Preparation of Red Phosphor \( \text{Sr}_2\text{Si}_5\text{N}_8: \text{Eu}^{2+} \) by Pellet Method and Its Optical Characteristics

Yuemei Lan, Dong Wang, Dongliang Xie, Junhao Tan, Bowen Li, Mei Zhang and Yan Chen *

School of Applied Physics and Materials, Wuyi University, Jiangmen 529020, China; wydxym@163.com (Y.L.); dongw@163.com (D.W.); ak1015882844@163.com (D.X.); j184335698606@163.com (J.T.); l19894226334@163.com (B.L.); lan1502221235@163.com (M.Z.)

* Correspondence: ychen15@wuyiu.cn; Tel.: +86-750-3296040

Abstract: Red \( \text{Sr}_2\text{Si}_5\text{N}_8: \text{Eu}^{2+} \) phosphor with excellent properties was successfully synthesized by pellet method, an effective synthesis technology presented in this work. The influence of reactive conditions such as pellet pressure, position of samples in carbon powder, and \( \text{Eu}^{2+} \) ion concentration on the properties of crystallinity, particle size, and the photoluminescence properties of \( \text{Sr}_2\text{Si}_5\text{N}_8: \text{Eu}^{2+} \) phosphor were studied in detail. Our results show that the optimum preparation condition is 1500, 5 MPA pellet pressure, and the middle position in carbon powder. The phosphor has improved its efficiency under excitation of near UV and blue LEDs, and it emits red light at around 620 nm. In addition, red LEDs were successfully prepared by using \( \text{Sr}_2\text{Si}_5\text{N}_8: \text{Eu}^{2+} \) phosphor combined with UV-chips with maximum luminous efficiency at 9.443 lm/W, when the molar concentration of \( \text{Eu}^{2+} \) ion reached 0.001.

Keywords: light emitting diodes (LEDs); pellet method; red phosphors; photoluminescence; \( \text{Sr}_2\text{Si}_5\text{N}_8: \text{Eu}^{2+} \)

1. Introduction

At present, phosphor-converted white light-emitting diodes (PC-WLEDs) have attracted increasing attention due to their unique properties of longer life, lower power consumption, and more environment-friendly characteristics [1–5], compared with current commercial white LEDs devices, which are prepared by combining yellow phosphor \( \text{Y}_3\text{Al}_5\text{O}_{12}: \text{Ce}^{3+} \) and blue LED chips [6]. However, PC-WLEDs usually exhibit higher color temperature and poor color rendition due to the lack of a red light component [7,8]. Therefore, it is of great importance to synthesize red-emitting phosphor, which is suitable for excitation by blue LED chips.

Rare earth-doped nitride phosphors exhibit excellent luminescence properties, such as high thermal stability and luminous efficiency [9,10]. In particular, \( \text{M}_2\text{Si}_5\text{N}_8: \text{Eu}^{2+} \) (\( \text{M} = \text{Ca}, \text{Sr}, \text{Ba} \)) phosphors give a broad emission band from 570 to 680 nm due to the \( 5\text{d} \rightarrow 4\text{f} \) parity-allowed transition of \( \text{Eu}^{2+} \), when excited by blue or near UV LED chips. This means that \( \text{M}_2\text{Si}_5\text{N}_8: \text{Eu}^{2+} \) (\( \text{M} = \text{Ca}, \text{Sr}, \text{Ba} \)) is a good candidate for red-emitting phosphor, which can convert the blue or near UV light of LED chips into red light [11–13]. The most common synthesis technique for nitride phosphor is high-temperature reaction, where precursors (\( \text{Ca}_2\text{N}_2, \text{Sr}_2\text{N}_2 \) and \( \text{EuN} \)) are very sensitive to air and moisture [1,9,14,15]. Other common synthesis methods include carbothermal reduction and the nitridation of oxides, which can easily introduce impurities and make the phase impure. These issues impair the absorption and emission properties of the phosphor [10,16–19]. Therefore, a new synthesis method of \( \text{M}_2\text{Si}_5\text{N}_8: \text{Eu}^{2+} \) (\( \text{M} = \text{Ca}, \text{Sr}, \text{Ba} \)) phosphors without the above disadvantages are urgent, with great theoretical and practical importance.

In this work, we present a novel synthesis technology referred to as the pellet and reduction method, which combines the advantages of a mild synthesis condition and high purity. Moreover, the effects of pellet pressure, synthesis temperature, and \( \text{Eu}^{2+} \)
ion concentration on the photoluminescence properties of Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ phosphor are investigated in detail. Finally, red LEDs are successfully prepared by using Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ phosphor combined with UV-chips, and its luminescent properties are also studied.

2. Materials and Methods

Sr$_2$Si$_5$N$_8$: $x$Eu$^{2+}$ samples with different Eu$^{2+}$ ion concentrations ($x = 0.005, 0.010, 0.040, 0.100, 0.200, 0.400$) were prepared by the pellet and reduction method. The process of the pellet method is illustrated in Figure 1. First, raw materials SrCO$_3$ (99.99%), Si$_3$N$_4$ (99.95%), and Eu$_2$O$_3$ (99.99%) were taken in the weight of stoichiometric ratio, with a small amount of Polyvinyl alcohol (PVA) and NaF added, and then thoroughly ground in an agate mortar. Then, a 0.15 g mixture was pressed in a stainless-steel mold with the pressure of 5 MPa using a tablet press. After that, each sample was removed from the mold, buried into carbon powder in an alumina boat, and positioned at the center of a high-temperature tubular resistance furnace. The samples were sintered at 1450–1550 °C for 4 h in the atmosphere of N$_2$. Finally, the samples were polished after cooling to room temperature and ground into powder for subsequent tests.

![Figure 1. Synthetic route of Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ phosphors by the pellet method.](image)

The crystalline phase of the Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ samples was collected by X-ray powder diffraction (XRD) using a diffractometer (X’ Pert PRO, Panalytical, Endhoven, The Netherlands) with Cu Kα radiation at 40 KV and 30 mA. XRD patterns were collected in the range of 10–80°. Photoluminescence (PL) spectra and decay curves were obtained by a spectrofluorometer (FLS980, Edinburgh Instruments, Edinburgh, England) equipped with a 150 W Xe lamp. The morphology and size of particles were examined using a scanning electron microscope (SEM, NoVaTM Nano SEM 430, Jena, Germany).

The PC-LEDs devices were prepared by coating the synthesized phosphor on near-UV chips with an emission peak at 395 nm. The detailed process is presented in Figure 2. First, silicones (labeled as A and B glue) were mixed with the phosphors uniformly with a certain mass ratio. Then, the glue mixture was coated equally onto the chip. Finally, the LEDs were obtained after curing at 70 and 130 °C for 4 h. The photoelectric properties of all PC-LEDs devices were measured by a spectrophotometer (PMS 50, Evergreen Photo-E-Info Co. Ltd., Shanghai, China) with an integrating sphere with a diameter of 50 cm. The forward-bias current is 20 mA. All measurements were conducted at room temperature.
3. Results

3.1. Effect of Sintered Temperature

It is well known that sintered temperature is critical to the preparation of phosphors [4]. As a result, the study of appropriate action temperature is necessary. Figure 3a shows the XRD patterns of Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ phosphors with different reaction temperatures ($T = 1450, 1500, 1550$ °C). Major SrSi$_2$N$_2$O$_2$ and minor SiO$_2$ remained in the samples shown in Figure 3a, which indicates that 1450 °C is not enough for a high-purity Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ phosphor synthesis. A further increase in the reaction temperature to either 1500 or 1550 °C gave the produced phosphor a better match with a standard sample when comparing the XRD results with a JCPDS standard card (No. 85-0101). However, it is hard to determine the best synthesis temperature by the XRD patterns of the samples only. Figure 3b shows the emission spectra of the samples with sintered temperature at 1500 and 1550 °C. A broad emission band was found between 550 and 700 nm in both emission spectra, which are attributed to the 4$d$ $- 5$f transfer of Eu$^{2+}$ in Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ phosphors [20]. However, the emission intensity of the sample prepared at 1500 °C is 3.3 times as intense as that at 1550 °C. In conclusion, the optimum synthesis temperature is 1500 °C, according to the above discussion of XRD patterns and emission spectra.

3.2. Effect of Pellet Pressure

In order to further optimize the synthesis condition, the effect of pellet pressure was studied under 1500 °C. Figure 4a shows the XRD patterns of the samples with different pellet pressure values during preparation. As shown in Figure 4a, the main diffraction peaks of the sample prepared at 1 and 15 MPa can be indexed to pure Sr$_2$Si$_5$N$_8$ (JCPDS 85-0101). However, there are minor diffraction peaks of Si$_3$N$_4$, which suggests that impurity was produced with N$_2$ atmosphere and can be detected. A possible reason is that the raw material was not reacted completely in the sample at low pressure because of large...
intermolecular distance. In contrast, the density of the sample prepared at high pellet pressure is high enough, which results in N₂ being too hard to spread into the interior and reacting with internal raw materials to produce Si₃N₄. Moreover, all the diffraction peaks of the samples prepared at 5 and 10 MPa correspond to the orthorhombic phase Sr₂Si₅N₈ (JCPDS 85-0101), which indicates that Sr₂Si₅N₈: Eu²⁺ phosphors were synthesized at pellet pressure at 5 or 10 MPa.

![XRD patterns and SEM images](image)

**Figure 4.** (a) XRD patterns and (b) SEM images of the samples with different pellet pressure.

In order to study the effect of pellet pressure on the surface morphology of the phosphors, Figure 4b presents the SEM images of Sr₂Si₅N₈: Eu²⁺ phosphors prepared at different pellet pressure values. Many large and inhomogeneous particles were found in the SEM images of phosphors prepared at 1 and 10 MPa. The particles of the phosphors prepared at 5 and 15 MPa are more uniform and smaller than those at 1 and 10 MPa. However, the phosphor prepared at 15 MPa is agglomerated because of higher pellet pressure. This suggests that the optimum pressure for the synthesis Sr₂Si₅N₈: Eu²⁺ is 5 MPa by the pellet method.

Figure 5a shows the emission spectra of samples with different pellet pressure values. Generally, the emission intensity of the samples prepared at 1 and 5 MPa are larger than that at 10 and 15 MPa because of the impurity of Si₃N₄ in the samples of the latter. The emission of the sample prepared at 5 MPa is more intense than those at 1 MPa. In addition, the normalized emission spectra of the samples are presented in Figure 5b. There is a slight blue shift with the increasing of pellet pressure, which is harmful to improving the color rendition index and the correlated color temperature of a white LED device. As a result, 5 MPa is the best pellet pressure for the preparation of Sr₂Si₅N₈: Eu²⁺ phosphors in this study. To sum up, the optimum synthesis condition is 1500 °C and 5 MPa pellet pressure, as determined by analyzing the data of the XRD patterns, SEM, and the emission spectra.

![Emission spectra](image)

**Figure 5.** Emission (a) and normalized emission spectra (b) spectra of Sr₂Si₅N₈: Eu²⁺ phosphors prepared at different pellet pressure values.
3.3. Effect of Eu$^{2+}$ Concentration

It is well known that the doping concentration of luminescence center has a critical effect on the luminescent performance of the phosphor. Figure 6a presents the excitation spectra of Sr$_2$Si$_5$N$_8$:xEu$^{2+}$ phosphors. Monitoring the emission of Eu$^{2+}$ at 583–618 nm, the excitation spectra contains a broad band between 250 and 550 nm, which originates from the $4f^7 \rightarrow 4f^65d^1$ transition of Eu$^{2+}$. Figure 6b shows the emission spectra of Sr$_2$Si$_5$N$_8$:xEu$^{2+}$ phosphors. All the shapes of the emission spectra are similar and contain a broad asymmetric emission band, which are ascribed to $4f^65d^1 \rightarrow 4f^7$ transitions of Eu$^{2+}$ ion occupying two Sr sites in Sr$_2$Si$_5$N$_8$ [16]. Clearly, the emission intensity increased with increasing the Eu$^{2+}$ content from 0.5 to 1%. However, a further increase of Eu$^{2+}$ content from 1 to 40% had the opposite effect due to the concentration quenching effect. The optimal emission intensity was observed for the material doped with 1%. This is often ascribed to that during a nonradiative energy transfer from one activator to another, the probability of which increases with increasing the activator concentration [4]. The nonradiative energy transfer can be concretely expressed by the critical transfer distance ($R_c$), which is the distance between the activators at the quenching concentration. The $R_c$ can be roughly estimated by the Blasse formula, as shown in Equation (1) [3]:

$$R_c \approx 2 \times \left[ \frac{3V}{4\pi x_c^3N} \right]^\frac{1}{3},$$  

where $x_c$ is the critical concentration of Eu$^{2+}$, $N$ is the number of cation in the unit cell, and $V$ is the volume of the unit cell. In this research, $x_c = 0.01$ and $N = 2$. Therefore, the critical transfer distance 32.6 Å, which demonstrates that the energy transfer mechanism in Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ phosphors, is the electric multipolar interaction.

![Figure 6. Excitation (a) and emission (b) spectra of Sr$_{2.99}$Si$_5$N$_8$:xEu$^{2+}$ phosphors with various x values on CIE 1931 chromaticity diagram.](image)

In addition, the CIE color coordinates of Sr$_2$Si$_5$N$_8$:xEu$^{2+}$ phosphors can be adjusted by changing the Eu$^{2+}$ doping concentration, as shown in Figure 6c. The color coordinates are tuned from (0.5123, 0.4581) to (0.5679, 0.3927). The result indicates that Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ can give red emission excited by UV and blue light. It is an excellent candidate of red phosphor, suitable for UV and blue LEDs chips.

The emission spectra of Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ are the asymmetric broad emission band, which demonstrates that Eu$^{2+}$ may occupy more than one Sr$^{2+}$ crystallographic sites in Sr$_2$Si$_5$N$_8$: Eu$^{2+}$. In reality, there are two crystallographic Sr ion sites in the Sr$_2$Si$_5$N$_8$ lattice that have the coordination numbers of 8 (Sr1) and 10 (Sr2), respectively [16], as shown in Figure 7a. Sr$_2$Si$_5$N$_8$ forms an orthorhombic crystal structure with a space group of Pmn21(31) and $a = 5.71$ Å, $b = 6.822$ Å, $c = 9.341$ Å, $\alpha = \beta = \gamma = 90.0^\circ$, and $V = 363.9$ Å$^3$. Therefore, Figure 7b presents the fitted and decomposed components of emission spectrum of Sr$_{1.99}$Si$_5$N$_8$: 0.010Eu$^{2+}$ phosphors by Gaussian decomposition. The asymmetric emission band is divided into two Gaussian peaks located at 589 and 624 nm, respectively. Among them, the Gaussian peak located at 589 nm should be assigned to the Eu$^{2+}$ occupied...
on the Sr2 sites, due to the emission peak of Eu$^{2+}$ in the Sr2 site being located at the higher energy side of the spectra in the low Eu$^{2+}$ ion concentration region. Generally, Eu$^{2+}$ ions prefer to occupy the loose environment of the Sr2 site in the low Eu$^{2+}$ ion concentration region first, and then gradually occupy the Sr1 site with the increasing of Eu$^{2+}$ ion concentration in the Sr$_2$Si$_5$N$_8$ lattice. Figure 7c presents the dependence of the emission peak position of the Sr$_{2-x}$Si$_5$N$_8$: xEu$^{2+}$ phosphors on Eu$^{2+}$ ion concentration. The emission peak position shifted from 595 to 637 nm as the concentration of Eu$^{2+}$ increased, which is also consistent with the above analysis.

![Figure 7](image)

**Figure 7.** (a) Crystal structure of Sr$_2$Si$_5$N$_8$; (b) experimental emission spectrum and fitted and decomposed components of emission spectrum by Gaussian deconvolution on an energy scale of Sr$_{1.98}$Si$_5$N$_8$: 0.010Eu$^{2+}$ phosphors; (c) the dependence of the emission peak position of Sr$_{2-x}$Si$_5$N$_8$: xEu$^{2+}$ phosphors on Eu$^{2+}$ ion concentration. Insert is the enlarged normalized emission spectra.

Nitrides have been widely used as red phosphors in LEDs [21], but the traditional synthesis methods of nitride phosphors always experience high temperature and long-time reaction processes. For example, it can be seen from Table 1 that multistep heat treatment requires high temperature, and both plasma-activated synthesis and high temperature solid-state methods require a long reaction time. Furthermore, the raw materials should be mixed homogeneously in a purified argon glove box for the phosphors synthesized by the high temperature solid-state method, plasma-activated synthesis, and low temperature modified solid-state metathesis. The sol-gel-nitridation method needs a tedious reaction process. For the synthesis method in this article, the reaction time is not long, and the steps are simple, which is an environmentally friendly preparation method.

### 3.4. The Application of Sr$_{2-x}$Si$_5$N$_8$: xEu$^{2+}$ Phosphors in LEDs

Considering the potentials of phosphors in LEDs devices, phosphor-converted LEDs were fabricated with red emitting Sr$_{2-x}$Si$_5$N$_8$: xEu$^{2+}$ phosphors, silicones, and 395 nm near-UV chips (shown in Figure 2). Figure 8a shows the electroluminescence spectra of the as-fabricated LEDs under a 20 mA forward-bias current ($I_F$). All electroluminescence spectra were found to contain a narrow emission peak and a broad emission band, which are assigned to the emission of UV LED chips and 4f$^6$5d$^1$→4f$^7$ transitions of Eu$^{2+}$ ion. Comparing the intensity of Eu$^{2+}$ ions, the emission intensity of UV LED chip gradually weakened with the increasing of Eu$^{2+}$ ion concentration, which illustrates that this phosphor can absorb the light emitted by 395 nm UV chips effectively. In addition, the broad emission band shifted to a longer wavelength with the increasing of Eu$^{2+}$ ion concentration, which is consistent with the photoluminescence spectra. Table 2 presents the chromaticity coordinates of the as-fabricated LED based on 395 nm UV-chip and Sr$_{2-x}$Si$_5$N$_8$: xEu$^{2+}$ phosphors under 20 mA forward-bias current. To sum up, the above results show that Sr$_{2-x}$Si$_5$N$_8$: xEu$^{2+}$ phosphors can convert the light of UV-LED chips into red light.
The performance of the Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ phosphors fabricated by various methods.

| Preparation                        | Preparation Condition | CIE (x,y)        | Size (um) | $\lambda_{em}$ (nm) | Ref.       |
|-----------------------------------|-----------------------|------------------|-----------|---------------------|------------|
| Pellet method                     | 1500 °C + 5 MPa       | (0.5902, 0.3749) | ~7        | 620                 | This work |
| Low temperature modified solid-state metathesis | 1300 °C + 6 h + H$_2$/N$_2$ | (0.6382, 0.3612) | 5~10     | 628                 | [21]      |
| Sol-gel-nitridation method        | 1300 °C + 3 h         | (0.615, 0.385)   | ~8        | 617                 | [22]      |
| Plasma-activated synthesis        | 1250 °C + 6 min       | ~                 | ~1        | 626                 | [18]      |
| Multi-step heat treatment         | 1400 °C + 3 h         | ~                 | ~         | 613                 | [23]      |
| High temperature solid-state method | 1400 °C + 9 h + H$_2$/N$_2$ | ~             | ~         | 612                 | [24]      |
| Acetate reduction synthesis       | 1600 °C + 6 h + N$_2$ | (0.638, 0.359)   | 5         | 619                 | [25]      |

Figure 8. (a) Electroluminescence spectra of the as-fabricated LEDs based on 395 nm UV-chip and Sr$_{2-x}$Si$_5$N$_8$: xEu$^{2+}$ phosphors under 20 mA forward-bias current; (b) luminous efficiency of as-fabricated LEDs with different Eu$^{2+}$ concentration ($x$) under $I_F = 20$ mA.

| $x$ Values | 395 nm UV Chips + Sr$_{2-x}$Si$_5$N$_8$: xEu$^{2+}$ CIE(x, y) | $x$ | $y$ |
|------------|-------------------------------------------------------------|-----|-----|
| 0.005      | 0.5852, 0.3837                                             |     |     |
| 0.010      | 0.5902, 0.3749                                             |     |     |
| 0.040      | 0.6367, 0.3597                                             |     |     |
| 0.100      | 0.6600, 0.3379                                             |     |     |
| 0.200      | 0.6749, 0.3237                                             |     |     |
| 0.400      | 0.6790, 0.3183                                             |     |     |

The luminous efficiency of as-fabricated LEDs based on red-emitting Sr$_{2-x}$Si$_5$N$_8$: xEu$^{2+}$ phosphors under 20 mA forward-bias current were investigated systematically, as shown in Figure 8b. The luminous efficiency of the as-fabricated LEDs increases first to reach a maximum value with $x = 0.010$, then decreases gradually with the increasing of the Eu$^{2+}$ concentration. The maximum of the luminous efficiency is 9.443 lm/W. A good consistency can be concluded between the variation of the luminous efficiency of the as-fabricated LED with that of the emission spectra of phosphors.

4. Conclusions

The pellet method, a novel synthesis technology of phosphors, was presented in this work, by which excellent red Sr$_2$Si$_5$N$_8$: Eu$^{2+}$ phosphor was successfully synthesized.
Compared with traditional synthesis methods, this method shows advantages of simplicity and mild conditions, and therefore it has the potential in practical application. The obtained phosphors showed good excitation property with a broad excitation band between 250 and 600 nm. The emission spectra show a broad asymmetric emission band at 583–618 nm, and we found that optimal Eu\(^{2+}\) molar concentration was \(x = 0.010\). Finally, the red LEDs were successfully prepared by combining Sr\(_2\)-Si\(_8\)N\(_8\) \(\times\) Eu\(^{2+}\) phosphor with UV-chips. The color coordinates of the as-fabricated LEDs based on 395 nm chips can be tuned from (0.5852, 0.3837) to (0.6790, 0.3183) with the adjustment of Eu\(^{2+}\) ion concentration, and the luminous efficiency of the as-fabricated LEDs can reach the maximum of 9.443 lm/W when the Eu\(^{2+}\) molar concentration was \(x = 0.010\). In conclusion, the pellet and reduction method is an excellent method for the synthesis of red Sr\(_2\)Si\(_8\)N\(_8\): Eu\(^{2+}\) phosphor.

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**Data Availability Statement:** The data used to support the findings of this study are available from the corresponding author upon request.

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**Conflicts of Interest:** We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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