Structures and luminescence properties of Eu^{2+}- doped α-sialon phosphors for UV-LED

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Abstract Eu^{2+}-doped α-sialon phosphor was synthesized and structures and various luminescence properties were studied. High crystalline Ca$_{0.8}$Al$_{2.8}$Si$_{9.2}$O$_{1.169}$N$_{14.94}$ phase was successively obtained for undoped and Eu^{2+}-doped samples. Eu^{2+}-doped α-sialon phosphor exhibited wide absorption in ultra violet (UV) and visible range, and high broad emission band peaking at from 570 to 582 nm. The optimum compositions and process conditions was obtained from 0.75 mol% Eu^{2+}–doped Ca$_{0.8}$Al$_{2.8}$Si$_{9.2}$O$_{1.169}$N$_{14.94}$ fired at 1650 °C for 2 h in 30% H$_2$–70% N$_2$ atm. In addition, fabrication of UV-light emitting diode (LED) lamp using this phosphor was conducted and the optical properties were measured. Relative quantum efficiency of the phosphor and luminous efficiency of the lamp were 83.66% and 35.28 lm/W, respectively. Those results indicated that Eu^{2+}-doped α-sialon phosphor in this study was a good candidate for UV-LED light source.

Keywords Eu^{2+} · α-Sialon · Phosphor · UV-LED · Structures · Luminescence properties · Process conditions

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1 Introductions

Recently, white LED was under a rapid development for new light source, which had merits such as a high efficiency, long life-time and low power consumption [1–3]. In the first generation of white LED, blue-emitting (460 nm) chip packaged with Y$_3$Al$_5$O$_{12}$:Ce^{3+}(YAG) yellow phosphor, namely, blue-LED has been used [2, 3]. However, a low color rendering index (CRI) of blue-LED limited its commercialization as a new light source. Therefore, there were enormous researches for the next generation of white LED consisted of UV-emitting (380×420 nm) chip with red, green, blue (RGB) or red, yellow, green, blue (RYGB) phosphors (UV-LED) [4, 5].

Especially, phosphors excited in UV-range around 400 nm have been rarely reported because most existing oxide phosphors were excited below far from 400 nm. On the other hand in nitride host, higher covalency of nitrogen than that of oxygen makes its excitation band locate in higher wavelength. In addition, larger ligand-field splitting due to nitrogen broadens emission band. Therefore, there have been lots of researches on oxynitride or nitride phosphors in the last few years [6–16].

As an oxynitride phosphor, Eu^{2+} doped α-sialon was widely studied as a yellow phosphor [6–14]. Actually, sialon ceramics has been developed for structural engineering applications because of good mechanical and chemical properties such as strength, hardness, thermal shock resistance and wear resistance [17–19]. These ceramics were stabilized by incorporation of Y, Li, Ca or rare earth oxide elements [19]. Krevel et al. reported Ce^{3+}- and Eu^{2+}-doped M-α-sialon (M = Y, Ca) could be applied for green and yellow phosphors [6]. Ca-α-sialon has the maximum excitation peaks at 254 and 365 nm and the maximum

emission peak at 580 nm. Xie et al. synthesized Ce^{3+}- or Eu^{2+}-doped α-sialon using hot pressing (HP) and gas pressure sintering (GPS) [7–10]. Phosphor synthesized by GPS showed emission band at 590 nm and became a good candidate for blue LED. Fabrication of this phosphor with blue LED has been conducted by Sakuma and luminous efficiency of 25.9 lm/W was achieved at room temperature with a forward-bias current of 20 mÅ [11]. Eu^{2+}-doped β-sialon has been also studied and green light was emitted [12]. Recently, Eu^{2+}-doped Ca,Y-α-sialon with emission at over 590 nm were reported [13, 14]. However, those phosphors required relatively difficult process such as GPS or carbothermal reduction process (CRN) to obtain a single α phase. In this study, Eu^{2+}-doped Ca-α-sialon phosphor was synthesized by conventional solid state reaction method using horizontal tube furnace, and structures and luminescence properties of this phosphor were analyzed. In addition, from the fabrication of UV-LED lamp using this phosphor, we evaluated the possibility of applying this phosphor to yellow phosphor in RYGB ones for UV-LED as a new lighting source.

2 Experimental

Eu^{2+}-doped Ca-α-sialon phosphors were prepared by a solid state reaction method. $CaCO_3$ (Acros, 99.9%), AlN (kojundo, 99.9%), α-Si_3N_4(LC Stark, α content 90%, oxygen content <1.2%) and Eu_2O_3 (kojundo, 99.9%) were used as the as-received raw materials. After weighed out in the appropriate amounts, sample powders were subsequently mixed and ground in high-purity isopropyl alcohol using ball milling for 4 h. After being dried at 90 °C, sample powders were transferred into the alumina boat. Subsequently, those mixtures were fired in a horizontal tube furnace at 800 °C for 2 h in N_2 atm to evaporate CO_2 from $CaCO_3$. Second annealing was carried out at various temperatures under flowing various H_2–N_2 mixed gas controlled by mass flow controller. After firing, the samples were gradually cooled down in the furnace.

X-ray diffraction (XRD, Rigaku, DMAX 2000) pattern analysis was conducted using Cu-Kα radiation ($\lambda = 1.5418$ Å). For analysis of luminescence characteristics, diffuse reflectance was measured by a spectrophotometer (Shimadzu, UV3101PC). $BaSO_4$ (reflection ×100%) was measured in advance for calibrations. The excitation and emission spectra were achieved by luminescence spectrometer (Perkin-Elmer, LS50B) equipped with 200 W Xe-lamp and red-sensitive photo-multi-tube (Hamamatsu, R928). To evaluate the possibility as a yellow phosphor for warm-white UV-LED light, bullet type LED lamp was fabricated with various amounts of the phosphor and optical properties were measured. The UV-LED chip was die-bonded on the cup at the lead pin and

connected to the other lead by wire bonding. Various amount of phosphor powders were dispersed into transparent Si resin. The mixture of resin and phosphor powders was poured into the chip-bonded cup and cured in oven. Using the same resin, a lens was formed by casting and second curing was conducted at higher temperature. We have measured the various optical properties such as radiant power, radiant flux, emission spectra, and commission international de L'Eclairage (CIE, France, 1931) chromaticity coordinates using integrated sphere of 10-inch diameters and spectrometer (Lapsphere, CDS1100). To reduce a measuring error as possible, ten lamps were prepared for each measuring sample.

3 Results and discussion

Figure 1 shows XRD patterns of (a) undoped and (b) 10 mol% Eu^{2+}-doped samples fired at 1650 °C for 2 h in 30% H_2–70% N_2 atm. Patterns of all the samples were completely matched with those of hexagonal α-sialon ($Ca_{0.8}Al_{2.8}Si_{9.2}O_{1.169}N_{14.94}$ (JCPDS #33–0261)) phase with P31c space group. Until doping concentration of Eu^{2+} was 10 mol%, no another phase was detected except unreacted AlN (JCPDS #79–2497). Generally, α-sialon has been synthesized using HP or GPS process to gain a single α phase [14, 15]. In this work, however, high crystalline α-sialon phase was successively achieved using conventional tube furnace annealing.

Eu^{2+}-undoped and doped α-sialon powders were fired at 1650 °C for 2 h in 30% H_2–70% N_2 atm and diffuse reflection spectra of those samples were measured as shown in Fig. 2. Sample powder without Eu^{2+} doping exhibited a gray white daylight color, which indicated no absorption in visible range as shown in spectra. The estimated absorption edge was around 280 nm, which was clearly corresponded to
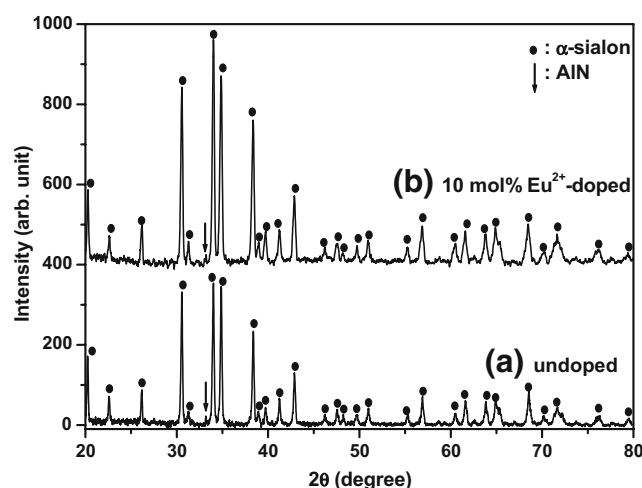

Fig. 1 XRD patterns of (a) undoped and (b) 10 mol% Eu^{2+}-doped samples fired at 1650 °C for 2 h in 30% H_2–70% N_2 atm
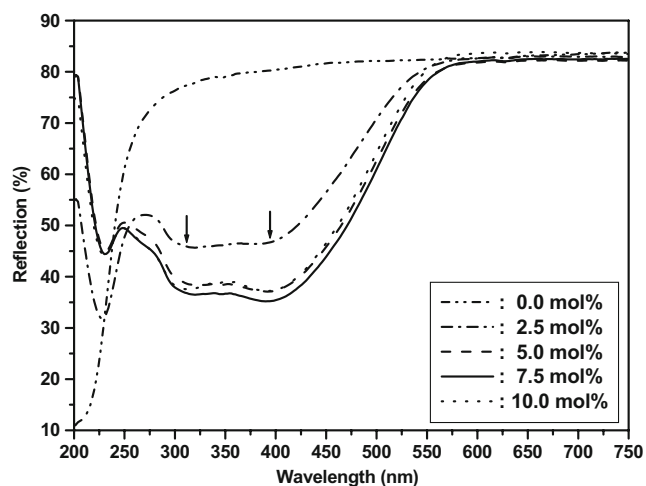
Fig. 2 Diffuse reflectance spectra of various amount of Eu^{2+}-doped samples fired at 1650 °C for 2 h in 30% H_2–70% N_2 atm

transition between conduction and valence band of host lattice. As Eu^{2+} was doped, the daylight color of powders changed into bright yellow. When 2.5 mol% Eu^{2+} was doped, two additional broad bands were detected peaking at 310 and 395 nm, obviously from absorption of doped Eu^{2+} ions. With increase of doping concentrations, red shift of reflection edge was detected, but negligible. The maximum absorption was obtained when doped Eu^{2+} concentration was 7.5 mol%.

The excitation and emission spectra were obtained for the samples with various Eu^{2+} doping concentrations (Fig. 3). All the samples were fired at 1650 °C for 2 h in 30% H_2–70% N_2 atm. In excitation spectra, all the samples showed strongest peaks at 393 nm and a few peaks ranged in 400×490 nm. Four small peaks positioned between 410 and 460 nm were proved as dummy ones from Xe-lamp because these peaks always appeared regardless of the phosphors. The other peaks were obviously attributed to 4f–5d inner transition of Eu^{2+} ion. Generally, excitation bands from 4f–5d transition of rare-earth metal in oxide
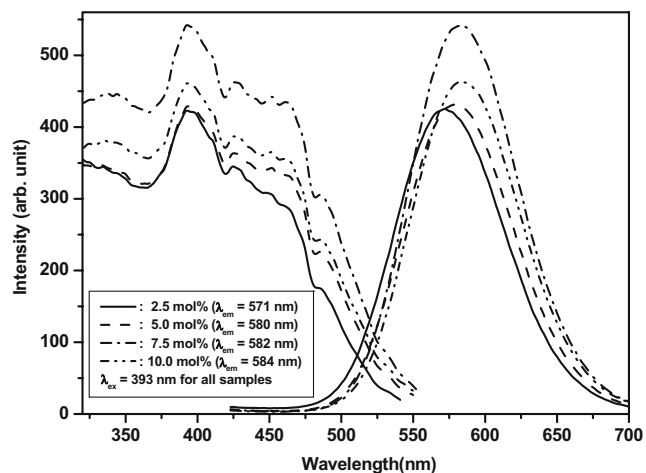
host appeared below 400 nm with narrow band width. The broad excitation band ranged in 350×520 nm indicated that nitrogen around activator strongly influence on energy levels of Eu^{2+} ions (nephelauxetic effect). It was noticeable that excitation bands completely matched with those of the reflection spectra. This result showed that excited energy from the incident light was effectively transferred to the lowest level of 5d shell without dissipation. With increase of doping concentration, noticeable change of the excitation spectra was not observed. From above results, Eu^{2+}-doped α-sialon in this research might be proper for UV as well as blue LED applications.

In the emission spectra, broad emission band was observed and slightly red-shifted from 571 to 584 nm proportional to Eu^{2+}-doping concentrations. Broader emission band than that of general oxide host might be due to the high crystal-field splitting of 5d levels of Eu^{2+} ions. In addition, the red shift of the emission bands with increase of the doping concentration could be explained by the increase of Eu^{2+} incorporations into matrix. More distortion of host lattice from incorporations of large Eu^{2+} ions resulted in larger crystal-field splitting around the activator. The similar phenomena had been reported in Eu^{2+}-doped $M_2Si_5N_8$ system (M = Ca, Sr, ba) [15, 16]. The maximum emission intensity was gained when 7.5 mol% Eu^{2+} was doped.

Photoluminescence properties with process conditions such as firing temperature and atmosphere were researched. Figure 4 exhibits the excitation and emission spectra of samples fired at various temperatures in 30% H_2–70% N_2 atm. With increase of firing temperatures, noticeable peak shifts were not detected, and the maximum intensity was gained from the sample fired at 1650 °C. Different from the excitation spectra, the emission spectra changed with firing temperatures. As the temperature increased, the strongest
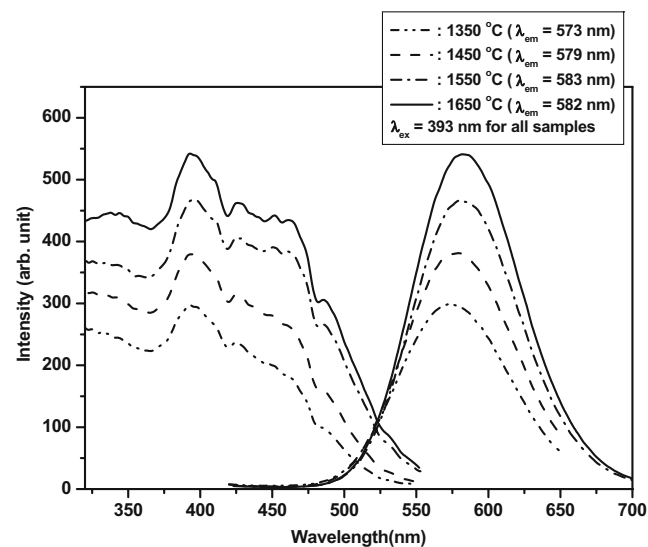

Fig. 3 Excitation and emission spectra of various amount of Eu^{2+}-doped samples fired at 1650 °C for 2 h in 30% H_2–70% N_2 atm

Fig. 4 Excitation and emission spectra of 7.5 mol% Eu^{2+}-doped samples fired at various temperatures for 2 h in 30% H_2–70% N_2 atm
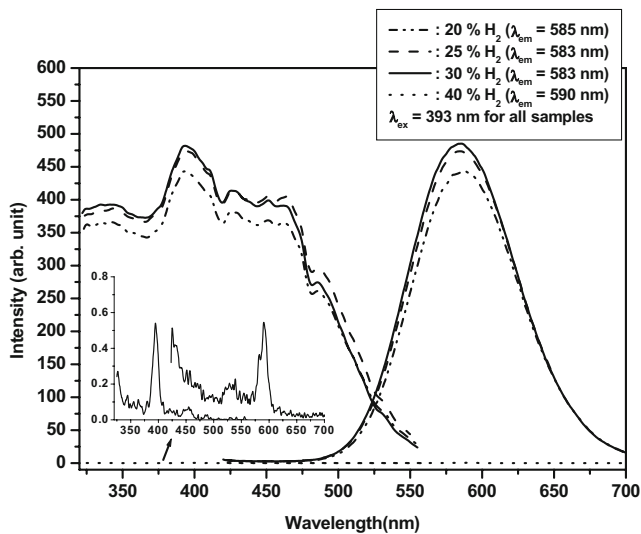
Fig. 5 Excitation and emission spectra of 7.5 mol% Eu^{2+}-doped samples fired at 1650 °C for 2 h in various atmospheres

peak moved from 573 to 582 nm, and this movement was terminated when the temperature was 1550 °C. Form the results, when higher heat energy was supplied, larger crystal-field splitting also occurred from the incorporation of Eu^{2+} ions into a matrix.

Firing atmosphere did not change the excitation and emission bands except the intensity. Figure 5 shows the excitation and emission spectra of samples fired at 1650 °C in H_2–N_2 atm with various H_2 contents. The inset is magnified spectrum of sample fired under 40% H_2–60% N_2 atm. The maximum intensity was gained from the sample fired in 30% H_2–70% N_2 atm. After fired under flowing 40% H_2–60% N_2 mixed gas, the sample was completely molten. We crushed this sample and measured luminescence properties as shown in the inset. Only sharp excitation and emission peaks with negligible intensity were detected. These spectra were often observed when Eu^{2+} ions were not properly positioned in matrix, but generally at grain boundary or surface. This might be explained by that high reduction lowered melting temperature of host, consequently, Eu^{2+} ions precipitated from molten host.

To evaluate the possibility of being applied for UV-LED light, sample powders were packaged with UV-LED chip and electrode for measuring the luminous efficiency. We selected 7.5 mol% Eu^{2+}-doped α-sialon fired at 1650 °C for 2 h in 30% H_2–70% N_2 atm. Before the measurement of phosphor's efficiency, luminescence characteristics of UV-LED chip only with Si resin were measured. The peak wavelength was 403.2 nm with full width at half maximum (FWHM) of 15 nm. Radiant power was 10.3 W with a forward-bias of 20 mA. CIE chromaticity coordinates at excitation wavelength of 403.2 nm was (0.1721, 0.016). After the phosphors with various amount were applied, relative quantum efficiency of phosphor was calculated

from the below equation. W_{bare} means the radiant power from chip with bare Si resin which phosphor powders were not mixed. W_{chip} and $W_{phosphor}$ mean radiant powers from LED chip and phosphor, respectively, when phosphor powders were applied. Ideally, W_{bare} must be equal to $W_{chip} + W_{phosphor}$ when all energy from chip transferred to phosphor powders. However, there is always a difference between W_{bare} and $W_{chip} + W_{phosphor}$ because of the heat loss during the operation.

$$\text{Relative quantum efficiency} = W_{phosphor} / \left(W_{bare} - W_{chip} \right)$$

Figure 6 shows the emission spectra of LED lamp consisted of transparent Si resin and various amount of phosphors (3, 5, 7%). The inset shows the summary of optical properties of the lamp. The emission peak from the chip was shown around 403 nm and decreased largely with increase of mixed phosphor amounts. The broad emission band from the phosphor was also shown with maximum and dominant wavelength of 583 and 591 nm, respectively. The emission intensity and peak position from phosphor were rarely changed with increase of the applied phosphor amounts. When 3% phosphor powders were applied, relative quantum efficiency of 83.66% was gained. With increase of amount of applied phosphor, the efficiency decreased. Although the decrease of $W_{phosphor}$ was negligible, the large decrease of W_{chip} was occurred, which became main factor for the decrease of efficiency as a result. The large decrease of W_{chip} indicated that when more powders were mixed, the more reflection by phosphor powders occurred, and reduced the escaping light outward as a consequence. When 3% phosphor was applied, the luminous efficiency was 35.28 lm/W, which is better than that of conventional incandescent lamps. The typical luminous efficiency of incandescent lamps is 16×18 lm/W
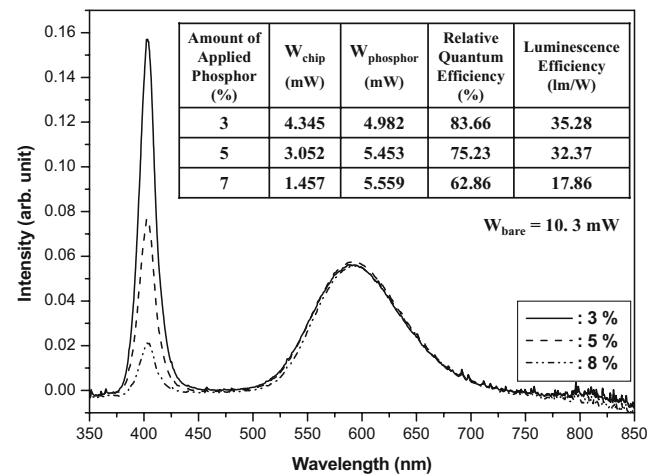

Amount of Applied Phosphor (%)	W_{chip} (mW)	$W_{phosphor}$ (mW)	Relative Quantum Efficiency (%)	Luminescence Efficiency (lm/W)
3	4.345	4.982	83.66	35.28
5	3.052	5.453	75.23	32.37
7	1.457	5.559	62.86	17.86

W_{bare} = 10. 3 mW

Fig. 6 Emission spectra of UV-LED lamp consisted of various amount of phosphor samples fired at 1650 °C for 2 h in 30% H_2–70% N_2 atm. Inset is summary of the optical properties of UV-LED lamp

[12]. CIE chromaticity coordinates of the lamp were changed from (0.4536, 0.4237) to (0.5330, 0.4958). From above results, Eu^{2+}-doped α-sialon phosphor was proved to have potential to be applied for UV-LED light source.

4 Conclusions

Eu^{2+}-doped α-sialon phosphor was synthesized using conventional annealing system, and structure and luminescence properties were measured. Hexagonal $Ca_{0.8}Al_{2.8}Si_{9.2}O_{1.169}N_{14.94}$ phase was successively obtained and no changes were observed with increase of Eu^{2+} doping concentrations. Eu^{2+}-doped α-sialon phosphor exhibited wide absorption in UV and visible range and broad emission band peaking at 570×582 nm. The optimum process condition was gained from the sample firing at 1650 °C for 2 h in 30% H_2–70% N_2 atm. From measuring the luminescence properties of the fabricated UV-LED lamp with this phosphor, high relative quantum efficiency (83.66%) and luminous efficiency (35.28 lm/W) were obtained. From the results, Eu^{2+}-doped α-sialon phosphor synthesized in this study was proved to be a good candidate for UV-LED lamp phosphor.

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