

Synthesis and optical properties of $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ red phosphor for application to white LEDs

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In recent years, SiN_4 -based covalent nitride materials, including nitridosilicates, and nitridoaluminosilicates have been extensively studied as good host lattices for white light-emitting diodes (LEDs). In this study, Eu^{2+} -doped strontium nitridosilicate ($\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$) red phosphor was successfully synthesized using a direct reaction among strontium carbonate (SrCO_3), Eu_2O_3 , and Si_3N_4 . The single-phase $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ phosphor was obtained by firing at 1550°C for 2 hrs under a 0.4 MPa ($\text{N}_2 + 4\% \text{H}_2$) atmosphere. The synthesized $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ phosphor presented a broadband excitation spectrum between 300 and 500 nm, which matches well the blue emission (400–460 nm) of current InGaN LEDs. The temperature dependence of the photoluminescence properties of the prepared $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ phosphor was investigated from 25 to 200°C , and the activation energy (ΔE) for thermal quenching was determined by Arrhenius fitting. This phosphor, with an encapsulant, was incorporated into an InGaN LED ($\lambda_{\text{max}} = 440 \text{ nm}$), and the CIE chromatic coordinates and color rendering index of the white light were measured from 20 to 100 mA.

Key words: White LEDs, $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$, Phosphor, Photoluminescence, Thermal quenching.

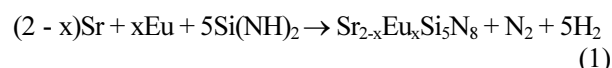
Introduction

Low-cost, easily fabricated white light-emitting diodes (LEDs) with a high degree of brightness have drawn much attention since the discovery that cool white-light emission could be generated by combining the blue emission of an InGaN diode chip with the yellow luminescence of the $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}^{3+}$ (YAG : Ce^{3+}) phosphor [1–4]. However, this white light has a low color rendering index (CRI) because the emitted yellow light lacks sufficient red emission. To obtain a good color rendering, warm white light output within a phosphor can be generated by two methods. One is to compensate for the red deficiency of a YAG : Ce^{3+} -based LED by using a separate red light [5], and the other is to combine a UV chip with red-, green-, and blue-emitting (RGB) phosphors [6]. For both methods red phosphors that can be efficiently excited by an InGaN LED chip are in great demand.

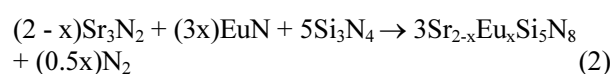
In recent years, SiN_4 -based covalent nitride materials, such as nitridosilicates, nitridoaluminosilicates, and other nitrides have been extensively studied as good host lattices for LEDs; these materials include $\text{M}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ and $\text{MAlSiN}_3 : \text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [7–15]. Among these phosphors, $\text{M}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ has demonstrated high luminescence intensity and very low thermal quenching. Several approaches have been used in attempts to

synthesize $\text{M}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ phosphors, including a traditional solid-state reaction method using nitride raw materials and a reaction between metals and silicon diimide $\text{Si}(\text{NH})_2$ [10,16]. These materials are not only expensive but also very sensitive to oxygen and moisture; thus, $\text{Si}(\text{NH})_2$ is difficult to prepare from pure grade reagents. The carbothermal reduction and nitridation (CRN) method can significantly degrade the optical properties of phosphors, because the obtained phosphors can be easily contaminated by residual carbon [7, 9].

Two common synthetic strategies for $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ have been proposed in the literature [17]. The first one involves the reaction of stoichiometric amounts of strontium metal and europium metal with silicon diimide [$\text{Si}(\text{NH})_2$] in a radio-frequency furnace:



The second one involves the reaction of strontium nitride (Sr_3N_2) and europium nitride (EuN) with silicon nitride (Si_3N_4) in a horizontal tube or graphite furnace under a nitrogen atmosphere:



The raw powders such as $\text{Si}(\text{NH})_2$ and EuN are not only expensive but also commercially unavailable, so they have to be synthesized in the laboratory first. Furthermore, the powder must be mixed in a dry,

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nitrogen-filled glove box because the raw materials are very sensitive to oxygen and moisture. Thus, both of the above-mentioned synthetic methods involve complex multistep procedures, difficulty in handling the materials, high costs, and low yields. Recently, the CRN method has been used to produce $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ according to the following chemical reaction:



This method will certainly introduce residual carbon into the phosphor, reducing its absorption and emission significantly. To remove the residual carbon, it is necessary to anneal the powder in air or oxygen at temperatures above 600 °C. However, no red emission is observed for $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ after heat treatment at 600 °C for 2 hrs, because Eu^{2+} is oxidized to Eu^{3+} [17]. This implies that the residual carbon in the synthesized powder is still not completely removed. Therefore, it is highly desirable to develop an inexpensive, straightforward, and efficient method to synthesize a high-brightness $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ red phosphor for industrial applications, and this remains an important task for materials engineers.

Here, we report a novel synthetic route to $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ red phosphor based on a direct reaction among strontium carbonate (SrCO_3), Eu_2O_3 , and Si_3N_4 . All the raw materials used are commercially available and relatively inexpensive, and the raw powders can be handled in an ambient atmosphere, so the reaction is a simple, efficient, and high-yield route to $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$. The crystal structure and the photoluminescence (PL) properties of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ phosphor were investigated. White LEDs based on a combination of an InGaN LED chip ($\lambda_{\text{max}} = 440 \text{ nm}$) and the $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ phosphors were fabricated and evaluated, along with the thermal quenching of the PL.

Experimental

$\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ red phosphors were prepared by a solid-state reaction of SrCO_3 and Si_3N_4 with the ratio of 2 : 1. $\alpha\text{-Si}_3\text{N}_4$ (SN-E10, Ube Industries), Eu_2O_3 (Shin-Etsu Chemical Co. Ltd.), and SrCO_3 (Sigma-Aldrich) were used as starting powders and mixed in ethanol for 2 hrs. The concentration of Eu^{2+} was fixed at 2.0 at% with respect to Sr^{2+} . After drying, the powder mixture was fired at 1550 °C for 2 hrs at 0.4 MPa ($\text{N}_2 + 4\% \text{ H}_2$) using a gas-pressure sintering furnace with a graphite heater. The fired powder sample was washed in a 5% nitric acid solution for 30 min at room temperature to eliminate oxide phases. The washed phosphor powder was dried for 12 hrs at 90 °C using a drying oven. The phases of the synthesized phosphor powder were identified using X-ray diffraction (XRD, Cu K α , 40 kV, 30 mA, Rigaku) at a scan rate of 3 °/min. The oxygen and nitrogen contents were measured by an O/N analyzer (EMGA-550, HORIBA).

Contour maps of 2D and 3D PL spectra of the prepared phosphor samples were obtained using a spectrophotometer (FluoroMate FS-2, SCINCO). The temperature quenching behavior was measured between 25 and 200 °C using a 450 W xenon lamp as an excitation source. Prototype white-LED devices were fabricated by applying a synthesized mixture of $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ red phosphor, $\beta\text{-SiAlON} : \text{Eu}^{2+}$ green phosphor (commercial), and transparent silicone resin on an InGaN LED ($\lambda_{\text{max}} = 440 \text{ nm}$). The device was then encapsulated in a phosphor/silicone mixture, with the mixture placed directly on the headers, and cured at 150 °C. After the packaging was completed, the device with the phosphor was measured in an integrating sphere under various DC forward-bias conditions [18].

Results and Discussion

Because $\text{Sr}_2\text{Si}_5\text{N}_8$ and $\text{Eu}_2\text{Si}_5\text{N}_8$ are isostructural (space group: $\text{Pmn}2_1$) [19], and Sr^{2+} and Eu^{2+} have similar ionic radii [20], a complete solid solution of $(\text{Sr}_{1-x}\text{Eu}_x)_2\text{Si}_5\text{N}_8$ is formed. As the optimized Eu^{2+} concentration is well known to be 2.0 at% (vs. the Sr sites) [21], a typical sample of $\text{Sr}_{1.96}\text{Eu}_{0.04}\text{Si}_5\text{N}_8$ is selected for characterization in this work. Fig. 1(a) shows the XRD pattern of the obtained phosphor after firing at 1550 °C for 2 hrs. All of the peaks are indexed as the $\text{Sr}_2\text{Si}_5\text{N}_8$ phase, as shown in Fig. 1(b) (JCPDS: 85-0101). The real structure of $\text{Sr}_2\text{Si}_5\text{N}_8$ is considered to be orthorhombic with $Z = 2$, $a = 571.00 \text{ pm}$, $b = 682.20 \text{ pm}$, and $c = 934.10 \text{ pm}$ [22]. As ideal $\text{Sr}_2\text{Si}_5\text{N}_8$ and $\text{Eu}_2\text{Si}_5\text{N}_8$ are isotopic, and the ionic radius of Eu^{2+} (130 pm) is nearly equal to that of Sr^{2+} (127 pm), Eu^{2+} doping has little influence on the structure, as shown in Fig. 1. The O/N analysis revealed a small amount of

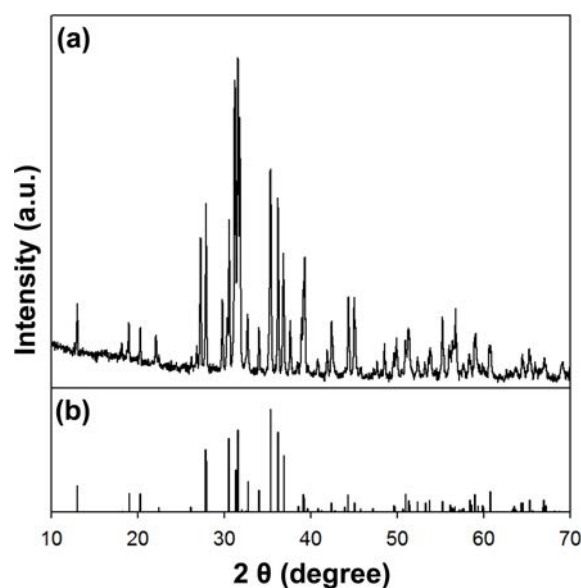


Fig. 1. XRD patterns of the (a) synthesized $\text{Sr}_2\text{Si}_5\text{N}_8 : \text{Eu}^{2+}$ sample and (b) JCPDS standard of $\text{Sr}_2\text{Si}_5\text{N}_8$ (85-0101).

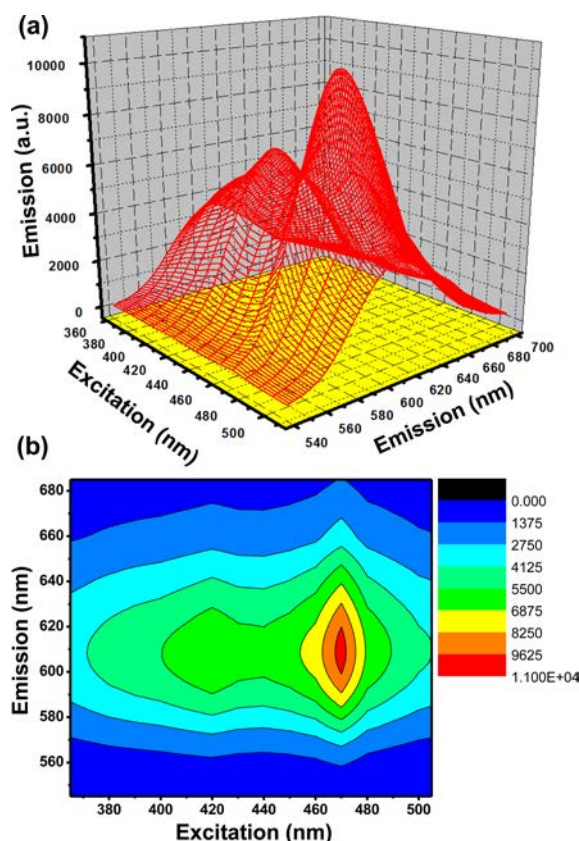


Fig. 2. (a) 3D and (b) 2D PL (excitation and emission) contour maps of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor.

oxygen (about 0.6 wt%). The charge imbalance is assumed to be compensated by the slight evaporation of Sr during the high-temperature sintering process, according to a previous work [21].

To determine the optimal excitation and emission conditions, 3D and 2D contour maps of the PL were obtained. Fig. 2 shows the 3D and 2D PL (excitation and emission) contour maps of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor. The excitation spectra, which were taken at 615 nm, are all very similar, with a sharp major peak at 470 nm. This is a characteristic excitation transition of the Eu^{2+} ion, corresponding to a direct Eu^{2+} ion ($4f^7 4f^6 \leftrightarrow 5d$) transition [12–14]. As shown in Figs. 2(a) and 2(b), the 3D and 2D contour maps of the PL indicated that the strongest emission wavelength is near 615 nm and occurs under excitation in a wavelength range of 380 to 470 nm.

The PL spectra of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor are plotted in Fig. 3. The excitation spectrum ($\lambda_{\text{emi.}} = 615 \text{ nm}$) consists of two broad bands covering UV to visible wavelengths, where the excitation of the Eu^{2+} ion ($4f^7 \rightarrow 4f^6 5d$) is dominant. Generally, the 5d levels of Eu^{2+} ions that are not shielded from the outside environment split regularly under ligand fields, exhibiting, for example, O_h or T_d symmetry, and the number of split levels is determined by the local symmetry around the Eu^{2+} ions [23]. For $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$, however, the complicated coordination environments of the two crystallographic

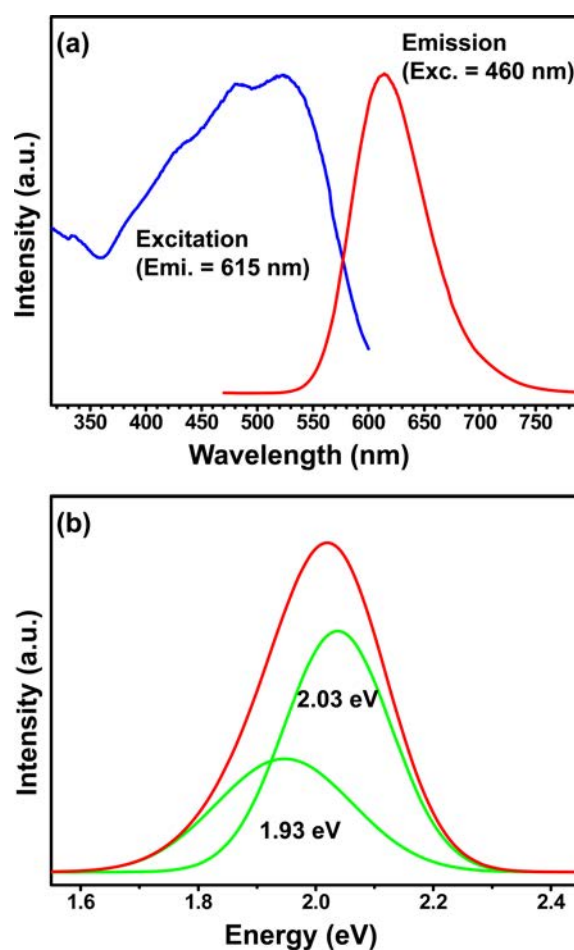


Fig. 3. (a) PL spectra of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ powder sample. (b) Gaussian deconvolution of the emission peak on an energy scale (eV).

Sr^{2+} sites (with coordination numbers of 8 and 10, respectively) make it impossible to resolve the excitation band precisely. Nevertheless, the 5d state is assumed to separate into two energy levels according to the two broad bands located at 320 and 460 nm. Such similarity in the excitation spectra is also observed in the $\text{Ca-a-SiAlON}:\text{Eu}^{2+}$ [24] and $\text{MAL}_2\text{S}_4:\text{Eu}^{2+}$ [25] phosphors. The excitation energy can be transferred nonradiatively from the host to the activator, resulting in red light emission. It is noteworthy that the strong absorption at 400–470 nm matches perfectly the emission of commercial blue light GaN or InGaN LEDs. The broad band emission (peaking at 615 nm) of the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor under excitation at 460 nm is assigned to the allowed $4f^6 5d^1 4f^7$ transition of the Eu^{2+} ion. Owing to the highly covalent environment around Eu^{2+} ions (the nephelauxetic effect), which effectively lowers the center of gravity of the 5d orbitals of Eu^{2+} ions, the emission of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ is observed in a fairly wide wavelength region than compared to that of other silicate or borate phosphors [26].

Considering the two crystallographic Sr sites in $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ with the coordination number of 8 and

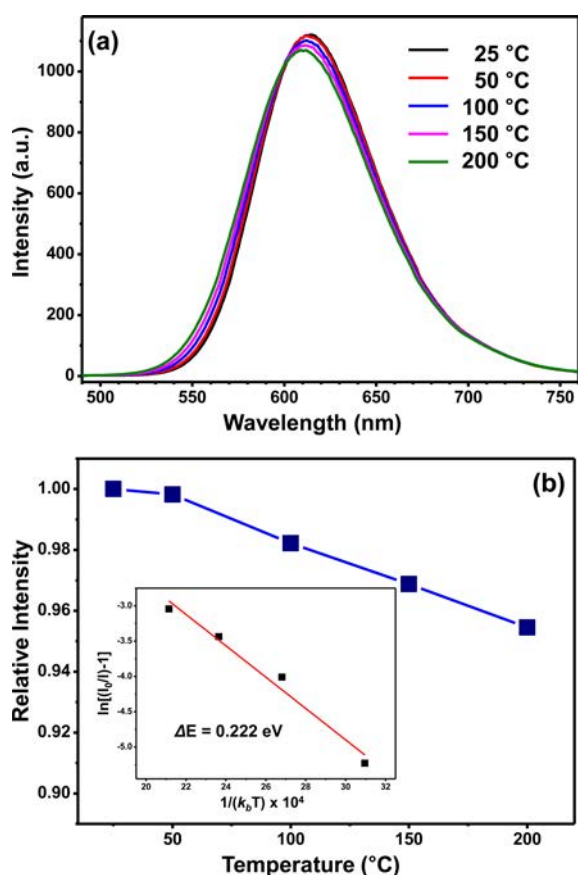


Fig. 4. (a) Emission spectra of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor powder measured at 25 to 200 °C. (b) Temperature dependence of emission peak intensity in this temperature range. The graph in the inset depicts an Arrhenius fitting of the emission intensity in the measured temperature range with the calculated activation energy for thermal quenching (ΔE).

10 [27], the emission is expected to be separated into two bands. In the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$, however, only broadband emission with a full-width at half-maximum of about 75 nm is observed even at room temperature. This phenomenon suggests that the two Sr sites have similar crystallographic environments, so eventually the two emission bands overlap. As shown in Fig. 3(b), the broadband emission can be deconvolved well on an energy scale into two Gaussian curves peaking at 1.93 and 2.03 eV (610.8 and 642.5 nm).

Furthermore, the rigid host structure based on the vertex-linked SiN_4 reduces the thermal quenching effect. Fig. 4(a) shows emission spectra of the prepared $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor as a function of the measurement temperature. Fig. 4(b) shows the temperature-dependent emission intensity of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor. When the temperature increases from 25 to 200 °C, the emission band peak at 615 nm shows almost no shift, and the emission intensity is decreased by only 5% of the initial value. In $\text{M}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ ($\text{M} = \text{Sr}, \text{Ba}$) phosphors, the thermal quenching effect depends strongly on the Eu^{2+} concentration, and contributes dominantly to the energy migration from $\text{Eu}(\text{site } 2)^{2+}$ to $\text{Eu}(\text{site } 1)^{2+}$,

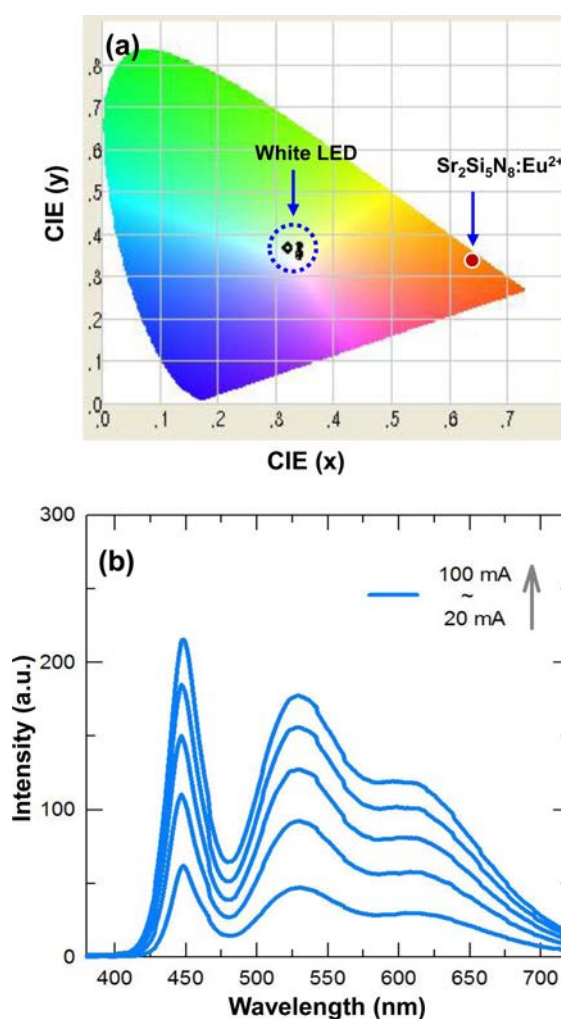


Fig. 5. (a) CIE chromatic coordinates of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor powder and white LED under different forward-bias currents. (b) Electroluminescence of the white LED (InGaN LED + phosphors) under different forward-bias currents.

which is followed by nonradiative emission [28]. In this work, the concentration of the Eu^{2+} activator is set at 2 at% (vs. the Sr sites). Thus, the high-energy emission becomes dominant, and energy migration is suppressed to the fullest extent. When the temperature is increased to 100 °C, at which white LEDs usually operate, the emission intensity of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor remains about 98% of that measured at room temperature. For application in white LEDs, the low temperature quenching effect helps maintain the chromaticity and brightness of the output white light.

To further understand the temperature dependence of the PL intensity and to determine the activation energy for thermal quenching, the Arrhenius equation was fitted to the thermal quenching data as shown in the inset of Fig. 4(b). According to the classical theory of thermal quenching, the temperature-dependent emission peak intensity can be described by the expression: [29]

$$I(T) = \frac{I_0}{1 + A \exp\left(\frac{-\Delta E}{k_B T}\right)} \quad (4)$$

where I_0 is the initial intensity, $I(T)$ is the intensity at a given temperature T , A is a constant, ΔE is the activation energy for thermal quenching, and k_B is Boltzmann's constant. The graph in the inset of Fig. 4(b) plots $\ln[(I_0/I(T)-1)]$ versus $1/(k_B T)$ and shows a straight line up to $T = 200$ °C. The best fit following Eq. (4) gives an activation energy ΔE of 0.222 eV.

Commission Internationale de l'Eclairage (CIE) 1931 chromaticity coordinate (x, y) of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor is (0.632, 0.328), as shown in Fig. 5(a). In the display field, however, white light with a high CRI is expected, which can be realized by adopting an RGB model. Here we also present two phosphor-converted LEDs fabricated by combining an InGaN blue LED chip with red $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ and a green phosphor, $\beta\text{-SiAlON}:\text{Eu}^{2+}$ [30]. The electroluminescence spectra of the fabricated white LEDs under a forward-bias current from 20 to 100 mA are shown in Fig. 5(b). The CIE chromatic coordinates of the device under 20 mA were (0.33, 0.38), and the CRI was about 92.

Summary

The $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ red phosphor was successfully synthesized using a direct reaction among strontium carbonate (SrCO_3), Eu_2O_3 , and Si_3N_4 . The XRD results showed that Eu^{2+} doping has little influence on the structure, and a small amount of oxygen (about 0.6 wt%) was detected by O/N analysis. The 3D and 2D contour maps of the PL indicated that the strongest emission wavelength is near 615 nm and occurs under excitation in a wavelength range of 380 to 470 nm. The strong absorption of the synthesized $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ red phosphor at 400–470 nm matches perfectly the emission of commercial blue light GaN or InGaN LEDs. The broad-band emission (peaking at 615 nm) under excitation at 460 nm was assigned to the allowed $4f^6 \rightarrow 5d^1 4f^7$ transition of Eu^{2+} ions. The activation energy (ΔE) for thermal quenching was determined to be 0.222 eV by Arrhenius fitting. When the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ red phosphor, with an encapsulant, was incorporated into an InGaN LED ($\lambda_{\text{max}} = 440$ nm), the CIE chromatic coordinates of the device under 20 mA were (0.33, 0.38), and the CRI was about 92.

Acknowledgments

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