phosphors as a function of sintering temperature

The lifetime decay curves from $4f^65D^1 \rightarrow 4F^7$ transition of Eu^{2+} are shown in Figure 6. Decay curve of the all samples can be fitted by a double-exponential function,

$$I(t) = I_1\exp(-t/\tau_1) + I_2\exp(-t/\tau_2) \rightarrow \ln I(t) = \ln[I_1\exp(-t/\tau_1) + I_2\exp(-t/\tau_2)] + C \quad (1)$$

where I is a luminescence intensity at time, I_1 , I_2 and C are constants, τ_1 and τ_2 are decay times. The lifetime for the emission of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ sintered at $1300\text{ }^\circ\text{C}$ sample is $\tau_1 = 9.739\text{ }\mu\text{s}$ and $\tau_2 = 38.643\text{ }\mu\text{s}$. This decay properties are independent on sintered temperature or defects on $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ powders such as CaAl_2O_4 and SiO_2 . It is explained that $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ phosphors have same emitting mechanism ($4f^65D^1 \rightarrow 4F^7$ transition of Eu^{2+}) and similar emission region.

Figure 7. CIE 1931 color coordinates of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor sintered at $1300\text{ }^\circ\text{C}$. The inset picture shows the photographs of blue light emission by near-UV light

Table 1. CIE 1931 color coordinates of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor sintered at $1300\text{ }^\circ\text{C}$

Sintering temperature ($^\circ\text{C}$)	X	Y
1100	0.176	0.166
1200	0.172	0.158
1300	0.168	0.144
1400	0.171	0.156
1500	0.175	0.172

CIE 1931 chromaticity coordinates of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor for different sintering temperature displayed in Table 1. In addition, CIE 1931 color coordinate of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor was presented in Figure 7. The CIE coordinate of $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphor sintered at $1300\text{ }^\circ\text{C}$ located at blue region (0.168, 0.144), and CIE coordinate of other samples are almost similar values.

4 Conclusions

The $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ phosphors were prepared by a solid state reaction method. The sintering temperature influences the structural properties, which were confirmed by analysing the XRD patterns, SEM images and luminescence properties. XRD patterns indicate that phosphors have mixed phases of both $\text{CaAl}_2\text{Si}_2\text{O}_8$ (JCDPS 41-1486 triclinic) and CaAl_2O_4 (JCDPS 34-0440 Monoclinic). The Eu^{2+} ion was well occupied in monoclinic crystalline structure. Luminescence properties of

$\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ have PL ($\lambda = 440$ nm) and PLE ($\lambda = 350$ nm) maximum intensity at 1300 °C. PL spectra have emission region extending to green region. Hence, based on the short life time, CIE coordinates and wide blue region of the broad PL spectra, $\text{Ca}_{0.88}\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}_{0.12}$ could be a potential blue color emitting candidate, which can be used to improve the quality of white.

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