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# Effects of full-range Eu concentration on Sr<sub>2-2x</sub>Eu<sub>2x</sub>Si<sub>5</sub>N<sub>8</sub> phosphors:

# a deep-red emission and luminescent thermal quenching

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# Abstract

To fabricate white-light-emitting diodes (white LEDs) with high color-rendering index or full light spectrum emission, the discovery of more efficient deep-red emitting phosphor materials is essential. In this paper, we have synthesized a series of  $Sr_{2-2x}Eu_{2x}Si_5N_8$  ( $0 \le x \le 1$ ) solid-solution compounds, and have systemically investigated effects of full-range Eu concentration on their luminescence. Their emission band maximum can be largely tuned from 610 to 725 nm by increasing Eu content. Reabsorption at low  $Eu^{2+}$  concentration while both the energy transfer and Stocks shift at high  $Eu^{2+}$  concentration account for this large spectral red-shift. Luminescent thermal quenching performance gets worse with  $Eu^{2+}$  concentration increasing. The compound with x = 0.15 possesses the best crystallinity and the highest luminescence intensity with the peak position around 660 nm, and still maintains 88.5% room-temperature intensity at 400 K, indicating that great potential for the application as a deep-red phosphor.

**Keywords:** Nitride phosphor;  $Sr_2Si_5N_8$ ;  $Eu^{2+}$  concentration; Deep-red; Thermal luminescent quenching

# **1** Introduction

In the recent years, white light emitting diodes (w-LED) lamps fabricated by blue chips combined with phosphors have wide applications. As is well known, LED phosphor plays a key role in LED lighting quality, such as luminous efficiency, color-rendering index (CRI), and thermal stability etc. The continuous improvement of LED phosphors makes possible their using for high quality LED lighting. Currently, the commercial phosphors for LED lamps include (Y, Gd)<sub>3</sub>(Al, Ga)<sub>5</sub>O<sub>12</sub>: Ce<sup>3+</sup> (maximum emission covering 525~580 nm) [1-2], (Ca, Sr)AlSiN<sub>3</sub>: Eu<sup>2+</sup> (610~660 nm) [3-8], (Ba, Sr)<sub>2</sub>SiO<sub>4</sub>: Eu<sup>2+</sup> (515~525 nm) [9-10], A<sub>2</sub>BF<sub>6</sub> (A = Na, K, Rb, Cs; A2 = Ba, Zn; B = Si, Ge, Ti, Zr, Sn): Mn<sup>4+</sup> (narrow band emission, ~630 nm) [11-13], SrLiAl<sub>3</sub>N<sub>4</sub>:

 $Eu^{2+}$  (narrow band emission, ~650nm) [14-15] and  $BaSi_2O_2N_2$ :  $Eu^{2+}$  (~490 nm) [16-18]. However, the phosphors with emission wavelength longer than 660 nm (deep-red emission) are urgently demanded in many LED applications, such as full-spectrum illumination, colorful decoration lighting and plant growing lighting.

The d-f parity-allowed electric dipole transition of activator ions (e.g.,  $Eu^{2+}$  and  $Ce^{3+}$ ) can achieve high-intensity emission [19]. The wavelengths of absorption and emission can be tuned by the host lattice because of the strong interaction between the 5d-electron and the neighboring anion ligands. Compared to fluorides and oxides, nitrides can cause larger centroid shift of 5d energy levels and lead to a red shift of the excitation/emission spectra. Among the nitride phosphors, red-emitting  $M_2Si_5N_8:Eu^{2+}$  (M = Ca, Sr, Ba) phosphors have attracted significant attention for their outstanding performance in w-LED applications [20-26]. The structure of  $M_2Si_5N_8$  was determined in 1995 [27]. In order to tune luminescent properties, researchers investigated the effect of cation replacement on M sites [22], or co-substitution of Al-O for Si-N [28-29]; however, these tunings failed to shift emission peak wavelength to deep-red range.

The  $Sr_2Si_5N_8$  phosphors doped solely with  $Eu^{2+}$ ,  $Mn^{2+}$  [20],  $Ce^{3+}$  [30], and co-doped with  $Eu^{2+}$  and  $Tm^{3+}$  [23] were investigated in detail. Compared with red  $Eu^{2+}$ emission in these host lattices,  $Mn^{2+}$  and  $Ce^{3+}$  usually give weaker emission, which is less suitable for application in LED package, although they can show various emission bands from green to deep red. The  $Tm^{3+}$  and  $Eu^{2+}$  co-doped  $Sr_2Si_5N_8$  red phosphor also shows emission intensity weaker than of  $Sr_2Si_5N_8:Eu^{2+}$ , but it is more suitable as an afterglow red phosphor [31-34]. Therefore, up to now, it should be mentioned that  $Eu^{2+}$  ion is the most promising activator for  $Sr_2Si_5N_8$  host lattice, which can emit broad emission bands derived from  $4f^65d-4f^7$  transition.

Eu<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> has the same crystal structure with Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>, and the ionic radius of Eu<sup>2+</sup>, Sr<sup>2+</sup> are very close (0.117 nm for Eu<sup>2+</sup> vs. 0.118 nm for Sr<sup>2+</sup> under six coordination). Therefore, a completely miscible solid solution Sr<sub>2-2x</sub>Eu<sub>2x</sub>Si<sub>5</sub>N<sub>8</sub> is expected to form in the range of x = 0-1. Generally, with the increase of Eu<sup>2+</sup> concentration, the emission spectrum shifts to red region due to re-absorption or energy transfer. However, the luminescence efficiency and thermal stability would decrease due to concentration quenching effect. In this paper, we have synthesized a series of compounds Sr<sub>2-2x</sub>Eu<sub>2x</sub>Si<sub>5</sub>N<sub>8</sub> (x = 0-1), and investigated the effect of full-range Eu<sup>2+</sup> concentration on luminescence properties. We find that the Eu<sup>2+</sup> concentration effect is in greatly different in previously reported systems. Sr<sub>2-2x</sub>Eu<sub>2x</sub>Si<sub>5</sub>N<sub>8</sub> with x = 0.15 gives the maximum integrated intensity at around 660 nm and shows brilliant luminescent thermal quenching resistance. The origins of these phenomena are also discussed in details.

# **2** Experimental Section

#### 2.1 Synthetic procedures

Synthesis of  $Sr_{2-2x}Eu_{2x}Si_5N_8$  ( $0 \le x \le 1$ ) solid solution compounds. The raw materials,  $Sr_3N_2$  and EuN were prepared by nitridation of the corresponding pure metals (metallic strontium and calcium, block, 99.9%, Beijing Founde Star Science &

Technology Co, Ltd.) in a tube furnace with high purity  $N_2$  (99.999%) flow. The as-prepared metal nitrides and  $Si_3N_4$  (fluorescent grade, UBE) were weighed out in stoichiometric ratio, ground and mixed in an agate mortar. Then, the homogeneous mixtures were transferred into BN crucibles, which were fired in the high temperature sintering furnace at 1700  $\Box$  for 8 h under a  $N_2$  atmosphere of 1.2 MPa. It is noteworthy that all the above-mentioned processes were carried out in a purified nitrogen glovebox, where both the oxygen and moisture content were maintained below 1 ppm. Finally, the synthesized samples were ground into powder and sieved in nylon screen of 200 mesh for measurements.

**Fabrication of phosphor converted LEDs.** First, the blue LED dies ( $\lambda_d$ : 455.0~457.5 nm) were attached with silver adhesive on the lead-frame of the commercial surface mounted device (SMD) packages of 5730 type (plastic sizes of length 5.7 mm and width 3.0 mm). Then, the LED dies were connected to the two electrodes by gold wires. The phosphors and silicone resin were weighed out according to a proper mass ratio, then dispensed by a standard deposition method. After that, the LED devices were fabricated by coating the mixture of phosphors and silicone resin homogeneously to the LED dies. The obtained LEDs were thermally cured at 80  $\square$  for 1 h and then 150  $\square$  for 2 h.

## 2.2 Characterization

The X-ray diffraction (XRD) data of as-prepared samples were checked by a Rigaku SmartLab high-resolution X-ray diffractometer with Cu K $\alpha$ 1 radiation ( $\lambda$  = 1.5406 Å) at 40 kV and 40 mA in the 2 $\theta$  range from 10 to 80°. The Rietveld refinement was conducted using the FullProf Suit package. The photoluminescent (PL) and photoluminescent excitation (PLE) spectra were measured by Edingburgh FLS920 fluorescence spectrophotometer using a xenon lamp as the excitation light source. The time-resolved photoluminescence spectra at 11K were performed by Spex Fluorolog 2 spectrofluorometer equipped with a helium flow cryostat. The emitted photons were collected with a Hamamatsu R928P photomultiplier. The crystalline morphology of as-prepared powders were characterized by Analytical Scanning Electron Microscope (JSM-6510A). The electro-luminescence spectra and correlated color temperature (CCT) of the fabricated LEDs were carried by using UV-VIS-near IR Spectrophotocolormeter (PMS-80, EVERFINE PHOTO-E-INFO Co., LTD) with an integrating sphere (diameter = 0.3 m).

# **3 Results and discussion**

# 3.1 Crystal Structure

The crystal structure of the obtained  $Sr_{2-2x}Eu_{2x}Si_5N_8$  ( $0 \le x \le 1$ ) phosphors were characterized by X-ray powder diffraction (XRD). According to previous report,  $Sr_2Si_5N_8$  and  $Eu_2Si_5N_8$  are isostructural with the orthorhombic compounds crystalized in space group Pmn2<sub>1</sub> (No.31) [35]. As shown in Fig. 1, all the diffraction patterns are well matched with both the calculated patterns of  $Sr_2Si_5N_8$  (ICSD No. 401500) [27] and  $Eu_2Si_5N_8$  (ICSD No. 59257) [36]. There are no obvious diffraction peaks from impurity phases. This indicates that all the phosphor samples are in pure phase state. Therefore, the  $Sr_{2-2x}Eu_{2x}Si_5N_8$  ( $0 \le x \le 1$ ) solid solution phosphors can be obtained by



substituting  $Eu^{2+}$  ions for  $Sr^{2+}$  ions, that is in consistent with previous reports [37-38].

**Fig. 1.** XRD patterns of  $Sr_{2-2x}Eu_{2x}Si_5N_8$  ( $0 \le x \le 1$ ) phosphor samples.





The results of Rietveld refinement show that the lattice constants of  $Sr_2Si_5N_8$  are a = 5.761(2), b = 6.819(1), c = 9.340(3) Å, and V = 363.85 Å<sup>3</sup>. For Eu<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>, they are a = 5.708(1), b = 6.812(2), c = 9.332(7) Å, and V = 362.91 Å<sup>3</sup>. Both sets of parameters are in good accordance with the results of Schnick and Huppertz et al. [27, 39]. It is accepted that there are two kinds of Sr sites in Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>, namely, Sr1 and Sr2.

The Sr1 cage is larger than that of Sr2 due to longer average Sr-N bond length [40]. Researchers have different opinions concerning which site, i.e. Sr1 or Sr2, is preferable for Eu<sup>2+</sup> substitution. Piao et al. [38] argued that the Eu<sup>2+</sup> ions tend to occupy the loose sites (Sr1) first and then the tight sites (Sr2). However, Xie et al. [40] believed that the Eu<sup>2+</sup> ions tend to be evenly distributed over both Sr1 and Sr2 sites regardless of Eu<sup>2+</sup> concentration. In Fig. 2, the dependence of unit cell volume on Eu<sup>2+</sup> concentration is shown. The volume shrinkage on *x* increase is caused by the slightly smaller ionic radius of Eu<sup>2+</sup> compared with Sr<sup>2+</sup>. However, the slope at low Eu<sup>2+</sup> concentration (x  $\leq 0.05$ ) is larger than that at high Eu<sup>2+</sup> concentration (x > 0.05). Therefore, it can be inferred that at low Eu<sup>2+</sup> concentration, Eu<sup>2+</sup> ions occupy the looser Sr1 sites preferentially, resulting in a lager decreasing rate of unit cell volume (slope 1) corresponding to the opinion by Piao et al. At higher Eu<sup>2+</sup> concentration, however, Eu<sup>2+</sup> ions occupy the Sr1 and Sr2 sites evenly, resulting in a smaller decreasing rate (slope 2) corresponding to the opinion by Xie et al.



**Fig. 3.** The diffuse reflection spectra (a), PLE spectra (b) and PL spectra ( $\lambda_{ex} = 450$  nm) of Sr<sub>2-2x</sub>Eu<sub>2x</sub>Si<sub>5</sub>N<sub>8</sub> ( $0 \le x \le 1$ ) phosphors, (d) the emission peak wavelength and normalized integrated intensity as a function of Eu concentration. For the PLE spectra (c), the monitored wavelength is the peak wavelength corresponding to emission spectrum.

Fig. 3a shows the diffuse reflection spectra of  $Sr_{2\text{-}2x}Eu_{2x}Si_5N_8~(0\leq x\leq\!\!1)$  with

different Eu<sup>2+</sup> concentrations. For all Eu<sup>2+</sup> containing samples, there is a strong absorption band covering UV to visible-light region. By comparison with the reflection spectrum of pure Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>, we ascribe the 300~350 nm range to host absorption and the 380~500 nm range to the  $4f^7-4f^65d$  transition of Eu<sup>2+</sup> ions. At low  $Eu^{2+}$  concentrations, the reflection spectra are very similar to these reports by Li et al. and Horikawa et al. [37, 41] The absorption is intensified with increasing  $Eu^{2+}$ concentration and the band edge shifts to longer wavelengths. Similarly, there are two excitation bands in the PLE spectra (Fig. 3b) which are easy to distinguish when  $x \leq x$ 0.1 because there is a valley between them. However, when  $x \ge 0.15$ , the valley gradually disappeared and the two-excitation bands turn into one continuous excitation band in the range 300~550 nm. At low doping concentration, the  $Eu^{2+}$  ions are far separated from each other in the host, their 5d energy levels are extended in a smaller range and, so, the two-excitation bands are recognizable. However, as the  $Eu^{2+}$  concentration going up, the distance between  $Eu^{2+}$  ions is shortened. Then the 5d orbitals overlap more with each other, leading to a continuous and very broad excitation band.

Fig. 3c and 3d gives the PL spectra of  $Sr_{2-2x}Eu_{2x}Si_5N_8$  ( $0 \le x \le 1$ ) as a function of  $Eu^{2+}$  concentration. Generally, due to concentration quenching, the integrated intensity will reach the highest value at low concentration. Piao et al. [38] reported that the quenching concentration of  $Eu^{2+}$  ions in  $Sr_2Si_5N_8$  is about 0.02. Above 0.06, the emission intensity will decrease very fast. However, we find that the integrated intensity gets its maximum at x = 0.15, although the maximum peak intensity is at x = 0.02. The activator ions concentration is less than 0.05 in most inorganic luminescent materials [42]. Such a high  $Eu^{2+}$  concentration is quite abnormal among  $Eu^{2+}$ -doped phosphors, which will be discussed in SEM analysis part later. The PL spectra also show a significant redshift of the emission maximum changing from orange region (610 nm, x = 0.0025) to a very deep-red region (725 nm, x = 1.0). Generally, reabsorption, energy transfer and Stocks shift could move the emission spectrum to longer wavelengths. In the next part, we will analyze the cause of the red shift.



**Fig. 4.**  $Eu^{2+}$  concentration dependence of the luminescence decay lifetime for  $Sr_2Si_5N_8:Eu^{2+}$  phosphors monitoring at three different emission wavelengths (610, 660 and 710 nm).

Reabsorption is caused mainly by the overlap between low energy side of PLE spectrum and the high-energy side of the PL spectrum. The energy transfer refers to the process that a certain excitation center transfers all or part of the excitation energy to another luminescent center [43]. The energy transfer among Eu<sup>2+</sup> ions in different crystallographic sites via electric dipole-dipole interaction could also result in redshift [44]. Reabsorption and energy transfer often co-exist and can be distinguished by luminescence decay lifetime analysis. Typically, reabsorption delays the de-population rate of excited electrons, and the decay lifetime will be prolonged. On the contrary, decay lifetime will be shortened due to energy transfer [45].

The luminescence decay lifetime was measured under three detecting wavelengths, 610 nm for high-energy emission, 660 nm for intermediate-energy emission and 710 nm for low-energy emission. The results in Fig. 4 show that the decay lifetime varies with detecting wavelength and Eu<sup>2+</sup> concentration. At low Eu<sup>2+</sup> concentration ( $x \le 0.1$ ), the lifetime decreases at 610 nm, while increasing at both 660 and 710 nm upon increasing Eu<sup>2+</sup> concentration. This is an indication of reabsorption process. At high  $Eu^{2+}$  concentration (x > 0.10), however, the lifetime decay curves show downward trend at all the three detecting wavelengths, suggesting that energy transfer surpasses reabsorption in the contribution to redshift. At the same time, low temperature time-resolved photoluminescent spectrum (TRPL) is another useful means for further study of energy transfer [46]. As shown in Fig. 5, at very low  $Eu^{2+}$ concentrations such as x = 0.0025 and x = 0.02, the emission profile keeps almost unchanged during the time from 100 to 1000 ns, which verifies that energy transfer rarely occurs in samples at very low  $Eu^{2+}$  concentration. When the  $Eu^{2+}$  concentration increases to x = 0.05, the emission peak begins to shift to longer wavelengths, and this redshift becomes more significant at a higher  $Eu^{2+}$  concentration (x = 0.15). The

relative intensity of the high-energy emission band decreases with increasing  $Eu^{2+}$  concentration due to energy transfer among different crystallographic sites. At x = 1.0, the lifetime of pure  $Eu_2Si_5N_8$  jumps out of the decreasing trend, and the reason is not very clear; this maybe is due to more perfect lattice for end-member compound  $Eu_2Si_5N_8$  resulting in less probability of the non-radiative transition.

The Stocks shift, which is greatly influenced by the rigidity of crystal structure, is another important factor for the spectral redshift. In this paper, the Stocks shift  $\Delta S$  is estimated by twice the energy difference between  $\lambda_{em}$  and  $\lambda_0$ , in which  $\lambda_{em}$  refers to the maximum emission wavelength and  $\lambda_0$  stands for the zero-phonon line characterized by the crossing point between PL and PLE spectra [45]. The  $\lambda_{em}$ ,  $\lambda_0$  and  $\Delta S$  are compiled in Table 1 and plotted in Fig. 6. At low Eu<sup>2+</sup> concentrations (x  $\leq 0.1$ ), we find that the Stocks shift  $\Delta S$  almost keep unchanged (around 2800 cm<sup>-1</sup>), as well as the positions of zero-phonon line, because a small amount of Eu<sup>2+</sup> substituting for Sr<sup>2+</sup>, has very limited influence on the Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> crystal structure rigidity. However, as the Eu<sup>2+</sup> concentration increases (x > 0.1), the rigidity is weakened by the large-amount substitution of Eu<sup>2+</sup> ions, and, then, the  $\Delta S$  increases rapidly leading to the spectral redshift.

Therefore, the redshift of emission spectrum is mainly caused by reabsorption at low Eu<sup>2+</sup> concentrations ( $x \le 0.1$ ), although a small part contribution from energy transfer cannot be excluded. The redshift is mainly caused by both energy transfer and Stocks shift at high Eu<sup>2+</sup> concentrations (x > 0.1).



**Fig. 5.** Time-resolved photoluminescence of  $Sr_{2-2x}Eu_{2x}Si_5N_8$  (*x* = 0.0025, 0.02, 0.05, 0.15) phosphors at 11 K.

<b>Table 1.</b> Data on the f-d spectroscopic parameters of $Eu^{2+}$ in $Sr_{2-2x}Eu_{2x}Si_5N_8$ phosphors					
r	$\lambda_{em}$	λο	$\Delta S_{\mu}$	FWHM	Integrated Emission
л	( <i>nm</i> )	( <i>nm</i> )	$(cm^{-1})$	( <i>cm</i> <sup>-1</sup> )	Intensity(a.u.)
0.0025	610	561	2870	2114	0.69
0.005	612	564	2781	2139	0.77
0.01	614	566	2794	2121	0.82
0.015	616	568	2738	2145	0.88
0.02	618	570	2738	2142	0.88
0.03	624	572	2926	2308	0.92
0.05	628	576	2905	2349	0.93
0.1	638	581	3052	2511	0.92
0.15	658	597	3128	2627	1.00
0.2	665	602	3175	2587	0.99
0.4	676	605	3467	2787	0.82
0.5	682	609	3526	2966	0.75
0.6	687	612	3568	3029	0.77
0.7	695	616	3680	3339	0.66
0.9	725	623	4506	3312	0.57
1	725	621	4635	2996	0.50
3400 <b>a</b> 3200 3200 2800 2600 2400 2200 2000 0.	- FWHM	4 0.6 0.8 X	.0 Учем/ <b>пш</b>	$ \begin{array}{c} 740 \\ 720 \\ 700 \\ 680 \\ 660 \\ 640 \\ 620 \\ 600 \\ 0.0 \\ 0.2 \end{array} $	(b) (b) (c) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c)
5000 <u>c</u>	<b>●</b> —ΔS		<b>,</b>	$\begin{array}{c} 630 \\ 620 \end{array} \qquad $	

**Fig. 6.** (a) FWHM, (b) the maximum emission wavelength  $\lambda_{em}$ , (c) Stocks shift  $\Delta S$ , (d) the position of zero-phonon line  $\lambda_0$  as a function of Eu concentration. All data on these values are listed in Table 1.

1.0

0.6

0.4

X

0.8

600 590-

580

570 560

0.0

0.2

0.4

x

0.6

0.8

1.0

3.4 SEM Analysis.

0.0

0.2

<sup>1</sup>-W2/S∇ 3500

3000

2500



Fig. 7. SEM images of  $Sr_{2-2x}Eu_{2x}Si_5N_8$  phosphors with various  $Eu^{2+}$  concentrations.

As mentioned before, the luminescent intensity of phosphor is controlled by many factors. Generally, the specific wavelengths of absorption and emission band are mainly determined by the chemical compositions and crystal structure, which can be altered by cation or anion substitution. However, some luminescent properties, such as emission intensity or emission efficiency, are not only closely associated with the compositions and structures, but also related to morphology. To optimize those parameters for higher luminescence efficiency, a series of systematic experiments are essential.

In this work, we find that the Eu<sup>2+</sup> concentration has a significant impact on the morphology of Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphor. Fig. 7 gives the typical SEM images of Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> phosphor with different Eu<sup>2+</sup> concentrations. As shown in Fig. 7a, the grains of phosphor at x = 0.0025 are very small and many of them are agglomerated. With Eu<sup>2+</sup> concentration increasing, larger-size grains appear among fine powders in Fig. 7 b-7d. To our surprise, when it comes to x = 0.15, as can be observed in Fig. 7e, the crystal grains are formed in very good morphology, with few ultra-fine or agglomerated particles. Most of the grains possess the size of 30 µm in length and 10 µm in diameter, and they also have clean, defectless surfaces. However, the morphology of grains deteriorates again when  $x \ge 0.20$ , which is shown in Fig. 7f-7i. As a result, it is reasonable to correlate the highest integrated emission intensity at such a high Eu<sup>2+</sup> concentration (x = 0.15) to the well-crystalized grain morphology.

From the above SEM result, we can draw a conclusion that the  $Eu^{2+}$  concentration is of great influence on the crystallinity of the  $Sr_2Si_5N_8$  phosphor. This is an interesting result and, later, we try to consider the reasons. Generally, the Gibbs free energy and entropy of the system will have a large change when a new constituent is added. The thermodynamic condition changes with varying  $Eu^{2+}$  concentration; this will have an important effect on the nucleation and crystal growth. Our experimental results show that the composition  $Sr_{2-2x}Eu_{2x}Si_5N_8$  with x = 0.15 is most favorable to crystalline with  $Sr_2Si_5N_8$ -type structure and therefore have highest emission intensity.



#### **3.3 Temperature-Dependent Luminescence Properties**

**Fig. 8.** (a) Temperature dependence of the normalized integrated emission intensity for  $Sr_{2-2x}Eu_{2x}Si_5N_8$  (0.0025  $\le x \le 1.0$ ) phosphor. The inset gives the integrated emission intensity at 400 K relative to that at room temperature. (b) The relationship of emission intensity and integrated intensity of  $Sr_{2-2x}Eu_{2x}Si_5N_8$  (x = 0.15) with increasing temperature.



**Fig. 9.** Temperature dependence of the emission spectra for  $Sr_{2-2x}Eu_{2x}Si_5N_8$  (0.0025  $\leq x \leq 1.0$ ) excited at 450 nm from 77 to 500 K.

For general phosphor-converted LED lighting, the phosphor layer temperature can reach as high as 400 K, so the luminescent thermal quenching performance of the phosphor must be evaluated. It is well established that the emission intensity of most rare-earth-doped inorganic phosphors decreases with the rising temperature because of larger non-radiative transition rate [47-48]. For a better understanding of luminescent thermal quenching in  $Sr_2Si_5N_8:Eu^{2+}$  phosphor, the emission intensity was measured as a function of temperature from 300 to 500 K at different  $Eu^{2+}$  concentrations. All the emission spectra were excited at 450 nm. The results are shown in Fig. 8a. The inset in Fig. 8a gives the relative integrated emission intensity at 400 K (relative to that at room temperature) as a function of *x*. The luminescent quenching becomes more pronounced with the  $Eu^{2+}$  concentration increasing.

Nevertheless, the  $Sr_2Si_5N_8:Eu^{2+}$  phosphor shows outstanding luminescent thermal quenching resistance. Particularly, for the compositions with low  $Eu^{2+}$  concentration ( $x \le 0.05$ ), the integrated emission intensity at 400 K is about 95% relative to that at room temperature. Even at high  $Eu^{2+}$  concentration (x = 0.15, in Fig. 8b), the intensity still keeps about 88.5% intensity, showing better thermal stability than that of commercial YAG:  $Ce^{3+}$  (3.33% Ce) yellow phosphor [49-50], which could satisfy the requirement of thermal stability for most phosphor-based LEDs. When the  $Eu^{2+}$  concentration exceeds x = 0.4, the spectral intensity drops very fast with the increasing temperature due to large excitation migration. The abnormal thermal quenching curve for pure  $Eu_2Si_5N_8$  is ascribed to the extremely perfect lattice of this end-member. Considering the commercial application of  $Sr_2Si_5N_8:Eu^{2+}$  phosphor, the doped  $Eu^{2+}$  concentration is suggested less than 0.2.



**Fig. 10.** (a-c) Temperature dependence of emission spectrum deconvoluted by two Gaussian peaks (dashed curves) corresponding to Sr1 site (Peak 1) and Sr2 site (Peak 2) for sample with x = 0.05; (b) temperature dependence of integrated intensity of Peak 1 and Peak 2.

Besides, we observed a blue shift of emission spectrum with the increasing temperature for all the samples. At low  $Eu^{2+}$  concentrations (x = 0.0025, 0.02 in Fig. 9a-9b), the blue shift is very small. It is getting more pronounced as  $Eu^{2+}$  concentration going up (x = 0.05, 0.15, 0.7, 1.0 in Fig. 9c-9f). This can be explained by the two-peak emission behavior. As mentioned above, there are two kinds of luminescent centers in  $Sr_2Si_5N_8:Eu^{2+}$  corresponding to the Sr1 and Sr2 sites.  $Eu^{2+}$  ions

in the Sr1 sites give a high-energy emission (Peak 1), and those in the Sr2 sites give a low energy emission (Peak 2). Take the sample with x = 0.05 for example, which is illustrated in Fig. 10. We deconvoluted the temperature dependence of the emission spectra by two Gaussian peaks, which belong to Peak 1 and Peak 2. The integrated intensity of the two peaks are decreasing with temperature. However, the dropping rate for Peak 1 is slower than that of Peak 2, which results to the blue shift of the emission spectra with increasing temperatures.

## **3.5 Applications in LED lighting**

To evaluate the device performance for the as prepared  $Sr_2Si_5N_8:Eu^{2+}$  (x = 0.15) phosphor, LEDs for different applications were packaged. Based on  $Sr_2Si_5N_8:Eu^{2+}$  (x = 0.15) deep red phosphor, Fig. 11a gives the photograph of the pure red light LED device, the blue light is totally absorbed by red phosphor and converted to red light through the red phosphor which has the advantage of lower cost over pure red light chips in the area of indicator and decoration lighting. Fig. 11b gives the photograph of the violet light LED device, which can be used in the area of plant growing lighting. Fig. 11c gives the photographs of full-spectrum white light LED device, in which the commercial green phosphor of  $Y_3(Al, Ga)_5O_{12}:Ce^{3+}$  (~525 nm, commercial phosphor) and BaSi<sub>2</sub>O<sub>2</sub>N<sub>2</sub>: Eu<sup>2+</sup> (~490 nm, commercial phosphor) was extra added. It shows a high CRI performance (Ra > 95, R1~R15 > 90), which have a relative wide application in high quality white LED lighting.



**Fig. 11.** Photographs of fabricated LED devices based on  $Sr_{2-2x}Eu_{2x}Si_5N_8$  (x = 0.15) phosphor. (a) red light; (b) violet light; (c) full-spectrum white light. The corresponding spectra are showing in the right side.

#### **4** Conclusions

A series of  $Sr_{2-2x}Eu_{2x}Si_5N_8$  ( $0 \le x \le 1$ ) solid-solution phosphors were obtained by

high temperature solid-state reaction. The Eu<sup>2+</sup> ions can be completely incorporated into the Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub> lattice forming a complete solid solution. The significant redshift of the emission spectra changing from orange region (610 nm, at x = 0.0025) to deep-red region (725 nm, at x = 1.0) is realized by adjusting Eu<sup>2+</sup> concentration. The reabsorption at low Eu<sup>2+</sup> concentration while both the energy transfer and Stocks shift at high Eu<sup>2+</sup> concentration account for the spectral red-shift. The luminescent thermal quenching resistance is analyzed in detail and the result indicates that thermal quenching gets worse with the increasing Eu<sup>2+</sup> concentration. Even though, at 400 K the compound with x = 0.15 still maintains 88.5% room-temperature intensity. The deep red phosphor of Sr<sub>2</sub>Si<sub>5</sub>N<sub>8</sub>:Eu<sup>2+</sup> (x = 0.15) was package into LED devices, showing great potential for the application in decoration lighting, plant growing lighting and high quality white LED lighting.

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- 1. A full-range  $Sr_{2-2x}Eu_{2x}Si_5N_8$  ( $0 \le x \le 1$ ) solid solution was synthesized.
- 2. Largely tunable red emission band from 610 to 725 nm by adjusting Eu content.
- 3. High quenching concentration and high thermal quenching temperature for  $Eu^{2+}$  emission.