

Luminescence properties of Eu_2O_3 -doped $\text{Ca}_2\text{Si}_5\text{N}_8$ phosphors

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Using Eu_2O_3 to dope, Eu^{2+} -activated $\text{Ca}_2\text{Si}_5\text{N}_8$ phosphors were synthesized and their luminescence properties were investigated. Dark yellow and orange day-light-colored phosphors were achieved with broad and high absorption in the ultra violet (UV)/visible range of 300-550 nm. The photoluminescence characteristics with various Eu^{2+} -doping concentrations were observed. The oxidation from Eu_2O_3 influenced not only emission but also the excitation spectra of the phosphors. Broad band emissions were achieved and the strongest peak positions were shifted from 588 to 613 nm with an increase of the dopant, Eu_2O_3 concentration. A large emission tunability and a high solubility of activators-h absorption in the UV range and broad red emission make phosphors in this study excellent candidates for UV-light emitting diode (LED) conversion phosphors.

Key words: Eu^{2+} , $\text{Ca}_2\text{Si}_5\text{N}_8$, Phosphor, Oxidation, UV-LED.

Introduction

Recently, white LEDs were under rapid development for general illumination, which have merits such as a high efficiency, long life-time and low power consumption [1,2]. In the first generation of white LEDs, blue-emitting (460nm) chips were packaged with $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}^{3+}$ (YAG) yellow phosphor, namely, blue-LEDs have been used [3,4]. However, a low color rendering index (CRI) of the blue-LED limited its commercialization as a new light source for a general illumination. Therefore, there was extensive research for the next generation of white LEDs consisted of UV emitting (380-420 nm) chips with red, green and blue phosphors (UV-LED) [5, 6].

In particular, phosphors excited in the UV range have been rarely reported because most existing oxide phosphors were excited far below 400 nm. On the other hand in a nitride host, the higher covalency of nitrogen than that of oxygen makes its excitation band be located in the UV range. In addition, larger ligand-field splitting due to nitrogen broadens the emission band. Among nitride phosphors, a red one is the most difficult to develop because it is known that oxidation of the host results in a blue-shift below 590 nm [6].

There have been various researches on nitride phosphors in the last few years [7-16]. As an oxynitride phosphor, Eu^{2+} -doped α -sialon was reported to emit yellow light which peaked at 580 nm [7, 8]. Eu^{2+} -doped $\text{SrSi}_2\text{O}_2\text{N}_2$ [9] and Eu^{2+} -doped $\text{MSi}_2\text{O}_{2-8}\text{N}_{2+2/3\delta}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [10] were also studied, and all of these phosphors exhibited green or yellow emission below 590 nm. It was said that the

emission peak positions of these phosphors depended on the amount of oxygen incorporated into the matrix [10]. On the other hand in a nitride without oxygen incorporations, various red phosphors have been reported [11-16]. Recently, a $\text{CaSiN}_2 : \text{Ce}^{3+}$ red phosphor was developed, but the excitation intensity around 400 nm was too low to be applied for a UV-LED [11]. In addition, it was reported by Uheda et al. that $\text{CaAlSiN}_3 : \text{Eu}^{2+}$ exhibited a red emission band which peaked at 650 nm and a high thermal quenching temperature, but this phosphor was synthesized only by gas pressure sintering [12]. Hoppe et al. reported red emission from a Eu^{2+} -doped was relatively low [13]. Li et al. also reported $\text{M}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) systems using EuN , Ca_3N_2 , Ba_3N_2 , Sr_3N_2 and Si_3N_4 as starting materials [14]. These systems showed high excitation intensity around 400 nm and broad concentrations. In addition, these systems were relatively easy to synthesize using normal pressure sintering.

It has been known that oxygen incorporations into the nitride lattice critically changed the luminescence properties. But, the study of oxidation effects on those of $\text{Ca}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ has rarely been reported. Therefore, $\text{Ca}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ phosphors were synthesized using Eu_2O_3 as the dopant and the oxidation effects from Eu_2O_3 on the luminescence properties of $\text{Ca}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ phosphors were investigated

Experimental

$\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ phosphors were prepared by a solid state reaction method. Ca_3N_2 (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 being weighed out in the appropriate amounts, sample powders were subsequently mixed and ground in high-purity normal-hexane using ball milling for 2 h. After being dried at 90 °C, sample powders

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were transferred into a BN crucible with a molybdenum cover. All the processes were carried out in glove box filled with purified nitrogen gas. Subsequently, these mixtures were fired in a horizontal tube furnace at 1,400–1,600 °C for 2 h under a flowing H_2 - N_2 mixed gas with various ratios controlled by mass flow controllers. After firing, the samples were gradually cooled down in the furnace.

X-ray diffraction (XRD, Rigaku, DMAX 2000) patterns using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) showed that $\text{Ca}_2\text{Si}_5\text{N}_8$ was formed as the main phase and there was also a secondary oxynitride phase such as $\text{CaSi}_2\text{O}_2\text{N}_2$ when Eu_2O_3 was used a dopant.

For analysis of luminescence characteristics, diffuse reflectance was measured by a spectrophotometer (Shimadzu, UV3101PC). BaSO_4 (reflection $\sim 100\%$) was measured in advance for calibration. The excitation and emission spectra were achieved by a luminescence spectrometer (Perkin-Elmer, LS50B) equipped with 200 W Xe-lamp and a red-sensitive photo-multi-tube (Hamamatsu, R928).

Results and Discussion

Undoped and Eu^{2+} -doped $\text{Ca}_2\text{Si}_5\text{N}_8$ powders were fired at 1,600 °C for 2 h in a 30% H_2 -70% N_2 atmosphere and the diffuse reflection spectra of these powders were measured. (Fig. 1.) The daylight color of undoped $\text{Ca}_2\text{Si}_5\text{N}_8$ was gray white, which indicated no absorption in the visible range as shown in Fig. 1. A sharp drop in reflectance was detected in range from 250 to 320 nm, which is identical to that in a previous study [14]. This absorption corresponded to a band-to-band transition in the host lattice. In the case of the 5 mol% Eu^{2+} -doped sample ($x = 0.10$), four additional absorption bands were detected with the strongest peaks at 260, 300, 395 and 490 nm. Obviously, these bands corresponded to the absorption by Eu^{2+} ions. In addition, the absorption edge shifted to a longer wavelength above 600 nm as the Eu^{2+} concentration

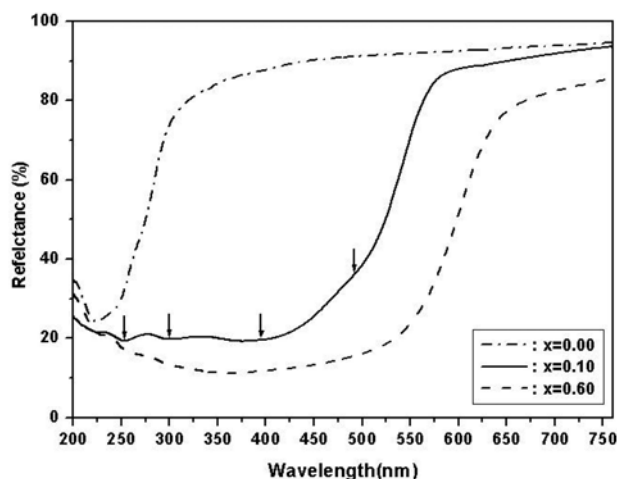


Fig. 1. Diffuse reflection spectra of $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ fired at 1,600 °C for 2 h in a 30% H_2 -70% N_2 atmosphere ($x = 0.00, 0.10, 0.60$)

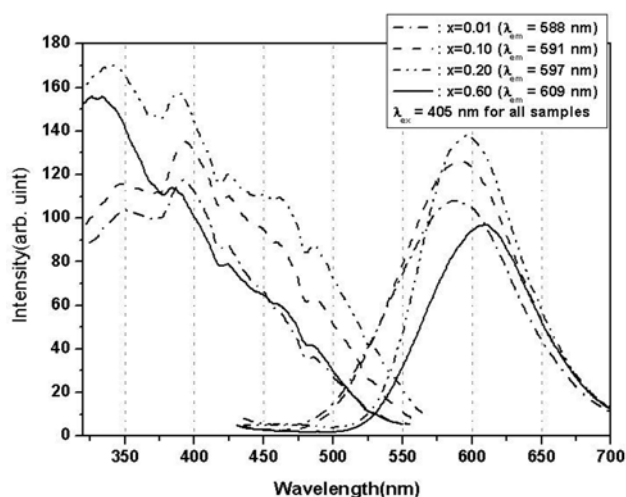


Fig. 2. Excitation and emission spectra of $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ fired at 1,600 °C for 2 h in a 30% H_2 -70% N_2 atmosphere ($x = 0.01, 0.10, 0.20, 0.60$).

increased. The daylight colors of these samples also changed from dark yellow to orange. This phenomenon can be explained by the distortion of the lattice. The larger Eu^{2+} ion replaced the Ca^{2+} ion, and resulted in an increased of distortion of lattice. In spite of the oxidation from the Eu_2O_3 , high and wide absorption was obtained. A broad absorption from around 400 to 560 nm could be evidence that the phosphor in this study is an excellent candidate for a warm-white UV- as well as a blue-LED.

Fig. 2 shows the excitation and emission spectra of $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ ($x = 0.01, 0.1, 0.2, 0.6$) fired at 1,600 °C for 2 h in a 30% H_2 -70% N_2 atmosphere. The excitation wavelength for the emission spectra was 405 nm for all samples and the emission wavelength for the excitation spectra was determined by the strongest peak wavelengths of emission. In the excitation spectrum, four bands were detected, whose strongest peaks were positioned around 350, 393, 460 and 487 nm. Obviously, these bands were from inner transitions of the 4f-5d levels in Eu^{2+} ions. The peak positions were the same as the ones reported previously for a $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ phosphor [14]. Small peaks positioned from 420–450 nm were shown to be dummy ones from the Xe-lamp because these peaks always appeared regardless of the phosphor. With an increase of x , the peak intensities positioned at 350, 393 nm increased relatively, but those of the other peaks in blue range decreased relatively. These phenomena indicated that oxygens replaced nitrogens neighboring Eu^{2+} ions, consequently, weakened ligand-splitting of activators. Consequently, the energy level density in the low energy range in the 5d level was reduced. It was noticed that for the sample with $x = 0.6$, broad absorption (reflectance $\sim 10\%$) was observed in the 450–550 nm range in the reflection spectra, but relatively very low excitation intensities were observed in the same range. From this result, it can be also said that the absorbed energy in this range could not be transferred effectively to the lowest 5d level to emit, and this energy might be

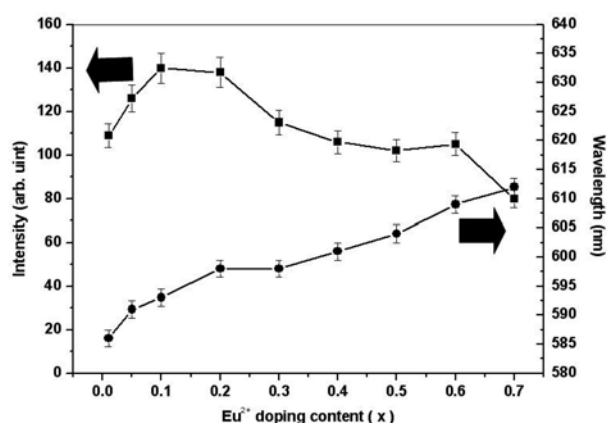


Fig. 3. Maximum emission intensities and their wavelengths of $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ fired at 1,600 °C for 2 h in a 30% H_2 -70% N_2 atmosphere.

dissipated as a heat.

In the case of emission spectra, the emission band shifted from 588 nm to 613 nm proportional to x . Generally, oxidation resulted in a blue shift of the emission band. In spite of further oxidation with an increase of x , the emission peak showed a red shift in this study. This red shift might arise directly from the crystal distortion by further incorporation of Eu^{2+} ions on Ca^{2+} sites.

Fig. 3. illustrates the maximum emission intensities excited at 405 nm and its wavelength of $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ fired at 1,600 °C for 2 h in a 30% H_2 -70% N_2 atmosphere. As shown, the emission wavelength linearly increased from 588 nm to 613 nm with an increase of x , and its intensity had a maximum value at $x = 0.1$. According to Li et al [14], red shift in $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ occurred in a small range (605-615 nm) and terminated when $x = 0.14$, which was explained by the large difference of ionic radius between Eu^{2+} and Ca^{2+} ions. However, $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ in this study exhibited a red shift over a large range, about 25 nm, with an increase of x . The red shift was terminated when $x = 0.7$, which means a higher solubility of Eu^{2+} ions. It was reported that a $\text{CaSi}_2\text{O}_{2-8}\text{N}_{2+2/38} : \text{Eu}^{2+}$ phosphor was known to emit yellow light peaking at 560 nm, [10] and $\text{CaSi}_2\text{O}_2\text{N}_2$ was also detected in samples in this study. Therefore, the broad shift starting from 588 nm was attributed to the oxynitride second phase in the matrix. A higher solubility of Eu^{2+} ions than that in previous studies could also be explained by the formation of second phase. Namely, extra Eu^{2+} ions were incorporated into the a second phase, consequently, the solubility of Eu^{2+} in this system increased. From the results of high a solubility and a wide emission band shift, it can be said that Eu_2O_3 -doped $\text{Ca}_2\text{Si}_5\text{N}_8$ phosphas have potential as UV-LED phosphors.

The photoluminescence properties as a function of process conditions were investigated. Fig. 4. shows emission spectra of $\text{Ca}_{1.4}\text{Eu}_{0.6}\text{Si}_5\text{N}_8$ fired at various temperatures for 2 h in a 30% H_2 -70% N_2 atmosphere. The inset shows a magnified emission spectrum of a sample fired at 1,300 °C. When the firing temperature was 1,300 °C, homogeneous powders with a yellowish green daylight color were formed. This

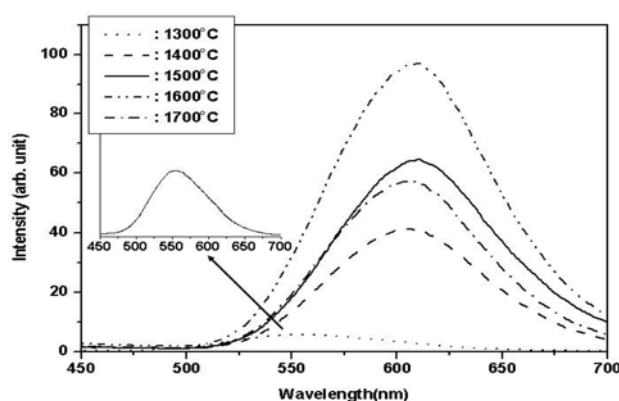


Fig. 4. Emission spectra of $\text{Ca}_{1.4}\text{Eu}_{0.6}\text{Si}_5\text{N}_8$ fired at various temperatures for 2 h in a 30% H_2 -70% N_2 atmosphere.

sample exhibited an emission band with the strongest peak at 560 nm, which was identical to that of $\text{CaSi}_2\text{O}_{2-8}\text{N}_{2+2/38}$ [10]. Thus, only an oxynitride phase was formed when insufficient energy was supplied for nitride formation. At a firing temperature of 1,400 °C, the emission band shifted toward 603 nm, and slightly shifted up to 609 nm, proportional to the firing temperature. This shift was terminated when firing temperature was 1,600 °C, and a further increase of firing temperature lowered the emission intensity without a further red shift. From there results, sufficient heat energy must be supplied to form a nitride phase.

Photoluminescence properties with firing atmosphere were also investigated. Fig. 5 shows emission spectra of $\text{Ca}_{1.4}\text{Eu}_{0.6}\text{Si}_5\text{N}_8$ fired at 1,600 °C for 2 h in various atmospheres. The inset shows a magnified emission spectrum of a sample fired in a 10% H_2 atmosphere. With an increase of H_2 content, the intensity of emission increased without a peak shift, and the maximum intensity was gained by firing in a 30% H_2 -70% N_2 atmosphere. It is worth noting that for the sample fired in a 10% H_2 -90% N_2 atmosphere, a glassy phase was partially precipitated within gray white powders, and negligible emission peaks in the

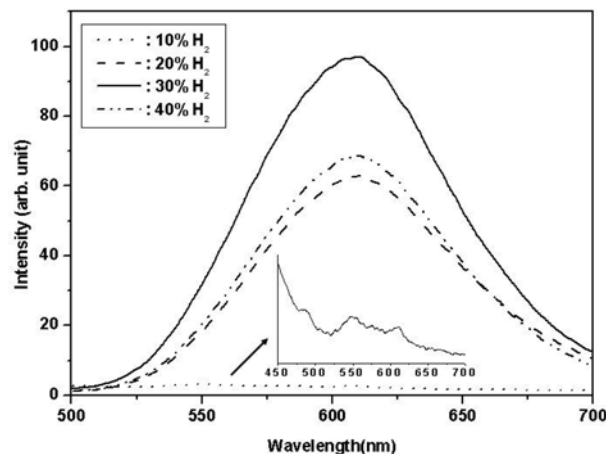


Fig. 5. Emission spectra of $\text{Ca}_{1.4}\text{Eu}_{0.6}\text{Si}_5\text{N}_8$ fired at 1,600 °C for 2 h in various atmospheres.

range 600-620 nm were formed. From this result, sufficient reduction must be carried out during the firing. Otherwise, oxygen in the sample lowered the melting point of the sample and formed a glass phase as a consequence. From the analysis of photoluminescence properties with process conditions, a high temperature and a sufficient reduction atmosphere were required for the formation of a nitride phase when Eu_2O_3 was used as a starting material.

Conclusions

Using Eu_2O_3 for doping, Eu^{2+} -activated $\text{Ca}_2\text{Si}_5\text{N}_8$ phosphors were synthesized and the luminescence properties were investigated. Oxygen from Eu_2O_3 might become a source of a second phase, namely $\text{CaSi}_2\text{O}_2\text{N}_2$ with oxygen incorporation into nitrogen sites in the host lattice. Consequently, this oxidation influenced not only emission peak shifts but also the solubility of activators. $\text{Ca}_{1.4}\text{Eu}_{0.6}\text{Si}_5\text{N}_8$ phosphor showed high absorption (absorption $\sim 90\%$) in a broad range (300-600 nm). The Eu^{2+} -activated $\text{Ca}_2\text{Si}_5\text{N}_8$ phosphor in this study had a high excitation intensity around 400 nm and a wide tunability in emission (588-613 nm), which is very applicable as a yellow or red phosphor for UV-LED. Further research on the structure and increasing the brightness will be carried out.

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