Formation of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ and Its Transformation to $\text{SrSi}_6\text{N}_8:\text{Eu}^{2+}$ Controlled by Temperature and Gas Pressure

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Firing temperature and gas pressure effect of synthesizing $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ were investigated. The emission intensity is positively correlated with the firing temperature under 0.1 and 0.5 MPa gas pressure. The $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ with the highest emission intensity was found at 1700°C and 1980°C under 0.1 and 0.5 MPa gas pressure, respectively. Although the maximum emission intensity of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ obtained under 0.5 MPa gas pressure condition is higher than that under 0.1 MPa, the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ synthesized under 0.5 MPa gas pressure in the temperature range from 1600°C to 1800°C have lower emission intensities than that synthesized under 0.1 MPa indicating that the melting of $\text{Sr}_3\text{N}_2$ is an important step for the formation of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$. Moreover, the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ undergoes phase transition into $\text{SrSi}_6\text{N}_8:\text{Eu}^{2+}$ completely after elongating the heating duration to 6 h at 1980°C under 0.5 MPa gas pressure. The same feature was observed under 0.1 MPa gas pressure after firing 8 h at 1750°C. Different heating durations led to different degrees of phase transition.

I. Introduction

Since the great breakthrough in the growth of highly quantum efficient Al, In, Ga, N–GaN thin film on lattice-mismatched substrates made by Nakamura and coworkers, white-light-emitting diodes (WLEDs) have become the most potential candidate to substitute traditional incandescent lamps because of their high brightness. The combination of an InGaN blue diode chips and a yellow luminescence such as Ce$^{3+}$-activated Y$_3$AlO$_{12}$ (YAG) leads to the formation of cold-WLEDs. Cold-WLEDs have a significant drawback in color-rendering property and thus are unable to realize the true color of an object. The reason for their low color-rendering index is the lack of red emission. To compensate the deficiency of cold-WLEDs, introducing a blue-to-red light-converting material is indispensable.

As a photo-conversion material, rare earth-doped silicon-based nitride and oxynitride have received significant attention because of their low thermal quenching, high chemical stability, and high conversion efficiency. The covalent bond between nitrogen and alkaline earth or rare earth ions strengthens the nephelauxetic effect and makes the silicon-based nitride a gazed red phosphor, such as $\text{M}_2\text{Si}_3\text{N}_8:\text{Eu}^{2+}$ (M = Ca, Sr, or Ba). Much effort has been exerted toward tuning the luminescence and thermal properties by substituting various amounts of alkaline earth ions and rare earth ions. More efficient synthesis methods have also been a topic in great demand. However, investigations on the phase transition between different nitride phosphors and the effect of heating temperature on the phase transition are relatively limited.

As the red phosphor with the highest quantum efficiency and the best thermal resistance among $\text{M}_2\text{Si}_3\text{N}_8:\text{Eu}^{2+}$ (M = Ca, Sr, Ba), $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ has received much attention. The synthesis of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ can be accomplished by the solid-state reaction (SSR) of nitrates, reaction of Sr metal or metal amide precursor (M = Sr, Eu) or SrCO$_3$/Sr (CH$_3$CO$_2$)$_2$ with silicon diimide Si(NH)$_2$ and carbothermal reduction and nitridation (CRN) under nitrogen atmosphere. The same reaction route is also used to synthesize different nitride phases, such as $\text{Sr}_2\text{Si}_5\text{N}_8$ and $\text{SrSi}_6\text{N}_8$. The decisive factors for the formation of these compounds are the heating temperature and the nitrogen–oxygen ratio of the reaction atmosphere. Thus, the reaction conditions should be critically controlled to obtain the pure phase of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$.

After mixing the reactants under glove box filling with nitrogen or argon, the reactant mixture was placed in a crucible. The crucibles used for sintering the phosphors were made by boron nitride (BN) or tungsten in order to reduce the oxide and carbon contaminations. Crude, the crucible mixture should be placed in a sealed plastic or steel box filling with nitrogen during transferring from glove box to furnace. Generally, the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ is synthesized by SSR of nitrates under normal pressure of N$_2$ or reductive atmospheres. The presence of oxygen always leads to the formation of yellow oxynitride phosphor which decreases the emission intensity of the red phosphor. The synthesis temperature is the other important factor that determines the efficiency and emission property of phosphors. The $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ is generally obtained in the temperature range from 1550°C to 1650°C by using the SSR method. This factor was considered only when the synthesis methods or precursors were changed. For example, the sintering temperature decreases to 1400°C–1500°C when using the CRN method and oxide as precursor. The systematic study on sintering parameters, such as sintering temperature, gas pressure, and duration, for one specific synthesis method was not found.

In this work, we present the sintering temperature effect on emission properties, and comparing range of the sintering temperature under 0.1 and 0.5 MPa. The sintering duration was also studied and the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ was found as a byproduct in this investigation.
II. Experimental Procedures

(1) Sample Preparation
Powdered samples of \( \text{Sr}_{2-x}\text{Si}_5\text{N}_8\cdot\text{Eu}^{2+} \) were prepared by SSR using strontium nitride (\( \text{Sr}_3\text{N}_2 \), Cerac, Milwaukee, WI, 99.5%, ~60 mesh), silicon nitride (\( \text{Si}_3\text{N}_4 \), Aldrich, 99.9%, Polk county, MI), and europium nitride (\( \text{EuN} \), Cerac, 99.9%, ~60 mesh) as starting materials. The \( x \) in \( \text{Sr}_{2-x}\text{Si}_5\text{N}_8\cdot\text{Eu}^{2+} \) was fixed at 0.02 based on the lowest thermal degradation shown by Yeh and coworkers. First, stoichiometric amounts of the nitrides were weighed out, ground, and mixed thoroughly in an agate mortar under Ar environment to prevent the oxidation of the reactants. The concentrations of oxygen and moisture in the environment were less than 1 ppm during grinding and mixing. The mixed powders were then transferred into a cylindrical BN crucible. Subsequently, the powder mixtures were placed in a gas-pressure-sintering furnace (FVPHP-R-5, FRET-25, Fujidempa Kogyo Co., Ltd., Osaka, Japan). After the furnace was evacuated to 2 \( \times \) 10\(^{-2} \) Pa, the evacuation of the furnace was stopped and nitrogen was introduced into the furnace until the gas pressure in the furnace reached a predetermined value. The powder mixtures were then fired at a temperature range of 1550°C–1980°C under flowing \( \text{N}_2 \) atmosphere of 0.1 and 0.5 MPa for 2–6 h.

(2) Characterization
All measurements were conducted on the carefully ground powder. In order to reduce the damages of the surface morphology resulted from grinding, the grinding process should be done carefully and the grinding time should be as short as possible. The variation in phase and the phase purity of the samples were analyzed by XRD with a D2 Phaser (Bruker, Billerica, MA) diffractometer operated with CuK\( \alpha \) radiation (\( \lambda = 1.5418 \) A). The data were gathered over a 2\( ^\circ \) range from 10\(^\circ \) to 70\(^\circ \) at intervals of 0.02\(^\circ \) with 5 s\(^\circ \) counting time. The PL excitation and emission spectra were obtained using FluoroMax-3 and Fluoromax-P spectrometers (HORIBA, Kyoto, Japan). The emission intensities of the \( \text{Sr}_{1.98}\text{Si}_5\text{N}_8\cdot\text{Eu}^{2+} \) synthesized in this study were compared with a commercial phosphor (0763, Grirem Advanced Materials Co., Ltd, Beijing, China.) in order to understand which condition is more suitable. A Commission International de l’Éclairage (CIE) chromaticity coordinate analysis was performed with an Isuzu optic cooperation software (Hsinchu, Taiwan). External and internal quantum efficiency measurements were done by Quantaurus-QY (Hamamatsu, Shizuoka, Japan.). All samples were analyzed at room temperature. The morphology of the powders was evaluated by scanning electron microscopy (SEM; Nova NanoSEM 450, FEI, Hillsboro, OR).

III. Results and Discussion

(1) Temperature Effect on \( \text{Sr}_{1.98}\text{Si}_5\text{N}_8\cdot\text{Eu}^{2+} \) Formation
The XRD patterns of the \( \text{Sr}_{1.98}\text{Si}_5\text{N}_8\cdot\text{Eu}^{2+} \) synthesized at 1600°C, 1800°C, 1900°C, and 1980°C for 2 h under 0.5 MPa nitrogen atmosphere are shown in Fig. 1. The spectra reveal that a single-phase \( \text{Sr}_{1.98}\text{Si}_5\text{N}_8\cdot\text{Eu}^{2+} \) was synthesized at these temperatures. All the peaks agreed well with the standard pattern of \( \text{Sr}_2\text{Si}_5\text{N}_8 \) (ICSD 401500), and no second phase was observed in all the spectra.

The PL spectra of the \( \text{Sr}_{1.98}\text{Si}_5\text{N}_8\cdot\text{Eu}^{2+} \) fired at 1600°C (black line), 1800°C (red line), and 1980°C (pink line) for 2 h are shown in Fig. 2. The excitation and emission spectra both agree with the XRD result. The peak shapes of the spectra are consistent with the work done by Li et al. The emission peaks excited by 460 nm radiation are all centered at 619 nm. The emission spectrum of \( \text{Sr}_2\text{Si}_5\text{N}_8\cdot\text{Eu}^{2+} \) was characterized by a broad full width of half magnitude (FWHM), 84–86 nm, and asymmetrical band composed of the emission radiations form \( \text{Eu}^{2+} \) occupying two different crystallographic sites. There is no obvious peak shift and broadening as changing firing temperature. The \( \text{Eu}^{2+} \) ions with smaller coordination number (CN = 8) emits the radiation with peak center at about 687 nm, whereas the \( \text{Eu}^{2+} \) ions with CN = 10 radiate the light with a peak center at about 628 nm. Thus, the change in distribution of \( \text{Eu}^{2+} \) positions can be monitored from the peak shapes of the emission spectra and the emission peak center. However, there is no significant variation in peak centers and shapes been observed in Fig. 2. This feature indicates the variation in firing temperature does not lead to change in the

| Table I. Peak Center, Internal and External Quantum Efficiency (QE) and Absorption of the \( \text{Sr}_{1.98}\text{Si}_5\text{N}_8\cdot\text{Eu}^{2+} \) Synthesized at 1600°C, 1800°C, 1900°C, and 1980°C Under 0.5 MPa \( \text{N}_2 \) Atmosphere |
|---|---|---|---|---|
| Firing temperature (°C) | Center (nm) | Internal QE (%) | Absorbance (%) | External QE (%) |
| 1600 | 616 | 86.1 | 86.6 | 74.5 |
| 1900 | 617 | 85.7 | 80.3 | 68.8 |
| 1980 | 616 | 91.0 | 68.9 | 62.7 |
| 1763 | 617 | 85.9 | 64.9 | 55.8 |
distribution of Eu$^{2+}$ position. More insights were revealed by the QE analysis. As shown in Table I, the internal QEs of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$ synthesized by different firing temperatures range from 91.0% to 85.7%. No apparent correlation was observed between firing temperatures and internal QEs, whereas the positive correlation was found between emission intensities and firing temperatures. On the other hand, the absorbance is trending up when the firing temperature is increased. This feature is more similar to that observed in emission intensities indicating that the increase in emission intensities results from the increase in absorbance. The improvement in absorbance is associated with a larger particle size and a smoother surface morphology. So we suggest the increase in emission intensities results from the growth of crystalline phosphor particles which has larger particle size and smoother surface morphology.

The excitation spectra show broad bands ranging from UV to visible light, which indicate that the phosphor can be applied to UV- and blue light-based WLEDs. The most important feature observed in this figure is the increase in the intensities of the peak at 619 nm with rising synthesis temperature. The peak intensity reaches its maximum at 1980°C synthesis temperature. Further rise in synthesis temperature to more than 1980°C leads to the formation of a black alloy from the decomposition of the phosphor.

To understand the dependence between synthesis temperature and emission intensity, SEM analysis was utilized. Figure 3 shows the SEM micrographs of the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$ synthesized at 1600°C, 1800°C, 1900°C, and 1980°C for 2 h under 0.5 MPa nitrogen atmosphere. As shown in Fig. 3(a), the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$ powder synthesized at 1600°C mainly consists of small particles with particle size less than 2 μm. The large particles with a diameter more than 5 μm are aggregated small particles but not actually “large particles”. As shown in Fig. 3(b), large particles start to form after heating at 1800°C. In this figure, many small particles are still observed on the large particles, and these small particles seem to be sintered on the large particles. This feature indicates that large particles form from the merging of small particles. As the heating temperature increase above 1900°C, the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$ powder mainly consists of large particles with a diameter more than 3 μm, and each particle looks like a crystal fragment as shown in Fig. 3(c). In Fig. 3(d), synthesizing Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$ at 1980°C leads to the formation of more large particles, and most of the particles have a particle size more than 5 μm. Moreover, flat crystal faces can be observed on these particles. The PL and SEM results apparently show that high synthesis temperatures lead to large particles, which result in high emission intensity. This particle effect of nitride phosphors is consistent with the investigations on cerium-doped yttrium aluminum garnet (YAG:Ce) and silicate yellow phosphors. Jang et al. suggested that the dependence between particle size and PL results from the luminous efficiency and scattering loss of the phosphors.

The temperature effect on particle size and PL emission intensity was also observed in an investigation under 0.1 MPa nitrogen atmosphere. Figure 4 shows the XRD patterns of the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$ synthesized at 1550°C, 1600°C, 1650°C, 1700°C, and 1750°C for 2 h under 0.1 MPa nitrogen atmosphere. The XRD pattern of the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$ synthesized at 1550°C for 2 h is apparently different from the others in the peak ratio and peak width, but the peak positions are similar to the standard spectrum. This feature suggests that sintering parameters such as temperature and duration are not sufficient for the formation of well-crystallized Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$, but they reach the threshold for the production of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$. The XRD patterns of the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$ synthesized at 1600°C, 1650°C, and 1700°C, respectively, show the formation of well-crystallized Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$. The XRD patterns indicate that the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$$_{0.02}$ synthesized at 1800°C, 1900°C, and 1980°C for 2 h under 0.5 MPa nitrogen atmosphere.
1700°C reveal the formation of pure-phase Sr1.98Si5N8:Eu2+0.02. In the XRD spectrum of the Sr1.98Si5N8:Eu2+0.02 synthesized at 1750°C, a trace of another phase was observed, as evidenced by the peak of 20 value at 31° (marked by the red arrow).

Figure 5 shows the PL spectra of the Sr1.98Si5N8:Eu2+0.02 fired at 1500°C, 1600°C, 1650°C, 1700°C, and 1750°C under 0.1 MPa nitrogen atmosphere for 2 h. The emission bands excited by 460 nm are centered at 619 nm with a FWHM range of 82–89 nm. The broad excitation bands from 250 to 600 nm indicate that the phosphor can be used in UV- and blue chip-based WLEDs. Both characteristics mentioned above again confirm the formation of Sr1.98Si5N8:Eu2+0.02. The emission intensities of the Sr1.98Si5N8:Eu2+0.02 synthesized at 1550°C (green line), 1600°C (pink line), 1650°C (blue line), and 1700°C (red line) under 0.1 MPa increased with the synthesis temperature. This feature is consistent with that observed in the experiments under 0.5 MPa; thus, this feature is supposed to result from the growth of particle size. High synthesis temperature promotes particle growth or merging of small particles into a large particle, which is more efficient in converting UV and blue light into red light. Emission intensity decreases as the synthesis temperature increases to 1750°C (black line). Based on the XRD results, the decrease in emission intensity is suggested to result from the presence of a second phase. Further increase in the synthesis temperature to 1800°C leads to the formation of a black alloy as observed in the high gas pressure experiments.

(2) **Gas Pressure Effect on Sr1.98Si5N8:Eu2+0.02 Formation**

To understand which condition is more appropriate for Sr1.98Si5N8:Eu2+0.02 synthesis, a commercial phosphor was used as reference to define the relative intensities of the phosphor synthesis in this study. As shown in Fig. 6, the Sr1.98Si5N8:Eu2+0.02 synthesized at 1980°C under 0.5 MPa for 2 h has the highest emission intensity, which is approximately 93% of the emission intensity of the commercial phosphor. The Sr1.98Si5N8:Eu2+0.02 synthesized at 1900°C, 1800°C, and 1600°C under the same condition have lower emission intensities, which are approximately 87%, 74%, and 66% of the emission intensity of the commercial phosphor, respectively. In the experiments under 0.1 MPa nitrogen atmosphere, the Sr1.98Si5N8:Eu2+0.02 with the highest emission intensity, which is approximately 90% of the emission intensity of the commercial phosphor, was obtained after 1700°C sintering for 2 h. The Sr1.98Si5N8:Eu2+0.02 synthesized at low temperatures of 1650°C, 1600°C, and 1550°C under the same condition have lower emission intensities, which are approximately 79%, 75%, and 57% of the emission intensity of the commercial phosphor, respectively. At a high synthesis temperature of 1750°C, a second phase forms and leads to a decrease in emission intensity that is 80% of the emission intensity of the commercial phosphor. The maximum relative emission intensities of the Sr1.98Si5N8:Eu2+0.02 synthesized at 0.5 MPa are higher than that synthesized at 0.1 MPa, thereby indicating that a high nitrogen atmosphere is more suitable for the synthesis of highly efficient Sr1.98Si5N8:Eu2+0.02. High nitrogen pressure are supposed to stabilize the Sr1.98Si5N8:Eu2+0.02 and suppress the decomposition reaction of Sr1.98Si5N8:Eu2+0.02. Thus, Sr1.98Si5N8:Eu2+0.02 can persist at a high temperature, and its particle size can grow further.

Another important feature is that the relative emission intensities is higher for 0.1 MPa as compared to 0.5 MPa in the range of firing temperature from 1600°C to 1800°C. The feature was associated with the change in melting point (m.p.) of the Sr3N2. The melting point of Sr3N2 (m.p. = 1630°C) is much lower than that of Si3N4 (m.p. = 1900°C). Thus, we supposed that the melting of the Sr3N2 may occur during heating and this process is a key step for the formation of Sr1.98Si5N8:Eu2+0.02. In the low gas pressure conditions, the Sr3N2 melts at 1030°C, thus the reaction between Sr3N2 and Si3N4 becomes a solid-liquid reac-

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**Fig. 4.** X-ray diffraction patterns of Sr1.98Si5N8:Eu2+0.02 fired at (a) 1750°C, (b) 1700°C, (c) 1650°C, (d) 1600°C, and (e) 1550°C under 0.1 MPa nitrogen atmosphere for 2 h, and (f) the standard X-ray diffraction patterns of Sr2Si3N8 [ICSD 401500].

**Fig. 5.** Photoluminescence spectra of Sr1.98Si5N8:Eu2+0.02 fired at 1550°C (green line), 1600°C (pink line), 1650°C (blue line), 1700°C (red line), and 1750°C (black line) under 0.1 MPa nitrogen atmosphere for 2 h (λex = 460 nm, λem = 619 nm).

**Fig. 6.** Relative intensities of Sr1.98Si5N8:Eu2+0.02 synthesized at various temperatures under nitrogen atmospheres of 0.1 and 0.5 MPa.
tion. Therefore, the reaction will be more thorough, and the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ will give better performance. Conversely, the higher gas pressure condition raises the melting point of Sr$_2$N$_2$ resulting in a higher reaction barrier. Thus, the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ synthesized under higher gas pressure in the temperature range from 1600°C to 1800°C give lower performance.

(3) Phase Transition from Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ to SrSi$_6$N$_8$:Eu$^{2+}$

In our investigations, sintering duration was also found as an important factor for synthesizing pure-phase Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$, more efficiently. Generally, Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ was synthesized by sintering the nitride reactants at a certain temperature for 2 h under nitrogen atmosphere in our studies. To obtain a well-crystallized Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ particles that are highly efficient, the sintering duration was tuned at 1980°C under 0.5 MPa nitrogen atmosphere. However, a white needlelike crystalline compound was observed after sintering for 4 h, as shown in Fig. 7. In Fig. 7(a), a wafer comprising red and white parts was obtained. The red part was supposed to be Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$, and the white part is similar to the second phase observed in the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ synthesized at 1980°C for 2 h under 0.1 MPa nitrogen atmosphere. To determine the composition of the second phase, the effect of sintering duration on the formation of this white crystalline compound/material was investigated.

To elucidate the composition and formation conditions of the white needlelike crystalline compound, XRD measurements were performed. As shown in Fig. 8, a series of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ was synthesized with a heating temperature of 1980°C and heating durations of 2, 4, 5, and 6 h under 0.5 MPa N$_2$ atmosphere. Comparing the XRD spectrum of the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ synthesized by sintering at 1980°C for 2 h [Fig. 8(e)] with the standard Sr$_2$Si$_6$N$_8$ XRD pattern [Fig. 8(f)] shows the formation of pure-phase Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$. Prolonging the heating duration to 4 h leads to the production of the second phase and a slight consumption of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ [Fig. 2(d)]. The diffraction patterns assigned to Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ are marked by asterisks (*) and those that belong to the other phase are marked by circles (○). After further prolonging the heating duration to 5 h, the signals of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ become quite weak. By contrast, the signals of the second phase become more intense. In Fig. 8(b), the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ is fully transformed into the second phase, the white needlelike crystalline compound, after heating for 6 h at 1980°C. Based on the comparison of Fig. 8(b) with the standard XRD pattern (ICSD 391265), we conclude that the second phase obtained from sintering Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ at 1980°C for more than 2 h is SrSi$_6$N$_8$:Eu$^{2+}$. The peak observed at 20 value of 31° is the most intense feature. This characteristic is identical to the work done by Yeh et al. who synthesized SrSi$_6$N$_8$:Eu$^{2+}$ at 1900°C for 6 h under 0.5 MPa nitrogen atmosphere.

The excitation spectra of the sample heated at 1980°C under 0.5 MPa N$_2$ atmosphere for different durations are shown in Fig. 9. The excitation spectra of the maximum emission wavelength at 455 and 619 nm were monitored and shown in Figs. 9(a) and (b), respectively. In Fig. 9(a), two principal excitation bands (≈295 and ≈365 nm) are observed below the middle of the UV range and near-UV range. The excitation spectra that track the emission wavelength at 455 nm correspond well with that of SrSi$_6$N$_8$:Eu$^{2+}$ reported by Yeh et al. Based on their density functional calculation, the first peak results from a general transition between the valence and conduction bands of the nitridosilicate host, and the others are caused by the N-vacancies in SrSi$_6$N$_8$:Eu$^{2+}$. The intensities of the two peaks increase with prolonged heating duration, indicating that long heating duration promotes SrSi$_6$N$_8$:Eu$^{2+}$ formation. In Fig. 9(b), the excitation spectra obtained from tracking the emission wavelength at 619 nm show broad bands covering the spectral range from 325 to 600 nm, which perfectly agree with the large crystal field splitting of Eu$^{2+}$ energy levels in Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$.20 The intensities of the broad peaks decrease with prolonged heating duration. The opposite trend observed in Figs. 9(a) and (b) corresponds with the emission spectra shown in Fig. 8.

![Image](https://example.com/image.png)

**Fig. 7.** Photo images of (a) the mixture consist of red and white parts in BN crucible, which can be carefully separated and milled into (b) white SrSi$_6$N$_8$:Eu$^{2+}$ powder and (c) red Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ powder.

![Image](https://example.com/image.png)

**Fig. 8.** X-ray diffraction patterns of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ fired at 1980°C for different durations: (b) 6, (c) 5, (d) 4, and (e) 2 h, and the standard X-ray diffraction patterns of (a) SrSi$_6$N$_8$:Eu$^{2+}$ [ICSD 391265] and (f) Sr$_2$Si$_6$N$_8$ [ICSD 401500]. (●: Sr$_2$Si$_6$N$_8$, ○: SrSi$_6$N$_8$: Eu$^{2+}$).
Fig. 10, indicating that SrSi$_6$N$_8$:Eu$^{2+}$ formation results from the consumption of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$.02.

The emission spectra of the sample fired at 1980°C under 0.5 MPa N$_2$ atmosphere for different durations show mainly two peaks at the maximum wavelength at 455 and 619 nm after excitation by 365 nm UV radiation (Fig. 10). The narrow peak at 455 nm implies that only one crystallographic Sr$^{2+}$ site in SrSi$_6$N$_8$:Eu$^{2+}$, which is ten coordinated, is being substituted by Eu$^{2+}$.18,25 The broad peak at 619 nm reveals that two crystallographic Sr$^{2+}$ sites, which are coordinated to eight and ten nitrogen atoms, are being substituted by Eu$^{2+}$.6, 20 The intensity of the peak at 455 nm increases with prolonged heating duration. On the contrary, the intensity of the peak at 619 nm shows the opposite trend. In the spectrum of the sample fired at 1980°C for 2 h, one peak is observed at 619 nm, which is the characteristic emission wavelength of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$.02, and only a trace of signal was found at 455 nm, which is the characteristic emission wavelength of SrSi$_6$N$_8$:Eu$^{2+}$.6,18 This feature indicates that Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$.02 is the main product under this condition. As the firing duration prolonged to 4 h, the peak area of the peak at 455 nm grows to approximately a quarter of that at 619 nm. In the emission spectrum of long heating duration (5 h), the peak areas of the peak at 455 and 619 nm are almost the same, and the intensity of the peak at 455 nm is almost two times that of the peak at 619 nm. After further prolonging the firing duration to 6 h, the peak at 619 nm almost disappears, and the remaining peak at 455 nm becomes intense. Instead of an orange-red Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$.02 powder, white-crystalline compound SrSi$_6$N$_8$:Eu$^{2+}$ is visually observed in the product.

Fig. 10. Emission spectra and color coordination of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$.02 sintered at 1980°C for 2 (red line), 4 (blue line), 5 (pink line), and 6 h (green line) under 0.5 MPa N$_2$ atmosphere with 365 nm excitation.

<table>
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<tr>
<th>Sintering duration</th>
<th>2 hours</th>
<th>4 hours</th>
<th>5 hours</th>
<th>6 hours</th>
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</thead>
<tbody>
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<td>Color Coordination (CIE (x,y))</td>
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<td>y</td>
<td>x</td>
<td>y</td>
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</table>
coordinates decrease with prolonged sintering duration. The emission color linearly changes from orange-red to blue, and the related internal and external quantum efficiency under 365 nm excitation also changes from 75.8% to 39.8% and 61.7% to 30.1%, respectively, as shown in Table II. Therefore, the color of the phosphor can be easily tuned by changing the sintering duration.

A phase transition from Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ to Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ also occurs under 0.1 MPa. As shown in Fig. 11, the PL spectra of the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ synthesized by sintering at 1750°C for 2, 4, 5, and 8 h under 0.1 MPa N$_2$ atmosphere reveal two emission bands at 455 and 619 nm under 365 nm excitation. The narrow peak at 455 nm is the emission characteristics of Sr$_2$Si$_5$N$_8$:Eu$^{2+}$, whereas the broad peak at 619 nm belongs to Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$. The Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ synthesized at 1750°C for 2 h under 0.1 MPa nitrogen atmosphere leads to the formation of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ and a trace of Sr$_2$Si$_5$N$_8$:Eu$^{2+}$. The observation on the small peak at 455 nm (black line in Fig. 11) clearly manifests the drop in emission intensity, whereas the same feature was observed after heating at 1980°C for 8 h under 0.1 MPa N$_2$ atmosphere with 365 nm excitation. The narrow peak at 455 nm is the emission characteristics of Sr$_2$Si$_5$N$_8$:Eu$^{2+}$, whereas the broad peak at 619 nm belongs to Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$. After sintering at 1750°C for 8 h under 0.1 MPa, the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ fully transforms into Sr$_2$Si$_5$N$_8$:Eu$^{2+}$.

IV. Conclusion

In this research, the temperature and gas pressure effect on Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ formation and the phase transition from Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ to Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ were studied. The PL spectra show that the emission intensities of Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ increase with increased sintering temperature. The best synthesis temperatures obtained in our study are 1700°C and 1980°C under 0.1 and 0.5 MPa nitrogen atmospheres, respectively. A comparison of the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ synthesized under these two conditions shows that the latter results in higher emission intensity, supposing that the high gas pressure condition stabilizes the Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$, whereas the same feature was observed after heating at 1980°C for 6 h, whereas the same feature was observed after heating at 1750°C for 8 h under 0.1 MPa nitrogen atmosphere. Although the mechanism of the transition from Sr$_{1.98}$Si$_5$N$_8$:Eu$^{2+}$ to Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ remains unclear, our research provides the experimental evidence and stage to understand the phase transition between nitridosilicates.

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References


