

Synthesis of $\text{CaSiAlN}_3 : \text{Eu}^{2+}$ phosphor by liquid phase precursor method

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The synthesis of $\text{Ca}_{0.92}\text{AlSiN}_3 : 0.08\text{Eu}^{2+}$ (CASN : Eu) phosphor was investigated by a carbothermal reduction and nitridation (CRN) reaction using a liquid-phase precursor (LPP) method. The carbon source for CRN reaction was prepared by a precursor of the LPP method, and carbonization of the precursor was carried out at 300 °C. CASN : Eu phosphor was constructed through the CRN reaction at synthesis temperatures of 1500 and 1600 °C. The obtained CASN : Eu phosphors were of a mixed powder with AlN. The main emission spectra of the CASN : Eu phosphors were located at 630 nm, and the main excitation spectra were in the range of 370-470 nm.

Key words: $\text{CaSiAlN}_3 : \text{Eu}^{2+}$, Phosphor, Nitride, LPP, CRN.

Introduction

White LEDs are emerging as one of the most promising eco-friendly light sources due to their lower energy consumption (and lower CO₂ gas emissions) than conventional incandescent lamps [1]. White light in LEDs can be realized by mixing multicolor LEDs or phosphor-converted LEDs (pc-LEDs). Phosphor-converted white LEDs (pc-WLEDs) have been developed for various lighting devices such as indicators, automobile headlights, decorative lamps, and LCD backlights due to their excellent properties such as superior life time [2], brightness, long lifetime, low applied voltage, and high power efficiency, which promise significant reductions in power consumption and environmental pollution [3, 4]. Since the excitation sources used for phosphors in LEDs are UV (360-410 nm) or blue light (420-480 nm), it is important that the phosphors have a high absorption of UV or blue light. The most commonly used phosphor in phosphor-converted LEDs is the yellow-emitting YAG:Ce phosphor [5]. The pc-LEDs also utilize other types of phosphors such as orthosilicates [6, 7], aluminates [8], and sulfides [9]. However, most oxide-based phosphors have a problem with low absorption in the visible-light spectrum. The luminescence properties of sulfide-based phosphors degrade significantly under ambient atmospheric conditions since they are thermally unstable and very sensitive to moisture. In order to obtain high-performance phosphors for LEDs, nitride-based phosphors are considered as good alternatives compared with oxide- and sulfide-based phosphors.

Luminescence properties of rare-earth-doped III-V group nitrides such as AlN, GaN, InGaN, and AlInGaN have been studied intensively due to their potential applications in blue-UV optoelectronic and microelectronic devices [10]. Silicon-based nitride phosphors have received significant attention in recent years because of their encouraging luminescent properties (excitability by blue light, high conversion efficiency, and the possibility of full color emission), as well as their low thermal quenching and high chemical stability, and high potential for use in white LEDs [11]. Recently, a new nitride system, CaAlSiN_3 (CASN), which is isostructural with ASi_2N_3 (A = Li, Na) and crystallizes in the Cmc2₁ space group [12], has drawn much attention due to its potential applications in white LEDs. CaAlSiN_3 (CASN) phosphors show interesting luminescent properties with a broad band emission in the range of 630-680 nm when doped with Eu^{2+} under excitation in the UV and blue visible range. The synthesis of high-quality CASN : Eu phosphors generally requires critical preparation conditions such as high temperature (≥ 1800 °C) and high pressure (≥ 10 Mpa) due to the chemical and thermal inertness of the starting materials [13]. In the present work, we utilized a novel liquid-phase-precursor (LPP) method demonstrated for other types of phosphors such as silicates and phosphates [14] to obtain CASN : Eu^{2+} phosphors at low synthesis temperature under normal atmosphere.

Experiment Section

$\text{CaAlSiN}_3 : \text{Eu}^{2+}$ (CASN) phosphors were synthesized by carbothermal reaction and nitridation (CRN) method based on a liquid-phase precursor (LPP) method called the LPP-CRN method. The synthesis route is as follows:

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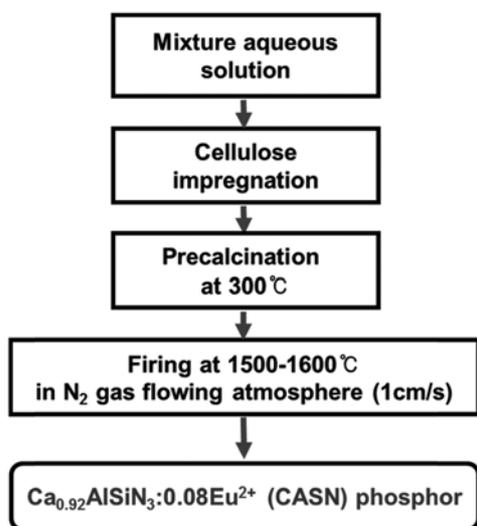
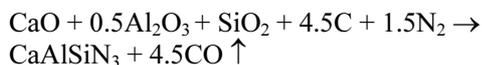


Fig. 1. Flow chart showing the synthesis procedure for CASN : Eu phosphor by LPP method.



The precursor of $\text{Ca}_{0.92}\text{AlSiN}_3 : 0.08\text{Eu}^{2+}$ phosphors was prepared via cellulose ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$, 20 μm , Aldrich) impregnation by an aqueous solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.0%, Aldrich), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.5%, Aldrich), $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.98%, Aldrich), and SiO_2 sol (20.0%, particle size 10 nm, Nissan Chemical Industries Ltd., Japan), which were dissolved in deionized water at mass fractions of 20.0 wt%, 50.0 wt%, 10.0 wt%, and 20.0 wt% in a stoichiometric ratio. The impregnation of the aqueous solution with a cellulose ratio of 50 wt% was carried out for 24 hrs. The impregnated cellulose was dried at 80 °C for 6 hrs and calcined in air at 300 °C for 3 hrs. The obtained particle precursor was ground thoroughly in a mortar and set into a carbon crucible positioned in an alumina boat, and then the alumina boat was inserted into a horizontal alumina tube furnace. The firing temperatures were 1500 °C and 1600 °C for 5 hrs with a heating rate of 5 °C/min in an N_2 atmosphere flowing at 1 cm/s. A brief flow chart of the LPP method is described in Fig.1.

The obtained samples were examined by a double scanning powder X-ray diffractometer (XRD, $\text{Cu K}\alpha$, $\lambda = 1.5406$, 40 kV, 20 mA, Rigaku) with a step size of 0.02° (2θ) and scan speed of $6^\circ/\text{min}$. The surface morphology was observed by scanning electron microscopy (SEM, HITACHI S-3000H, JEOL; FE-SEM, 7600, JEOL). The identified elements of the phosphor particles on the surfaces were measured by energy dispersive spectroscopy (EDS).

The photo-luminescence (PL) properties of the phosphors were evaluated using a uorescent spectrometer (Drasa PRO 5300, 500W, Korea) equipped with a xenon lamp as the excitation source. All the measurements were carried out at room temperature.

Results and Discussion

Fig. 2 shows the powder X-ray diffraction of CASN:Eu phosphors fired at 1500 °C and 1600 °C. The X-ray patterns of samples indicated a mixed phase of CaAlSiN_3 and AlN , corresponding to JCPDS # 39-0747 and 76-0566. The CASN : Eu phosphor obtained at 1500 °C showed low crystallinity and an amorphous pattern at $10\text{-}20^\circ$. The phosphor was more crystalline as the synthesis temperature increased.

Fig. 3 shows the SEM images of a precursor carbonized at 300 °C and CASN : Eu phosphor fired at 1500-1600 °C. The carbonized precursor had 100-nm nanosized particles, as shown in Fig. 3(a). The CASN : Eu particles with a size of $\sim 2 \mu\text{m}$ obtained at 1500 °C were agglomerated into flake shapes, as shown in Fig. 3(b). With increasing temperature, the CASN : Eu particles grew to $\sim 10 \mu\text{m}$ at 1600 °C, as shown in

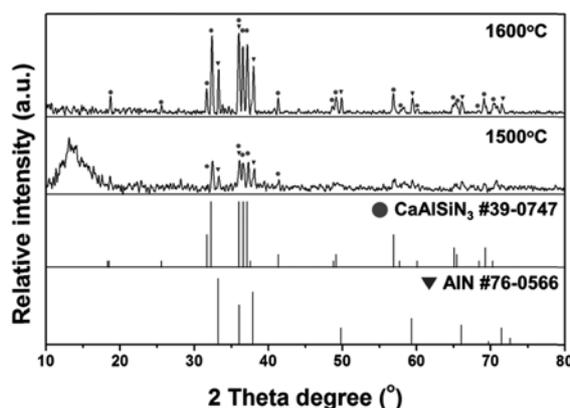


Fig. 2. X-ray diffraction patterns of CASN : Eu phosphor obtained at 1500-1600 °C by LPP method; ● CaAlSiN_3 (#39-0747), ▼ AlN (#76-0566).

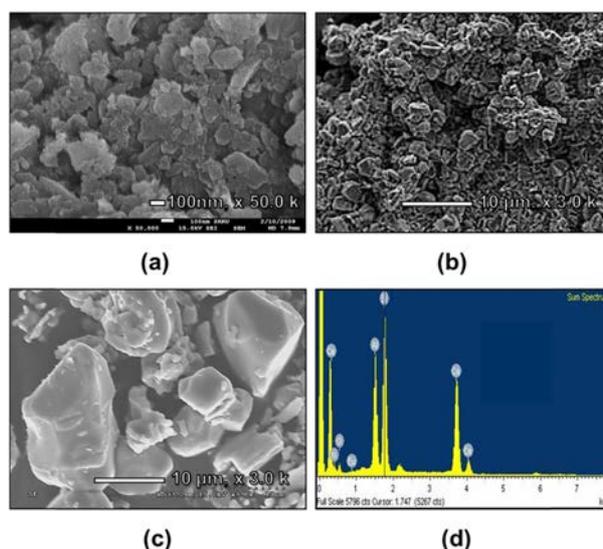


Fig. 3. SEM images of precursor prepared at 300 °C (a); CASN : Eu phosphors synthesized by LPP method at 1500 °C (b); 1600 °C (c); EDS measurement of CASN : Eu phosphor synthesized at 1600 °C (d).

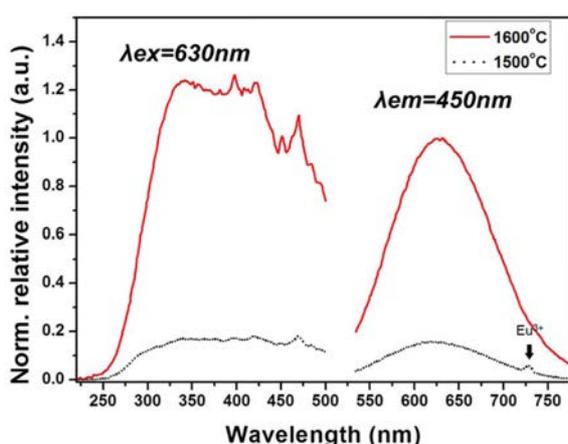


Fig. 4. PL properties of CASN : Eu phosphors synthesized by LPP method at 1500 °C (dot-line); 1600 °C (solid line).

Fig. 3(c). The sample consisted of Ca, Eu, Al, Si, O, and N elements, as confirmed by the SEM-EDS analysis shown in Fig. 3(d).

Fig. 4 shows the PL properties of the CASN : Eu phosphors fired at 1500 °C and 1600 °C. The broad excitation spectra, which were effective in UV and blue light, were due to the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} ions, and the emission spectra monitored at 450-nm excitation showed red emission at 620-630 nm due to the $4f^65d^1 \rightarrow 4f^7$ ($^8S_{7/2}$) transition. The emission properties of the samples at 1500 °C showed a little luminescence of Eu^{3+} ions at ~ 725 nm with f-f transition, indicating insufficient reduction of Eu^{3+} ions to Eu^{2+} ions. The emission intensity was 15% compared with that of the sample obtained at 1600 °C. This difference was due to the insufficient reaction at 1500 °C and low crystallinity. The photoluminescence excitation (PLE) spectra obtained by monitoring the 630-nm wavelength exhibited a broad band ranging from 220 nm to beyond 500 nm with a maximum located at 330-470 nm, indicating that the phosphor can be excited by ultraviolet (UV) light.

The small excitation band at about 240 nm takes place due to the electronic transition between the valence and the conduction bands of the CaAlSiN_3 host. The broad excitation bands are attributed to the electron transfer between $4f_7$ and $4f_65d_1$ of Eu^{2+} [15].

Therefore, the CASN : Eu phosphor monitored at 630 nm covered an intense excitation spectrum in the wavelength range of 330-470 nm, which matched well with the emission range of a blue LED chip.

Conclusions

$\text{Ca}_{0.92}\text{AlSiN}_3 : 0.08\text{Eu}^{2+}$ (CASN) phosphor was syn-

thesized at 1600 °C for 5 hrs under a flowing N_2 atmosphere (1 cm/s) by carbothermal reduction and nitridation (CRN) reaction using a liquid-phase precursor (LPP) method. The X-ray patterns of samples indicated a mixed phase of CaAlSiN_3 and AlN. The particle size of the precursor was ~ 100 nm, and the CASN particle size was ~ 10 μm . The broad excitation spectra were located from 220 nm to beyond 500 nm due to the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} ions, and the emission spectra monitored at 450 nm excitation showed red emission at 630 nm due to the $4f^65d^1 \rightarrow 4f^7$ ($^8S_{7/2}$) transition.

Acknowledgments

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