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LETTER

Luminescence properties of $SrSi_6N_8$:Eu^{2+}

**Kousuke Shioi · Naoto Hirosaki · Rong-Jun Xie ·
Takashi Takeda · YuanQiang Li**

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In the last few years, white light-emitting diodes (white-LEDs) have been the subject of increasing interest due to their potential applications in indicators, backlights, automobile headlights, and general illumination [1]. They possess many excellent features such as long lifetime, mercury free, high energy efficiency, and compactness. In the case of the phosphor-converted LEDs either organic dyes or inorganic phosphors have been used as down-conversion materials [1–5]. However, the lifetime of organic materials is too short, and some environmental problems arise from the preparation and use of inorganic phosphors as they contain toxic elements, such as sulfur, chlorine, and cadmium. To solve these problems, novel phosphors without environmental hazards should be developed.

Recently, rare earth doped (oxy)nitride phosphors are gaining considerable attention due to their promising luminescent properties that enable them to use in white-LEDs, fluorescent lamps, and flat panel displays (FPD). Typical examples are red $M_2Si_5N_8$ (M = Ca, Sr, and Ba) [6, 7], yellow Ca-α-SiAlON [8–11], green β-SiAlON [12], and yellow Ce-melilite [13]. Although several kinds of (oxy)nitride phosphors have been developed and showed their suitability for use in white-LEDs, the requirement of high color rendering and high efficiency lamps for general illumination catalyzes the continuous search for (oxy)nitride phosphors with suitable emission colors and high conversion efficiency. In this letter, we will report a blue-emitting nitride phosphor—$SrSi_6N_8$:Eu^{2+}—that can be excited by UV or near UV-LEDs, and may have applications in white-LEDs.

The structure of strontium silicon nitride ($SrSi_6N_8$) single crystals was reported by Stadler et al. [14], as shown in Fig. 1 and Table 1. Figure 1 was drawn with the visualization program VESTA [15]. As seen, the framework of $SrSi_6N_8$ differs from any other silicates, which contains SiN_4 tetrahedrons and direct Si–Si bonds in N_3Si–SiN_3. In the framework each nitrogen atom bridges three silicon atoms. The Sr^{2+} atoms are tenfold coordinated to N^{3-} anions at distances of 2.69–3.16 Å (see Fig. 2) [14].

Powder samples of $SrSi_6N_8$:Eu^{2+}, with europium concentration varying in the range of 0–3 at% with respect to strontium, were prepared from α-Si_3N_4 (SN-E10, Ube Industries Ltd.), $SrSi_2$ (Kojyundo Chemical Laboratory Co., Ltd.), and Eu_2O_3 (Shin-Etsu Chemical Co., Ltd.). The powder mixtures were synthesized by sintering at 1900 °C for 2 or 4 h under 0.9 MPa nitrogen atmosphere. The product phase was identified by X-ray powder diffraction (Model RINT-2000, Rigaku, Tokyo, Japan) using CuKα radiation. A single phase was confirmed by comparing the XRD pattern of the sample with the simulated pattern of ICSD#391265 data. The photoluminescence spectra of the powder phosphor were measured by fluorescent spectrophotometer (Model F-4500, Hitachi) at room temperature. The absorption spectra, temperature-dependent emission intensity, and the external quantum efficiency were measured by an intensified multichannel spectrophotometer (Model MCPD-7000, Otsuka Electronics Co Ltd).

The photoluminescence spectra and absorption of powder phosphors are shown in Fig. 3. The phosphor exhibits an intense blue emission upon UV or near-UV excitation. The emission spectrum consists of a single broad band with

K. Shioi (✉)
Corporate R&D Centers, Showa Denko K.K., 1-1-1 Ohnodai,
Midori-ku, Chiba 267-0056, Japan
e-mail: shioi.kousuke@nims.go.jp

N. Hirosaki · R.-J. Xie · T. Takeda · Y. Li
National Institute for Materials Science, 1-1 Namiki,
Tsukuba-shi, Ibaraki 305-0044, Japan

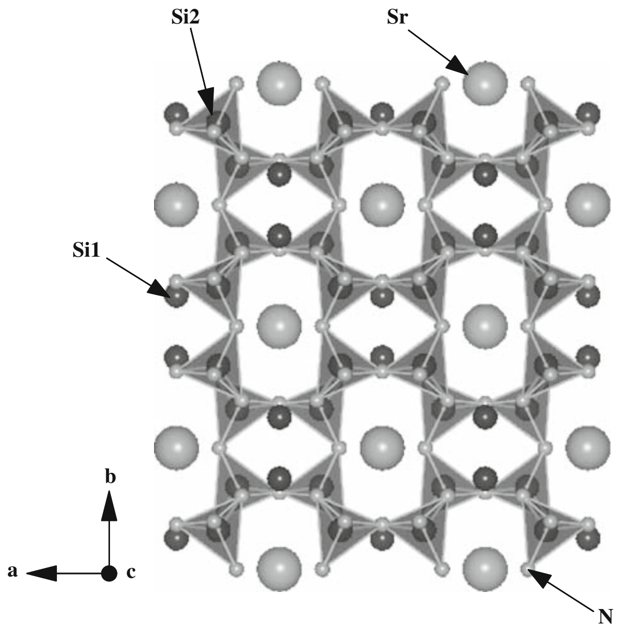

Fig. 1 Crystal structure of $SrSi_6N_8$ (ICSD#391265) along [001]

Table 1 Crystal structure and unit cell parameters of $SrSi_6N_8$

ICSD #391265			
Unit cell (Å)	7.855 (2)	9.260 (2)	4.801 (1)
Vol (Å^3)	349.21		
Z	2		
Space group	I m m 2		
Cryst Sys	Orthorhombic		

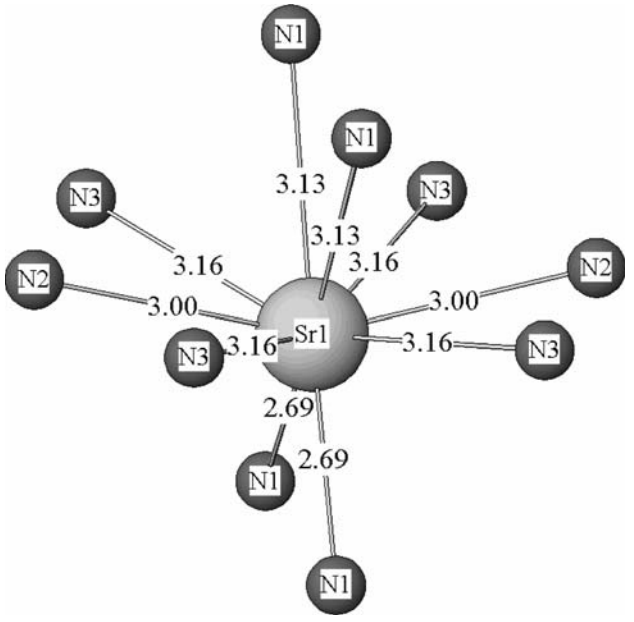

Fig. 2 Coordination of Sr^{2+} atoms and Sr^{2+} to N^{3-} distances (Å) in $SrSi_6N_8$ (ICSD#391265)

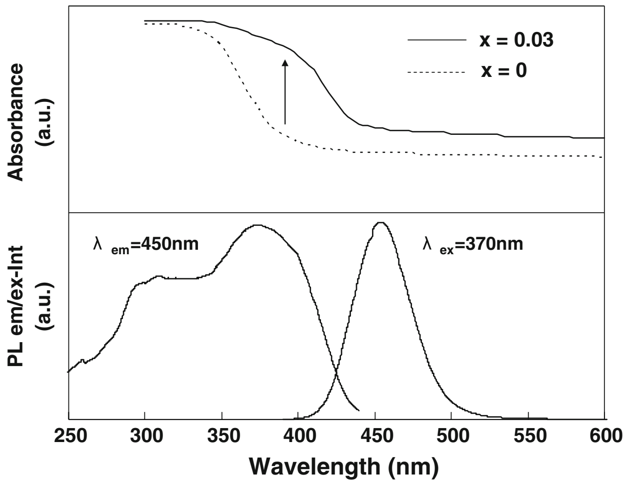

Fig. 3 Photoluminescence spectra and absorption of 0–3 at% Eu^{2+}-doped $SrSi_6N_8$

a maximum wavelength at about 450 nm. The full width at half maximum of the emission is about 44 nm. No red line emission from Eu^{3+} is observed, indicating that the valence of Eu ions in $SrSi_6N_8$ powders is divalent. Usually, Eu^{2+} activated (oxy)nitride phosphors such as $M_2Si_5N_8$:Eu^{2+} (M = Ca, Sr, and Ba) [6, 7] and Ca-α-SiAlON:Eu^{2+} [8, 11] show much longer wavelength emissions (e.g., red, yellow) than that of $SrSi_6N_8$:Eu^{2+}. The shorter emission wavelength in $SrSi_6N_8$:Eu^{2+} is due to the tenfold coordination of Eu^{2+} to N^{3-} anions (versus sixfold coordination in $M_2Si_5N_8$ (M = Ca, Sr, and Ba), sevenfold coordination in Ca-α-SiAlON), and large metal–ligand distances in $SrSi_6N_8$ [8], which results in weaker crystal-field splitting. For example, the average Sr–N distance in $SrSi_6N_8$ (0.3028 nm) is longer than that observed in Ca-α-SiAlON (0.2606 nm) and $Ca_2Si_5N_8$ (0.2652–0.2708 nm). The excitation spectrum consists of two broad bands centered at 310 nm and 370 nm, respectively. The absorption edge of the sample without Eu^{2+} is at about ~340 nm, whereas it shifts to ~380 nm of the sample with 3 at% Eu^{2+}.

The external quantum efficiency and internal quantum efficiency were calculated in the same way as described in the previous work [12]. At current synthesis conditions, the internal quantum efficiency of $SrSi_6N_8$:Eu^{2+} phosphor with Eu^{2+} concentration of 3 at% was 44 and 38% at the excitation wavelength of 370 nm and 405 nm, respectively, and the corresponding external quantum efficiency was 38 and 28%. As shown in Fig. 3, the absorbance of the same sample was 86, 73, and 41% at the excitation wavelength of 370, 405, and 500 nm, respectively. The low quantum efficiency can be interpreted by the strong absorption in the range of 430–600 nm, which leads to the consumption of a large number of photons in the emission of the phosphor. The strong absorption is perhaps due to impurities or the incompleteness of the host lattice of this phosphor. In other

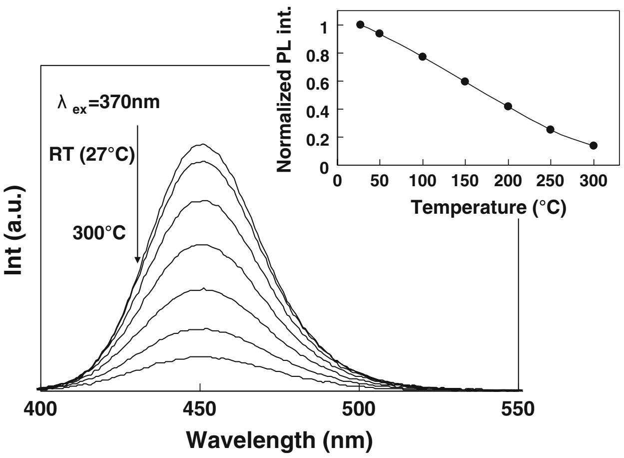

Fig. 4 Temperature-dependent emission intensity and emission spectra of 3 at% Eu^{2+}-doped $SrSi_6N_8$

words, it means that with decreasing the absorption in the range of 430–600 nm, the quantum efficiency of the phosphor will be improved.

Figure 4 presents the temperature-dependent emission intensity of $SrSi_6N_8:Eu^{2+}$ phosphor. It is observed that the thermal stability of $SrSi_6N_8:Eu^{2+}$ phosphor is not so high when compared to that of other (oxy)nitride phosphors. At 150 °C the phosphor can maintain about 60% of the intensity that measured at room temperature. Unfortunately, we still do not understand the exact reasons of the thermal stability of $SrSi_6N_8:Eu^{2+}$ phosphor and are making great efforts to do that. In addition, the emission spectra of this phosphor do not exhibit any shifts except the intensity as the temperature increases, indicative of its high stability of chromaticity against temperature.

Figure 5 shows the Commission International de l'Eclairage (CIE)1931 chromaticity coordinates of the $SrSi_6N_8:Eu^{2+}$, $AlN:Eu^{2+}$ [16], and $SrSiAl_2O_3N_2:Eu^{2+}$ [17] phosphors and National Television System Committee (NTSC) chromaticity coordinates. The chromaticity coordinates of $SrSi_6N_8:Eu^{2+}$ phosphor are $x = 0.15$ and $y = 0.048$. It is significantly better than that of $SrSiAl_2O_3N_2:Eu^{2+}$ ($x = 0.17$ and $y = 0.215$), and is superior to $AlN:Eu^{2+}$ (x = 0.139 and y = 0.106), and is close to $BaMgAl_{10}O_{17}:Eu^{2+}$ (x = 0.146 and y = 0.047) in the color purity. As seen, the chromaticity coordinates of the $SrSi_6N_8:Eu^{2+}$ phosphor is beyond NTSC, implying that a large color gamut can be realized. As mentioned above, usually, Eu^{2+} activated (oxy)nitride phosphors show much longer wavelength emissions than that of $SrSi_6N_8$. It means that (oxy)nitride phosphors with the large coordination numbers such as $SrSi_6N_8$ are suitable for a blue phosphor.

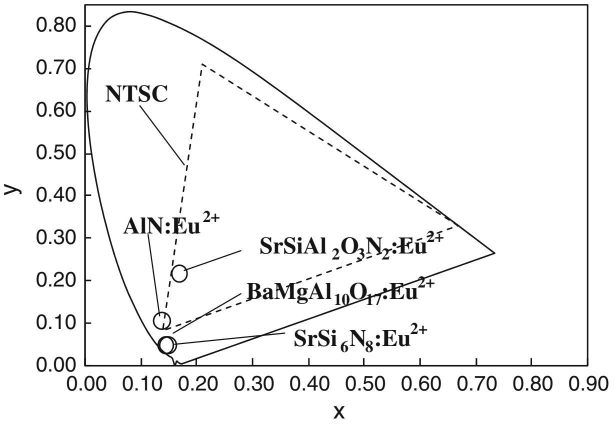

Fig. 5 CIE chromatic coordinates of 3 at% Eu^{2+}-doped $SrSi_6N_8$, $BaMgAl_{10}O_{17}:Eu^{2+}$, $AlN:Eu^{2+}$, and $SrSiAl_2O_3N_2:Eu^{2+}$

In summary, a blue-emitting $SrSi_6N_8:Eu^{2+}$ nitride phosphor was synthesized by the gas-pressure sintering method. This phosphor shows the wide excitation spectrum covering from 300 nm to 430 nm, and emits pure-blue light. It means that the $SrSi_6N_8:Eu^{2+}$ phosphor could be a good blue phosphor candidate for creating white-light when combined with a UV-LED and other green and red phosphors.

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