

Nitrogen Gas Pressure Synthesis and Photoluminescent Properties of Orange-Red SrAlSi₄N₇:Eu²⁺ Phosphors for White Light-Emitting Diodes

Jian Ruan,[†] Rong-Jun Xie,* Naoto Hirosaki,* and Takashi Takeda

Nano Ceramics Center, National Institute for Materials Science, 1-1Namiki, Tsukuba, Ibaraki 305-0044, Japan

Nitride phosphor SrAlSi₄N₇:Eu²⁺ was synthesized by gas pressure sintering of powder mixtures of Sr₃N₂, AlN, α -Si₃N₄, and EuN at 1750°C under 0.48 MPa N₂. The photoluminescent properties of SrAlSi₄N₇:Eu²⁺ were measured and analyzed. Two-peak emission from Eu²⁺ located at two different Sr sites in the SrAlSi₄N₇ host structure was observed. When the phorphors were excited at 410 nm, the highest emission intensity was found to be ~126% of that in YAG:Ce³⁺ excited at 460 nm. The highest relative emission intensity at 150°C was ~84.6% of that at 30°C. The highest external quantum efficiency acheived was 58.5%. SrAlSi₄N₇:Eu²⁺-based phosphors are potential for white light-emitting diodes.

I. Introduction

 $E_{\text{highly promoted by the development of white light$ emitting diodes (white LEDs) with characteristics of high efficiency, simple structure, and long life in the past decade.¹ The most common commercial white LED is combined of a blue-emitting InGaN chip and a yellow Ce³⁺-doped yttrium aluminum garnet (YAG:Ce³⁺) phosphor.² YAG:Ce³⁺-based white LED exhibits a high luminous efficiency, but its color-rendering index is limited to relatively low level by the color deficiency in the red- and blue-green of the phosphor.³ An alterative way to overcome this weakness is incorporation with additional phosphors, and extensive investigations have been devoted to these materials. Among them, rare-earth-doped (oxy)nitride phosphors have attracted increasing attention in recent years.^{3–15} They exhibit broad excitation bands covering the emission of the commercial InGaN near-UV and blue LED chips because of the strong nephelauxetic effect and large crystal-field splitting caused by the coordination of nitrogen atoms. Furthermore, higher thermal and chemical stabilities of nitride phosphors are expected because of their stiff frameworks in the host lattices based on [SiN₄] or [AlN₄] tetrahedra.¹⁰

Recently, novel nitrioalumniosilicate SrAlSi₄N₇ was reported.¹⁵ As shown in Fig. 1, SrAlSi₄N₇ has an orthorhombic structure (Pna2₁ symmetry) with unit cell parameter of a = 11.7 Å, b = 21.31 Å, and c = 4.95 Å and infinite chains of edge-sharing [AlN₄] tetrahedra in crystal structure. It is obvious that there are two different Sr lattice sites in SrAlSi₄N₇. Emission around 635 nm was observed in the SrAlSi₄N₇:Eu²⁺ and high quantum efficiency (QE) was also expected. However, the reported synthesis of SrAlSi₄N₇:Eu²⁺ based on radio-frequency furnace is usually baffled by the byproducts of microcrystalline Sr₂Si₅N₈. For practical applications, both high purity and crystallinity are required for the synthesized product. Therefore, applicable synthesis methods for the novel SrAlSi₄N₇:Eu²⁺ phosphor are still urgently required for mass production. Besides this, the study of

the detailed luminescent behaviors is also necessary for the estimation of its potential application in warm white LEDs.

In this work, well crystalline $SrAlSi_4N_7:Eu^{2+}$ nitride phosphors were synthesized by gas pressure sintering. The luminescent properties of $SrAlSi_4N_7:Eu^{2+}$ were investigated. Their thermal quenching properties and internal and external QE were also estimated; the results show $SrAlSi_4N_7:Eu^{2+}$ nitride phosphors are potential for white LED.

II. Experimental Procedure

(1) Preparation of $SrAlSi_4N_7:Eu^{2+}$

SrAlSi₄N₇:Eu²⁺-based phosphors were prepared by a solid-state reaction of high-purity reagents Sr₃N₂ (Kojundo Chem. Lab. Co. Ltd., Tokyo, Japan), AlN (Tokuyama Chem. Co. Ltd., Tokyo, Japan), α-Si₃N₄ (SN-E10, Ube Industries, Tokyo, Japan), and EuN. Starting materials (~ 2 g) with chemical composition of $Sr_{1-x}Eu_xAlSi_4N_7$ (referred to as SASN-x, where x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.10, respectively)were mixed properly in an agate mortar and then filled into a BN crucible under a continuously purified N₂ atmosphere in a glove box. Then, the mixtures were fired at 1750°C for 2 h under 0.48 MPa N₂ atmosphere in a gas pressure sintering furnace (FVPHR-R-10, FRET-40, Fujidempa Kogyo Co. Ltd., Osaka, Japan) with a graphite heater. Subsequently, the samples were mixed properly with additive AlN with contents equal to the first time and refired for 6 h under the same conditions, respectively. EuN was synthesized by the reaction of metallic Eu with N_2 at 850°C for 6 h in a tube furnace.

(2) Structure Characterization

The X-ray diffraction (XRD) pattern of the as-synthesized powder was analyzed using Rigaku RINT2000 system (Rigaku Co., Tokyo, Japan) using CuK α 1 (λ = 1.5408 Å), operating at 40 kV and 40 mA. Data were collected over 20 range of 10–60°, with a step width of 0.02° and count time of 12 s/step. The powder morphology was investigated by field-emission scanning electron microscopy (FESEM, JEOL-840A, JEOL Co., Tokyo, Japan).

(3) Luminescence Properties Measurement

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at room temperature using a fluorescent spectrophotometer (F-4500, Hitachi Ltd., Tokyo, Japan) with a 200 W Xe lamp as the excitation source. The QE of the samples were measured using a multi-channel spectrophotometer (MCPD-7000, Otsuka Electronics, Tokyo, Japan) with a 200 W Xe lamp as the excitation source. A white BaSO₄ powder was used as a standard reference for correction in the measurements of QE. The temperature-dependent photoluminescence (TDPL) spectra (30–200°C) were also conducted by the MPCD-7000 machine under excitation at 410 nm. The measurements of room-temperature time-resolved photoluminescence (TRPL) were carried out in a time-controlled single photon counting (TCSPC) system (FluoroHub, Horiba Jobin Yvon, Edison, NJ) with a TBX picoseconds photon detection module. The

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^{*}Member, The American Ceramic Society.

[†]Author to whom correspondence should be addressed. e-mail: bowkeeper@163.com



Fig. 1. Crystal structure of $Sr_{1-x}Eu_xAlSi_4N_7$. The Sr/Eu, Al, Si, and N atoms are marked in green, red, blue, and light gray, respectively.¹⁵

interchangeable nanoLED (370 nm, Horiba Jobin Yvon) was used as an excitation source.

III. Results and Discussion

(1) Synthesis and Structural Characteristics of SASN—x Phosphors

It was found that the pure SrAlSi₄N₇ phase was difficult to be acheived with starting raw materials mixed stoichiometrically. Additional AlN may be helpful to solve this problem. Figures 2(a) and (b) shows the XRD patterns of samples after the first firing (stoichiometrical compositon) and the second firing (additional AlN introduced). For comparison, the standard XRD patterns of Sr₂Si₅N₈ and SrAlSi₄N₇ (downloaded from ICSD website) were also shown in Figs. 2(a) and (b). The residual Si_3N_4 and AlN and a small amount of as-synthesized SrAlSi₄N₇ have been marked in Fig. 2(a). Very little amount of residual Sr₂Si₅N₈ has also been marked in Fig. 2(b). For better illumination, the main phases in those patterns were not marked, but they can be identified easily. It is clear that the main phase of the first firing products is Sr₂Si₅N₈ and only a little amount of SrAlSi₄N₇ can be obtained. On the other hand, the main phase of the second firing product is SrAlSi₄N₇ and almost no AlN or $Sr_2Si_5N_8$ phase can be recognized. The content of AlN seems to be very important for the synthesis of the $SrAlSi_4N_7$ phase. However, it is difficult to distinguish those residual AlN from XRD patterns after the second firing (Fig. 2(b)). Further investigation may be necessary for better understanding of the function and behavior of AlN in the growth of SrAlSi₄N₇ crystalline.

The designed compositions are $Sr_{1-x}Eu_xAlSi_4N_7$ (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.10) (SASN—x). The theoretical compositions of the final products should be $Sr_{1-x}Eu_xAl_2Si_4N_7$ (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.10) in mol% because of the additional AlN. The chemical composition of the sample was measured by an induction coupled plasma atomic emission spectroscopy method and an oxygen–nitrogen analyzer (TC-436, LECO, St. Joseph, MI). The results show that the actual compositions are almost the same as the theoretical ones. For



Fig. 2. (a) XRD patterns of samples after the first firing. Standard $Sr_2Si_5N_8$ and $SrAlSi_4N_7$ patterns were also shown for comparison. (b) XRD patterns of samples after the second firing. Standard $Sr_2Si_5N_8$ and $SrAlSi_4N_7$ patterns were also shown for comparison.

example, the actual and the theoretical compositions of the SASN—0.05 sample are [Sr: $22.0\pm0.1\%$, Eu: $2.11\pm0.01\%$, Al: $14.6\pm0.1\%$, Si: $30.0\pm0.1\%$, N: $28.7\pm0.02\%$, O: $097\pm0.06\%$, rest are unknown] and [Sr: 22.55%, Eu: 2.06%, Al: 14.61%, Si: 30.43%, N: 30.35%] in wt%, respectively. Little oxygen impurity was found because it is usually unavoidable from the starting materials and from the second contamination in the processing for all the nitride compounds.

The intensity distribution of diffraction peaks shown in Fig. 2(b) seems to be a little different from the standard pattern, especially for those samples with higher Eu concentrations. This may be ascribed to the preferred growth of $Sr_{1-x}Eu_xAlSi_4N_7$ crystallines along the *c*-direction [001] because of the infinite chains of edge-sharing [AlN₄] tetrahedra in the crystal structure as shown in Fig. 1.

The assumption can be supported by FESEM observations. Figure 3 shows the particle morphology images of SASN—0.01, 0.05, and 0.10 samples. It can be found that crystallines with a larger particle size and a more cylindrical shape were obtained with an increase in the Eu concentration. This is because lower temperature of the solid-state reaction can be estimated when higher content of Eu was used to replace the Sr in the Sr_{1-x}Eu_xAlSi₄N₇ crystalline. Figures 3(d), (e), and (f) show the crystalline particles with different shapes. As shown in Fig. 3(d), the crystallines with larger size usually show smooth surface on their head faces and adhered dozens of smaller particles on their side faces. Figure 3(e) indicates that the crystalline can epitaxially grow starting from the same face. Figure 3(f) shows an FESEM image with zoom



Fig. 3. (a)–(c) Morphology images of SASN–0.01, SASN–0.05, and SASN–0.10. (d)–(f) crystalline particles with different shapes ((a)–(c) \times 1000, (d)–(e) \times 3000, and (f) \times 20 000).

multiple of 20 000. Two types of particles can be observed: cylinder particle A with a diameter of ~1.0 µm and a length of ~4.0 µm, and amorphous particles B adhered in the two head sides of particle A. It can be observed that the side face of particle A is very smooth. This indicates that the axial growth of the cylindrical crystalline particles may play a dominant role in forming such a morphology. Although the particle morphology was found to be cylindrical in SASN:Eu²⁺ phosphors, we believed that the influence of phosphor sharp on their practical application will become weaker once those phosphors can be well milled and classified. A similar case can be found in Eu²⁺-doped β -SiAION phosphors, which have been applied successfully.

(2) Photoluminescent Properties of SASN—x Phosphors

The PL and PLE spectra of SASN—*x* samples are shown in Fig. 4(a). The PL spectra were measured with irradiations at 410 nm, while the PLE spectra were monitored at 620, 623, 625, 640, 645, and 650 nm for SASN—*x* (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.10) samples, respectively. The intensity has been normalized according the emission intensity of a standard YAG:Ce³⁺ (P46Y3) with excitation at 460 nm for comparison. As shown in Fig. 4(a), all samples exhibit broadband excitation and emission spectra. The excitation spectra consist of four bands at 320, 355, 410, and 460 nm. With an increase in the Eu concentration, only difference in excitation intensity was observed in the first two bands. On the other hand, both peak shifts and excitation intensity differences can be found in the last two bands. It is interesting that a quite plate excitation band from 350 to 400 nm was observed in the SASN—0.1 sample.

A single and broad emission band peaking at 620–650 nm was observed in all samples when the samples were excited at 355, 410, or 460 nm. For instance, the PL spectra of SASN—0.05 with excitation at the above-mentioned wavelengths are given in Fig. 4(b). The full-width at half-maximum (FWHM) is 115, 119, and 114 nm, respectively. With excitation at 410 nm, the FWHM is 125, 122, 121, 119, 114, and 113 nm for SASN—x (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.10), respectively, as seen in Fig. 4(a). The emission should be ascribed to $4f^65d^1-4f$ transition of Eu²⁺ ions because no characteristic emission of Eu³⁺ (sharp lines between 580 and 650 nm) was observed. It is suggested that Eu³⁺ were reduced to Eu²⁺ in a reducing carbon monoxide gas atmosphere using a graphite heater and in a nitrogen atmosphere.

In addition, the emission peak also exhibits an obvious redshift with an increase in the Eu concentration. Figure 5 shows the dependence of PL intensity and emission peak position of SASN—x samples as a function of Eu concentration. As seen, the emission peak shifted from ~610 to ~650 nm with an increase in the Eu concentration, while the PL intensity increased at first till x = 5% and then decreased gradually. The PL maximum value was observed in the SASN—0.05 sample. When it



Fig. 4. (a) Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of SASN—x (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.1) samples. (b) PL spectra of SASN—0.05 with excitation at 355, 410, and 460 nm.



Fig. 5. Eu concentration-dependent photoluminescence (PL) intensity and peak position of SASN—x (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.1) samples with excitation at 355, 410, and 460 nm.

was excited at 410 and 460 nm, the PL intensity was $\sim 126\%$ and $\sim 111\%$ of that observed in YAG:Ce³⁺ (P46Y3) with 460 nm excitation, respectively.

Table I shows the Eu²⁺ 5*d* excitation bands, emission band maximum, crystal-field splitting, and Stokes shifts of SASN—*x* (*x* = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.10) samples. The crystalfield splitting was estimated from the energy difference between the highest and the lowest observed 5*d* excitation levels of Eu²⁺. Stokes shifts were calculated from the energy difference between the lowest 5*d* excitation level (λ_{abs}) and the emission band of Eu²⁺ (λ_{em}). Limited to the resolutions of excitation spectra at room temperature, it is difficult to avoid the extra errors if the λ_{abs} was determined directly from the spectra. Therefore, the mirror-image relationship may be available to estimate the λ_{abs} for this work based on the Gaussian sharp of the observed emission peaks. The λ_{abs} was calculated by the formula as follows:

$$\lambda_{abs} = 2E_0 - \lambda_{em}$$

where E_0 is the zero-phonon line that can be determined at the intersection of the emission and excitation spectra. Then, the Stokes shifts were calculated as $\Delta S = \lambda_{abs} - \lambda_{em}$. As shown in Table I, the crystal-field splitting and Stokes shifts increased and decreased with an increase in the Eu concentration, respectively.

The energy levels of Eu²⁺ ions have been extensively studied. The broadband emission from the $4/^{6}5d^{1}-4f$ transition of Eu²⁺ ions has been observed in the color range from ultraviolet to red, which depends on the ligand-field splitting of the 5*d* levels caused by the host lattice. In this work, orange-red emission was observed in SASN—*x* samples because of the relatively large ligand-field splitting of the 5*d* levels and the low-energy center of gravity of the 5*d* states due to the high formal charge of N³⁻ and the nephelauxetic effect. The red-shift of emission peaks is commonly observed in rare-earth-doped phosphors, as the doping concentration increases. This phenomenon has been assigned to the re-absorption processes caused by the crossrelaxation and energy transfer among the active ions.¹⁶ The similar phenomenon observed in Figs. 4 and 5 could also be explained as the re-absorption processes.

In order to further understand the re-absorption process, a series of lifetime decay curves were recorded by monitoring the SASN—0.01 and SASN—0.10 samples in different wavelengths from 450 to 750 nm at 3 nm interval, and the TRPL spectra shown in Figs. 6(a) and (b) were obtained by slicing them, respectively. When the time interval was 1.4 ns, both the emission peaks A and B were apparently observed in the spectra. The occurrence of the two emission peaks may be assigned to the Eu^{2+} emission from the two different Sr lattice sites. The Eu^{2+} can enter the structure and occupy two distinct Sr^{2+} sites, in which one (referred to as Sr1) is coordinated by eight nitrogen ions with an average distance of 2.87 Å, and the other (referred to as Sr2) is coordinated by six nitrogen ions with an average distance of 2.71 Å. Because lower ligand field strength is expected in the former position based on its larger coordination number, Eu²⁺ occupying the Sr1 position should exhibit a higher-energy (shorter wavelength) emission peak. Therefore, the observed emission peaks A and B should be originated from the Eu²⁺ ions located in Sr1 and Sr2 positions, respectively.

As shown in Fig. 6, with the time interval prolonging, it was interesting to observe that the relative emission intensity of peak A rapidly descended, whereas that of peak B increased till the time interval was 2.9 ns and then descended gradually. An apparent red-shift of emission peak B was also observed in the both SASN—0.01 and SASN—0.1, while no apparent red-shift of emission peak A was found. In comparison with SASN—0.01, a higher relative intensity of emission peak B versus peak A was observed in the SASN—0.1 sample. This indicates that Eu²⁺ ions will occupy Sr2 sites taking precedence over Sr1 sites, when the Eu concentration increased from 1% to 10%.

The thermal quenching properties of SASN—x samples were also investigated. Figure 7(a) presents the TDPL spectrum of SASN—0.01 with 410 nm excitation. A slight blue-shift from 600 to 594 nm was observed in the spectra when the temperature increased from 30° to 200°C. This phenomenon can be ascribed to the thermally active phonon-assisted tunneling from the excited states of lower-energy emission band to those of higher-energy emission band in the configuration coordinate diagram.¹⁷

The temperature-dependent emission intensities of all SASN—*x* samples under 410 nm excitation are shown in Fig. 7(b). It can be found that the emission intensity of SASN—*x* (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.1) samples at 150°C remains 84.6, 83.6, 83.1, 77.2, 72.9, and 68.1% of that measured at 30°C, respectively. The activation energy for the thermal quenching was also estimated by the equation as follows¹⁸:

$$I(T) = \frac{I_o}{1 + A \exp\left(\frac{-\Delta E}{k_{\rm B}T}\right)}$$

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. As shown in the inset of Fig. 6(b), it can be concluded that the ΔE for

Table 1. The Eu²⁺ 5*d* Excitation Bands, Zero-Phonon Line (E_0), Emission Band Maximum (λ_{em}), Crystal-Field Splitting and Stokes Shifts (ΔS) of SASN—*x* (*x* = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.10, Respectively) Samples

SASN—x	Eu ²⁺ 5d excitation bands (nm)	E_0 (nm)	λ_{em} (nm)	Crystal-field splitting (cm ⁻¹)	$\Delta S \ ({ m cm}^{-1})$	FWHM (nm) at 410 nm
x = 0.01 x = 0.02 x = 0.03 x = 0.05 x = 0.075 x = 0.10	314±2, 353±2, 406±2, 472±2 (λ_{abs}) 313±2, 353±2, 406±2, 479±2 (λ_{abs}) 314±2, 355±2,407±2, 481±2 (λ_{abs}) 314±2, 356±2,410±2, 496±2 (λ_{abs}) 317±2, 356±2, 408±2, 505±2 (λ_{abs}) 315±2, 358±2, 412±2, 505±2 (λ_{abs})	546 ± 2 551 ± 2 553 ± 2 568 ± 2 575 ± 2 581 ± 2	$620 \pm 2 \\ 623 \pm 2 \\ 625 \pm 2 \\ 640 \pm 2 \\ 645 \pm 2 \\ 650 \pm 2 $	$10155 \pm 100 \\ 10546 \pm 100 \\ 10388 \pm 100 \\ 10480 \pm 100 \\ 10712 \pm 100 \\ 10056 \pm 10056 \pm 100 \\ 10056 \pm 10056 \pm 10056 \\ 10056 \pm 10056 $	$5057 \pm 100 \\ 4825 \pm 100 \\ 4790 \pm 100 \\ 4536 \pm 100 \\ 4298 \pm 100 \\ 4147 \pm 100 \\ 414$	125 122 121 119 114



Fig. 6. (a) Time-resolved photoluminescence (TRPL) emission spectra of SASN—0.01. (b) TRPL emission spectra of SASN—0.1.

SASN—0.01 is 0.235 eV, which is a little higher than the value (0.20 eV) reported in $Sr_2Si_5N_8$:Eu²⁺ phosphors. Besides the emission spectra, the external and internal QE of

Besides the emission spectra, the external and internal QE of SASN—x samples were also measured and calculated using the method described in Hirosaki *et al.*³ With excitation at 410 nm, the internal QE of SASN—x (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.10) are about 84.0, 83.1, 80.4, 71.2, 62.3, and 56.3%, respectively. The external QE in the wavelength range from 400 nm to 500 nm decreased gradually but the absorption increased with an increase in the Eu concentration. This finally leads to an initial increase in the external QE of SASN—x (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.10) are about 54.0, 58.0, 58.5, 57.5, 49.0, and 44.2%, respectively. Figure 8 shows the internal and external QE and absorption of SASN—0.05 as a function of excitation wavelengths. We believed that the external QE value can be improved by further purification and particle classification.

Orange-red-emitting nitride phosphors have been extensively studied and high external QE and thermal stability have been achieved. For comparison, the crystal structures and luminescent properties of $Sr_2Si_5N_8$, CaSiAlN₃, and SrAlSi₄N₇ are given in Table II. It can be found that the FWHM of SrAlSi₄N₇ is more than 25 nm broader than others, which indicates that a higher color-rendering index may be achieved after the incorporation of phosphor. This may be ascribed to the difference in their crystal structures. All of them are orthorhombic in the crystal system, but the [AlN₄] tetrahedras in SrAlSi₄N₇ connected with each other by edge-sharing and formed infinite chains in the crystal structure, while the [AlN₄] or [SiN₄]



Fig. 7. (a) The temperature-dependent photoluminescence (TDPL) of SASN—0.01 measured with increasing temperature from 30° to 200°C. (b) TDEL emission intensity of SASN—x (x = 0.01, 0.02, 0.03, 0.05, 0.075, and 0.1) samples. The inset shows an Arrhenius fitting of the emission intensity and calculated ΔE . All the spectra were measured with 410 nm excitation.

tetrahedras in $\rm Sr_2Si_5N_8$ and CaSiAlN₃ were connected by corner-sharing. And lower crystal-field splitting was achieved in SrAlSi_4N_7 in comparison with $\rm Sr_2Si_5N_8$ and CaSiAlN_3. Such a difference in the host lattice may result in higher vibronic intensity and stronger vibronic transition of Eu^{2+} ions in SrAlSi_4N_7 compared with Sr_2Si_5N_8 and CaSiAlN_3. This will lead to a



Fig. 8. Internal and external quantum efficiency (QE) and absorption of the SASN—0.05 sample.

Table II.	Crystal	Structures	and Photo	oluminescent	Properties	of Sr ₂ Si	$5N_8$	CaSiAlN ₃	, and SrAlSi	$_{4}N_{7}$
	•/						., .,			-

Formula	$Sr_{1.98}Eu_{0.02}Si_5N_8$	Ca _{0.992} Eu _{0.008} AlSiN ₃	$Sr_{0.97}Eu_{0.03}AlSi_4N_7$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pmn</i> 2 ₁ (No. 31)	<i>Cmc</i> 2 ₁ (No. 36)	<i>Pna</i> 2 ₁ (No. 33)
Lattice parameters (Å)	a = 5.710(1)	a = 9.8007 (4)	a = 11.742(2)
	b = 6.822(1)	b = 5.6497 (2)	b = 21.391 (4)
	c = 9.341 (2)	c = 5.0627 (2)	$c = 4.966 (1)^{\dagger}$
Coordination number (CN)	Sr1 = 10,	Ca = 5	Sr1 = 8,
	Sr2 = 8		$Sr2 = 6^{\dagger}$
Avenge bond length of M-N	Sr1 = 2.928,	Ca = 2.485	Sr1 = 2.87,
(M = Sr or Ca) (Å)	Sr2 = 2.865		$Sr2 = 2.71^{+}$
Shortest band length of	Sr1 = 2.542	Ca = 2.405	Sr1 = 2.653
M-N (M = Sr or $\tilde{C}a$) (Å)	Sr2 = 2.570		$Sr2 = 2.504^{\dagger}$
Emission peaks	625 nm	650 nm	625 nm [‡]
Excitation peaks	334, 395, 465, 505 nm	335, 450, 500, 564 nm	314, 355, 407, 481 nm [‡]
Crystal-field splitting (cm^{-1})	14 200	14 600	$10388\pm100^{\ddagger}$
Stokes shifts (cm^{-1})	3700	2500	$4790 \pm 100^{\ddagger}$
FWHM (nm)	86 nm at 450 nm	89 nm at 460 nm	116 nm at 460 nm ^{\ddagger}
Absorption	80% at 450 nm	80% at 460 nm	70% at $460~{ m nm}^{\ddagger}$
external QE	64% at 450 nm	76% at 460 nm	49.0% at $460 \text{ nm}^{\ddagger}$
Thermal quenching at 150°C	86% at 450 nm	87% at 450 nm	83.1% at $410 \text{ nm}^{\ddagger}$
References	Mueller-Mach and colleagues ^{9–11,19,20}	Uheda and colleagues ^{8,19}	[†] Hecht <i>et al</i> . ¹⁵
	2	-	[‡] This work

broader emission observed in SrAlSi₄N₇. Similarly, it can be found that the observed FWHM of Eu²⁺-doped SrAlSi₄N₇ decreases with increasing crystal-field splitting when Eu concentration increases, as shown in Table I.

As shown in Fig. 9, the emission peak position usually depends on the crystal-field splitting and the nephelauxetic effect in the Eu²⁺-doped (oxy)nitride compounds. Both of them will reduce the energy difference between the ground and the excited state of Eu^{2+} ions; hence, the excitation and emission bands at lower energies (i.e. longer wavelength) were observed in various phosphors. As shown in Table II, Eu^{2+} ions can occupy two different Sr lattice sites in SrAlSi₄N₇ with less CN and a little shorter average band length than those in Sr₂Si₅N₈. But both of them are much more and longer than those in CaSiAlN₃, respectively. These indicate that stronger nephelauxetic effect will be caused in SrAlSi₄N₇ than in Sr₂Si₅N₈, but it will be weaker than that in CaSiAlN₃. And the weaker crystal-field splitting in the SrAlSi₄N₇ will lead to higher energy of the lowest 5d-4f level and thus caused the emission observed at a wavelength shorter than that in CaAlSiN₃ and similar to that in Sr₂Si₅N₈.

Among the three above-mentioned nitride phosphors, SrAl-Si₄N₇ shows the weakest crystal-field splitting and comparable strong nephelauxetic effect with $Sr_2Si_5N_8$ but weaker than CaAlSiN₃. This is the reason why excitation bands at higher energy were observed in SrAlSi₄N₇.



4f⁷ ground state

Fig. 9. Schematic representation of the energy level of the Eu^{2+} ion in (oxy)nitride phosphors.

Stokes shift is the reflection of energy consumption during the electron relaxation from the lowest 5*d*–4*f* excitation band to emission band. Based on the Stokes shift model, higher thermal stability and internal QE of the PL should be achieved in the phosphors with smaller Stokes shift. This is in agreement with our results, that is, the Stokes shift occurs in the following sequence: CaSiAlN₃ < Sr₂Si₅N₈ < SrAlSi₄N₇. The thermal stability and internal QE will also be influenced by the impurity in the crystalline. This is the reason why stronger thermal quenching and lower internal QE were observed when the Eu concentration increased.

It should also be noted that $Sr_{0.9}Eu_{0.1}AlSi_4N_7$ shows a relatively plant excitation band in the wavelength range between 300 and 500 nm. This means that the sample is efficient for the excitation of blue GaN and near-UV InGaN chips and compatible with various blue, green, or yellow phosphors.²¹

IV. Conclusion

Novel orange-red SrAlSi₄N₇:Eu²⁺ nitride phosphors were synthesized by gas pressure sintering. The luminescent properties of SrAlSi₄N₇:Eu²⁺ were studied as a function of Eu concentration. The TRPL and TDPL spectra of SrAlSi₄N₇:Eu²⁺ were also measured. The SrAlSi₄N₇:Eu²⁺ phosphors were estimated to show good thermal quenching properties and high external QEs, which are potential orange-red down-conversion luminescent materials for white LEDs. The crystal structure and photoluminescent properties of SrAlSi₄N₇ were also compared with Sr₂Si₅N₈ and CaSiAlN₃. The results may be useful to anticipate the photoluminescent properties of other rare-earth ion-doped SrAlSi₄N₇ compared with Sr₂Si₅N₈ and CaSiAlN₃.

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