Paper

Preparation of Eu^{2+} -doped $\text{Ca}_2\text{Si}_5\text{N}_8$ by Carbothermal Reduction / Nitridation of Spray-pyrolyzed Oxide/nitride Powder and Its Luminescence Properties

Kazuaki YAMAGUCHI*, Hubertus T. HINTZEN**, Anne C. A. DELSING**, Hideki KUWAHARA***, Seiichiro KODA* and Kiyoshi ITATANI*

*Sophia University, Department of Materials and Life Sciences, Faculty of Science and Engineering

**Eindhoven University of Technology, Department of Chemical Engineering and Chemistry

***Sophia University, Department of Engineering and Applied Sciences, Faculty of Science and Engineering

Received April 18, 2011, Accepted October 5, 2011

ABSTRACT

The conditions for the preparation of regular-shaped Eu^{2+} -doped calcium silicon nitride ($(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$) powder were examined by the carbothermal reduction and nitridation (CRN) of oxide/nitride powder prepared by ultrasonic spray pyrolysis. Two kinds of silicon sources, *i.e.*, (i) colloidal silica (CS) and (ii) silicon nitride (Si_3N_4 ; SN), were used for the spray pyrolysis. Firstly, the solution containing $0.057 \text{ mol}\cdot\text{dm}^{-3} \text{ Ca}(\text{NO}_3)_2$, $0.140 \text{ mol}\cdot\text{dm}^{-3} \text{ CS}$ and $5.71 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3} \text{ Eu}(\text{NO}_3)_3$ was spray-pyrolyzed at 600°C , and the resulting powder was calcined at 800°C for 10 min in air. The single phase but agglomerated particles of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ were obtained when the CRN (the relative carbon amount to the stoichiometric amount (*m*): 1.5) of spray-pyrolyzed/calcined oxide powder was conducted at 1300°C for 2 h in nitrogen (N_2) atmosphere. Secondly, the solution containing $0.0285 \text{ mol}\cdot\text{dm}^{-3} \text{ Ca}(\text{NO}_3)_2$, $0.070 \text{ mol}\cdot\text{dm}^{-3} \text{ SN}$ and $2.855 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3} \text{ Eu}(\text{NO}_3)_3$ (one-half of the solution concentration compared to the case of CS utilization) was spray-pyrolyzed, and the CRN of spray-pyrolyzed oxide/nitride powder was conducted at 1500°C for 2 h to obtain $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ in N_2 atmosphere. The microscopic observation showed that this powder was composed of regular-shaped particles with sizes of approximately 2-3 μm . The excitation and emission peaks of this powder appeared at around 370 and 590 nm, respectively, showing the emission of orange light.

KEYWORDS: calcium silicon nitride, carbothermal reduction/nitridation, regular particle shape, luminescence

1. Introduction

A light emitting diode (LED) is a promising illumination source of the next generation. Compared to the most popular fluorescent lamp currently used in our life, it has noted advantages of energy saving, long operation life and mercury free¹⁾. The commercial white-LED generally consists of a blue emitting LED and a yellow-emitting phosphor (*e.g.*, Ce-doped yttrium aluminate garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$; YAG:Ce) and, therefore, has problem of poor red components²⁾. Recently, many researchers pay attention to the nitride phosphors from the viewpoints of (i) absorption of visible light and emission of longer wavelength light, and (ii) excellent thermal and chemical stabilities³⁾. However, the synthesis of nitride powder generally requires the heating operation at higher temperature, compared to the case of oxide and sulfide phosphors; moreover, the powder consists of irregular-shaped particles with wide size distribution.

Eu^{2+} -doped calcium silicon nitride ($(\text{Ca}_{1-x}\text{Eu}_x)_2\text{Si}_5\text{N}_8$) phosphor, which has three dimensional networks consisting of a SiN_4 -based tetrahedral structure, is a

promising material as an orange emitting component in white-LED⁴⁾⁵⁾. The phosphor particles are mainly prepared by the solid-state reaction of nitride compounds, *e.g.*, Ca_3N_2 and Si_3N_4 or carbothermal reduction and nitridation (CRN) of oxide/nitride compounds⁶⁾. The technique of solid state reaction may have the advantage to control the chemical composition but some problems on the high-purity, chemical homogeneity at the atomic level, regular particle shape, and homogeneous distribution of activator ions in the host material.

On the other hand, ultrasonic spray pyrolysis (USP) is a technique to instantaneously form the particles through (i) the introduction of droplets with a homogeneous mixture of the desired kinds and amounts of components in the heating zone, (ii) the precipitation of solid materials due to the evaporation of solvent, and (iii) the solid-state reaction among the solidified materials⁷⁾⁸⁾. The resulting powder has the noted luminescence properties, reflecting the characteristics of spray pyrolysis⁹⁾¹⁰⁾. The nitridation of oxide powder is further expected to be promoted using the powder prepared by USP, because the oxide powder is

composed of nanometer-sized particles containing homogeneously dispersed chemical components. On the basis of such background, this paper describes the research on the preparation of regular-shaped $(\text{Ca}_{1-x}\text{Eu}_x)_2\text{Si}_5\text{N}_8$ ($x = 0.01$) particles through the combination of USP and CRN techniques.

2. Experimental procedure

The objective compound, *i.e.*, $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$, was prepared by the combination of USP and CRN techniques. Two kinds of silicon sources, *i.e.*, (i) colloidal silica (CS) and (ii) silicon nitride (Si_3N_4 ; SN), were used for the spray pyrolysis. The kinds and concentrations of starting materials with the chemical composition of $(\text{Ca} + \text{Eu}) / \text{Si} = 0.40$ are shown in Table 1. The solution was sprayed using a vibrator with the frequency of 2.4 MHz and introduced into a furnace kept being heated at 600°C. The droplets were changed into solid materials, due to the evaporation of water vapor and the solid state reaction of precipitated metal salts⁷⁸⁾, and the powder was collected by filter paper. The resulting powder was calcined at 800°C for 10 min in air (Sample code: SP(CS)), or was used with no calcination (Sample code: SP(SN-1.0) and SP(SN-0.5)). These oxide/nitride powders were mixed with carbon (the relative carbon amount to the stoichiometric amount (*m*): 1.5) and then the CRN treatment was conducted under the optimum heating conditions ranging from 900 to 1600°C for 2 h in N_2 atmosphere.

Crystalline phases were identified using an X-ray diffractometer (XRD; RINT2100V/P, Rigaku, Tokyo) with monochromatic $\text{CuK}\alpha$ radiation generated at 40 kV and 40 mA. The morphology of the particles was observed using a field-emission scanning electron microscope (FE-SEM; SU-8000, accelerating voltage, 5 kV, Hitachi, Tokyo), after the particles had been coated with Pt-Pd in order to avoid charging effects. The chemical composition of the powder prepared by various techniques was examined using SEM/energy dispersive electron microanalyzer (EDX; E-1030). The photoluminescence spectra were measured using a fluorescent spectrophotometer (F-4500, Hitachi, Tokyo).

Table 1 Preparation conditions of the starting solutions for spray pyrolysis (total amount of solution: 250 cm^3)

Sample Code	$\text{Ca}(\text{NO}_3)_2$ mol·dm ⁻³	Colloidal silica mol·dm ⁻³ a)	Si_3N_4 mol·dm ⁻³	$\text{Eu}(\text{NO}_3)_3$ mol·dm ⁻³
SP(CS)	0.057	0.140		5.71×10^{-4}
SP(SN-1.0)	0.057		0.140	5.71×10^{-4}
SP(SN-0.5)	0.0285		0.070	2.855×10^{-4}

a) Concentration calculated on the basis of SiO_2 content in the colloidal silica.

Figure 1 FE-SEM micrograph and agglomerate diameter distribution of the powder spray-pyrolyzed at 600°C, using SP(CS)

3. Results and discussion

3.1 Preparation of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ from SP(CS)

The preparation conditions of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ from CS were examined by the combination of USP and CRN techniques. Firstly, FE-SEM micrographs of the spray-pyrolyzed powders are presented in Figure 1, together with the agglomerate-diameter distributions. Note that the agglomerate-diameter distributions were examined measuring the diameters of 200 agglomerates by sliding calipers. These powders were composed of spherical agglomerates, and the mean particle diameter obtained from SP(CS) was 0.96 μm . These agglomerates must be reflected by the drop diameters sprayed using ultrasonic vibrator. The drop diameter (G_{DROP}) formed by the use of ultrasonic vibrator is calculated as follows¹⁰⁾:

$$G_{\text{DROP}} = 0.34 \left[\frac{8\pi\sigma}{\rho f^2} \right]^{\frac{1}{3}} \quad (1)$$

where ρ is the droplet density, f is the frequency of the ultrasonic vibrator (≈ 2.4 MHz), and σ is the surface tension. The use of an ultrasonic vibrator produces droplets with diameters of typically 2.3 μm . Since the mean agglomerate diameters of powders obtained by the spray-pyrolysis of SP(CS) was below 1 μm , the solid agglomerate may be formed by the volume reduction due to the evaporation of water vapor from the droplets.

According to the XRD results, no marked compounds were detected from the spray-pyrolyzed powder. In order to check the phase changes during the heating, DTA-TG was conducted with the results being shown in Figure 2. Based upon the DTA curve, the exothermic event of SP(CS) started to occur at around 900°C. On the other hand, TG curve showed that the mass loss gradually occurred with temperature from 30 to 800°C. The

Figure 2 DTA-TG curves of the powder prepared by the spray-pyrolysis of SP(CS) in air (heating rate: $10^{\circ}\text{C}\cdot\text{min}^{-1}$)

exothermic event occurring above 800°C , therefore, must be related to the phase changes. In order to make clear the phase changes above 800°C , the crystalline phase was checked by using an X-ray diffractometer. Figure 3 shows the XRD patterns of powder obtained by the spray pyrolysis of SP(CS) at 600°C . No crystalline phase was detected, *i.e.*, broad background over the 2θ range of 20 to 40° , from the powder heated at 800°C . The reaction product, $\beta\text{-CaSiO}_3$, was detected from the powders heated at 1000 and 1200°C . Moreover, SiO_2 , as well as $\alpha\text{-CaSiO}_3$, were detected from the powder heated at 1300°C . Since

Figure 3 XRD patterns of the powders after the calcination of the powder prepared by the spray-pyrolysis of SP(CS) at 600°C
 ●: $\beta\text{-CaSiO}_3$ (JCPDS 42-550) ○: $\alpha\text{-CaSiO}_3$ (31-300) ○: SiO_2 (JCPDS 39-1425)

Note that the calcination time was 10 min at each temperature in air.

the $\beta\text{-CaSiO}_3$ was detected from the powders heated at $1000\text{--}1200^{\circ}\text{C}$, the exothermic event on the DTA curve (900°C) may be attributed to the crystallization of amorphous material to $\beta\text{-CaSiO}_3$ through the following chemical reaction:

The broad background in the 2θ range of 20 to 40° , which appeared in the XRD pattern at 800°C , corresponds to the X-ray reflection positions of CaSiO_3 . This fact indicates that CaSiO_3 may have the possibility of being present as amorphous material at 800°C . The CRN operation of amorphous material, *i.e.*, the replacement of oxygen atom with nitrogen, is expected to be conducted more homogeneously than that of crystalline material. On the basis of mass loss and amorphous state, the calcination of the powder obtained by the spray-pyrolysis of SP(CP) was conducted at a fixed temperature of 800°C for 10 min.

Figure 4 shows the typical XRD patterns of the powders after the CRN treatment of spray-pyrolyzed/calcined powder was conducted at each temperature for 4 h. Note that the carbon amount (m) added to the powder was fixed at 1.50, on the basis of our preliminary investigation ($1.0 \leq m \leq 2.0$). The crystalline phase of the powder CRN-treated at 900°C for 4 h was only C. The crystalline phases of the powder CRN-treated at 1100°C for 4 h were C and $\beta\text{-CaSiO}_3$. The crystalline phase of the powder CRN-treated at 1300 and 1500°C was only $\text{Ca}_2\text{Si}_5\text{N}_8$.

Phase changes during the CRN treatment of spray-pyrolyzed/calcined powder were examined on the basis of

Figure 4 XRD patterns after the CRN treatment (4 h) of the spray-pyrolyzed / calcined powder ($m: 1.5$)
 ○: $\text{Ca}_2\text{Si}_5\text{N}_8$ (JCPDS 82-2489)
 ▲: C (41-1487) ●: $\beta\text{-CaSiO}_3$

Note that the heat treatment of spray-pyrolyzed powder was conducted at 800°C for 10 min in air.

Figure 5 Phase changes during the CRN treatment (m : 1.5) of oxide powder prepared using SP(CS), together with typical FE-SEM micrograph

○: $\text{Ca}_2\text{Si}_5\text{N}_8$ ($2\theta = 35.2^\circ$; JCPDS 82-2489)

○: SiO_2 ($2\theta = 26.8^\circ$; 52-1425)

●: $\beta\text{-CaSiO}_3$ ($2\theta = 29.90^\circ$) ▲: C ($2\theta = 26.60^\circ$)

Note that the spray-pyrolyzed powder was calcined at 800°C for 10 min in air, and that CRN treatment was conducted at each temperature for 2 h in N_2 atmosphere.

the characteristic X-ray reflections of the compounds. Results are shown in Figure 5, together with FE-SEM micrograph. X-ray intensity of carbon started to decrease at 900°C and disappeared at 1200°C . Although $\beta\text{-CaSiO}_3$ and SiO_2 were present in the temperature range of 900 to 1300°C , only $\text{Ca}_2\text{Si}_5\text{N}_8$ existed above 1300°C . FE-SEM micrograph of the powder heated at 1300°C for 4 h indicated the presence of the irregular-shaped particles with sizes of around $1\text{--}5\text{ }\mu\text{m}$.

The carbothermal reduction process based upon the above phase changes may be expressed as follows:

Here $\beta\text{-CaSiO}_3$ may be formed by the reaction of CaO with SiO_2 (see Eq. (2)). It should be noted that the objective compound of $\text{Ca}_2\text{Si}_5\text{N}_8$ could be formed with the disappearance of C, and that the single phase of CaSi_5N_8 : Eu^{2+} , *i.e.*, $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$, could be obtained at the carbothermal temperature as low as 1300°C . Unfortunately, no regular-shaped particles could be obtained by the utilization of SP(CS).

3.2 Preparation of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ from SP(SN)

The single phase of $\text{Ca}_2\text{Si}_5\text{N}_8$ could be successfully prepared but the particle morphology was irregular by using the combined techniques of USP and CRN at temperature as low as 1300°C . We considered that the active mass transfer during the drastic substitution of oxygen for nitrogen in the CRN operation of the oxide

Figure 6 XRD patterns of the powders obtained by the spray pyrolysis of (a) SP(SN-1.0) and (b) SP(SN-0.5) at 600°C , together with FE-SEM micrographs

●: CaCO_3 (JCPDS, 47-1743)

powder may be one of the reasons not to control the particle morphology. Then we replaced the CS with SN in the spraying solution, from the prospect that the gradual CRN treatment may be expected to control the particle morphology, as well as the formation of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$. Figure 6 shows the typical XRD patterns of spray-pyrolyzed powder (SP(SN-1.0) and SP(SN-0.5)), together with FE-SEM micrographs. XRD pattern of the powder obtained by the spray pyrolysis of SP(SN-1.0) indicated the presence of amorphous materials (broad background) and CaCO_3 . The resulting powder was composed of agglomerates with sizes of around $0.2\text{ }\mu\text{m}$ (Figure 6(a)). On the other hand, XRD pattern of the powder obtained by the spray pyrolysis of SP(SN-0.5) indicated the presence of amorphous materials (broad background). The powder was composed of agglomerates with sizes of around $0.3\text{ }\mu\text{m}$ (Figure 6(b)).

The noted phenomenon regarding the crystalline phase of the powder obtained by the spray pyrolysis of SP(SN-1.0) was the formation of CaCO_3 . When the acidic solution containing $\text{Ca}(\text{NO}_3)_2$, Si_3N_4 and $\text{Eu}(\text{NO}_3)_3$ was spray-pyrolyzed at 600°C , the retarded reaction of Ca^{2+} with Si_3N_4 may preferentially form CaCO_3 , due to the reaction of Ca^{2+} with CO_2 present in the acidic solution. The formation of CaCO_3 seems to be restricted by the utilization of dilute solution of SP(SN-0.5), *i.e.*, the retarded reaction of Ca^{2+} with CO_2 .

Then CRN operation of the powder obtained by the spray pyrolysis of SP(SN-1.0) was conducted at a

Figure 7 XRD patterns of the powders after the CRN treatment of the powder prepared by the spray pyrolysis of SP(SN-0.5)
 O: $\text{Ca}_2\text{Si}_5\text{N}_8$ ▲: C △: Si_3N_4 (JCPDS 73-1210), ◆: unknown phase

Note that the CRN operation was conducted at each temperature for 2 h in N_2 atmosphere, and that m value was fixed at 1.5.

temperature between 1300 and 1500°C. The reaction products were Ca_2SiO_4 and unknown phases, as well as carbon. Thus no objective compound, $\text{Ca}_2\text{Si}_5\text{N}_8$, was obtained in the range of 1300 to 1500°C. On the basis of the information obtained above, the CRN treatment of the powder obtained by the spray pyrolysis of SP(SN-0.5) was conducted at a temperature between 1400 and 1600°C. The XRD results obtained are shown in Figure 7. When the CRN treatment was conducted at 1400°C for 2 h in N_2 atmosphere, the objective compound of $\text{Ca}_2\text{Si}_5\text{N}_8$, as well as C, Si_3N_4 and unknown phase, was found to form. When the CRN operation was conducted at 1500 and 1600°C, only $\text{Ca}_2\text{Si}_5\text{N}_8$ was detected from the powder.

The reaction to form $\text{Ca}_2\text{Si}_5\text{N}_8$ is shown as the following route:

The typical SEM micrographs of these powders are shown in Figure 8. When the CRN treatment was conducted at 1400°C, the particle sizes were around 1 μm . The particle size increased with increasing CRN temperature and attained approximately 2 μm at 1500°C and 3 μm at 1600°C. It should be noted that no marked agglomeration of particles was found in the resulting powder, and that the particle sizes of $\text{Ca}_2\text{Si}_5\text{N}_8$ prepared by the carbothermal reduction reported so far was approximately 20 μm ⁶⁾. The present particle sizes were about 1/10, compared to the previous report⁶⁾.

Figure 8 FE-SEM micrographs of the powder after the spray pyrolysis of SP(SN-0.5) and subsequent CRN treatment

Note that the CRN treatment was conducted at each temperature for 2 h, and that m value was fixed at 1.5.

The chemical compositions of resulting powders, *i.e.*, (i) the conventional solid state reaction (SSR) among CaCO_3 , Si_3N_4 and Eu_2O_3 and CRN treatment at 1550°C for 2 h, (ii) USP of the SP(CS) and subsequent CRN treatment at 1300°C for 2 h, and (iii) USP of the SP(SN-0.5) and subsequent CRN treatment at 1500°C for 2 h, are shown in Table 2. The chemical compositions of these powders measured by SEM/EDX were in good accordance with theoretical value. Overall, we successfully prepared the $\text{Ca}_2\text{Si}_5\text{N}_8$ through the combination of USP and CRN techniques, as well as the conventional SSR, and particle shape could be controlled by the utilization of spray pyrolysis of SP(SN-0.5).

3.3 Luminescence properties of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$

In Section 3.1 and 3.2, we have successfully prepared the single phase of Eu^{2+} -doped $\text{Ca}_2\text{Si}_5\text{N}_8$ powder. Then the excitation and emission spectra were examined using the powders obtained by the spray pyrolysis of SP(CS) and SP(SN-0.5). The results are shown in Figure 9, together with the case of powder obtained by the conventional CRN technique for comparison. These compounds showed a broad excitation band from 200 to 500 nm and emission at about 590 nm. The Eu^{2+} ion is responsible for the excitation band ($4f^7 \rightarrow 4f^65d$), and the emission peak is assigned to

Table 2 Chemical compositions (determined by SEM/EDX) of the powders prepared by the CRN treatment of various oxide/nitride powders

Sample Code	Ca	Si	Ca
	mol	mol	Si
SSR ^{a)}	28.6	71.1	0.402
SP(CS)	28.7	71.3	0.403
SP(SN-0.5)	28.5	71.5	0.399
TV ^{b)}	28.4	71.6	0.396

a) Solid State Reaction b) Theoretical Value

Figure 9 Excitation and emission spectra of various $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ powders

- (a) Conventional SSR-CRN techniques (1550°C, 2 h, N_2 atmosphere, $m = 1.5$)
- (b) USP-CRN techniques (SP(CS); 1300°C 2 h, N_2 atmosphere, $m = 1.5$)
- (c) USP-CRN techniques (SP(SN); 1500°C 2 h, N_2 atmosphere, $m = 1.5$)

the allowed $4f^{65}d^1 \rightarrow 4f^7$ transition of Eu^{2+} ion. Li *et al.*⁴ reported that the emission peak of $(\text{Ca}_{1-x}\text{Eu}_x)_2\text{Si}_5\text{N}_8$ for the excitation at 465 nm shifts from 605 to 615 nm with increasing x from 0.01 to 0.07. On the other hand, Piao *et al.*⁶ reported that the emission peak of $(\text{Ca}_{1-x}\text{Eu}_x)_2\text{Si}_5\text{N}_8$ prepared by CRN shifts from 596 to 612 nm with increasing x from 0.005 to 0.20. Such lowering of the emission peaks' wavelength must be associated not only with Stokes shift, covalency and crystal-field splitting of 5 d levels of Eu^{2+} , but also with particle size, lattice defects, *etc.* The understanding of this phenomenon, however, needs further investigation. It is noted that the emission of $(\text{Ca}_{1-x}\text{Eu}_x)_2\text{Si}_5\text{N}_8$ may be tuned by controlling the amount of Eu^{2+} .⁴⁶

The relative emission intensity of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ prepared using SN ($=0.452$) was higher than the case of the utilization of CS ($=0.0371$), and comparable to the case of SSR/CRN ($=0.494$). The low relative intensity of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ prepared using the CS may be associated with the poor crystallinity based upon the lower CRN temperature but is expected to improve when the CRN operation is conducted at higher temperature.

4. Conclusion

The conditions for the preparation of regular-shaped Eu^{2+} -doped $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ powder were examined by the CRN treatment of oxide/nitride powder prepared by USP. The objective compound $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ could be obtained when CS and SN were used as silicon sources.

The results obtained were summarized as follows:

- (i) The solution containing $0.057 \text{ mol}\cdot\text{dm}^{-3}$ $\text{Ca}(\text{NO}_3)_2$, $0.140 \text{ mol}\cdot\text{dm}^{-3}$ CS and $5.71 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ $\text{Eu}(\text{NO}_3)_3$ was spray-pyrolyzed at 600°C, and then the resulting powder was heat-treated at 800°C for 10 min. Single phase of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ could be obtained when the CRN ($m : 1.5$) of spray-pyrolyzed/heat-treated oxide powder was conducted at 1300°C for 2 h.
- (ii) The solution containing $0.0285 \text{ mol}\cdot\text{dm}^{-3}$ $\text{Ca}(\text{NO}_3)_2$, $0.070 \text{ mol}\cdot\text{dm}^{-3}$ SN and $2.855 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ $\text{Eu}(\text{NO}_3)_3$ was spray-pyrolyzed at 600°C, and then the CRN ($m = 1.5$) of spray-pyrolyzed oxide/nitride powder was conducted at 1500°C for 2 h to obtain $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$. This powder was composed of regular-shaped particles with sizes of 2 - 3 μm . The excitation and emission peaks of this powder appeared at around 370 and 590 nm, respectively, showing the emission of orange light; the relative emission intensities of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_2\text{Si}_5\text{N}_8$ prepared using SN was much higher than the case of CS.

References

- (1) Xie, R.-J. and Hirosaki, N.: Silicon-based oxynitride and nitride phosphors for white LEDs-a review, *Science Technology Advanced Materials*, Vol. 8(7-8), pp. 588-600 (2007).
- (2) Xie, R.-J., Hirosaki, N., Sakamura, K., Yamamuro, Y. and Mitomo, M.: Eu^{2+} -doped Ca- α -SiAlON a yellow phosphor for white light-emitting diodes, *Applied Physics Letter*, Vol. 84 (26), pp. 5404-5406 (2004).
- (3) Horikawa, T., Piao X., Fujitani, M., Hanzawa, H. and Machida, K.: Preparation of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors using various novel reducing agents and their luminescent properties, *Materials Science Engineering*, Vol. 1, pp. 012024-1-6 (2009).
- (4) Li, Y. Q., Van Steen, J. E. J., Van Kreveld J. W. H., Botty, G., Delsing, A. C. A., Disalvo, F. J., De with G. and Hintzen, H. T.: Luminescence properties of red-emitting $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) LED conversion phosphors, *J. Alloys and Compounds*, Vol. 417(1-2), pp. 273-279 (2006).
- (5) Li, H. L., Xie, R. J., Hirosaki, N. and Takeda, T.: Synthesis and luminescence properties of orange-red-emitting $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) light-emitting diode conversion phosphors by a simple nitridation of MSi_2 , *J. Applied Ceramic Technology*, Vol. 6(4), pp. 459-464 (2009).
- (6) Piao X., Horikawa, T., Fujitani, M., Hanazawa, H. and Machida, K.: Photoluminescence properties of $\text{Ca}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ nitride phosphor prepared by carbothermal reduction and nitridation method, *Chemistry of Letters*, Vol.35(3), pp. 334-335 (2006).
- (7) Lin, S. E., Borgohain, K. and Wei, W. C.: Praseodymium-doped photo-luminescent strontium

- indate nanoparticles by ultrasonic spray pyrolysis, *J. American Ceramic Society*, Vol. 89(10), pp. 3266-3269 (2006).
- (8) Itatni, K., Umeda, T., Musha, Y. and Ian J. Davies, I. J.: Microstructures of spherical calcium-phosphate agglomerates prepared by spray-pyrolysis and freeze-drying techniques, *Phosphorous Research Bulletin*, Vol. 20, pp. 47-60 (2006).
- (9) Roh, H. S., Kang, Y. C., Lee, C. H., Park, H. D. and Park, S. B.: Morphological control of Zn_2SiO_4 : Mn phosphor particles by adding citric acid in spray pyrolysis process, *Japanese J. Applied Physics Part 1*, Vol. 42(6A), pp. 3429-3433 (2003).
- (10) Kang, Y. C., Roh, H. S., Seo, D. J. and Park, S. B.: The effect of metal carbonate fluxes on the crystallinity, morphology, and photoluminescence characteristics of Y_2O_3 : Eu phosphor in spray pyrolysis, *J. Materials Science Letters*, Vol. 19(4), 1225-1227 (2000).
- (11) Lang, R. J.: Ultrasonic Atomization of Liquids, *J. Acoustical Society of America*, Vol. 34(1), pp. 6-8 (1962).