Crystal, electronic and luminescence properties of Eu$^{2+}$-doped Sr$_2$Al$_{2-x}$Si$_1+y$O$_7-x$N$_x$

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Abstract

The crystal and electronic structures, as well as the luminescence properties of Sr$_2$Al$_{2-x}$Si$_1+y$O$_7-x$N$_x$:Eu$^{2+}$ are reported. First-principles calculations energetically confirm that the Al and Si atoms are in partial ordering in the 2a and 4e sites in Sr$_2$Al$_2$SiO$_7$. In addition, the band structure calculation shows that Sr$_2$Al$_2$SiO$_7$ has an indirect band gap with an energy gap of about 4.07 eV, which is in good agreement with the experimental data ($\approx$ 5.3 eV) obtained from the diffuse reflection spectrum. The crystal structure of Sr$_2$Al$_2$SiO$_7$ can be modified by Si–N substitution for Al–O in the lattice with a maximum solubility of about $x \approx 0.6$. The average bond length of Eu Sr$_{O,N}$ slightly increases although the lattice parameters decrease with the incorporation of Si–N in Sr$_2$Al$_2$SiO$_7$:Eu$^{2+}$. Under excitation in the visible spectral region, Sr$_2$Al$_{2-x}$Si$_{1+y}$O$_{7-x}$N$_x$:Eu$^{2+}$ emits blue to yellow light with a broad emission band in the range of 480–570 nm, varying with both the Eu concentration and the $x$ value. The red shift of the emission band of Eu$^{2+}$ is associated with an increase in the crystal-field splitting and the covalency, which arise from the incorporation of nitrogen as well as the energy transfer between the Eu ions at high Eu concentrations. Moreover, the Eu ions have a strong effect on both the concentration quenching and the thermal quenching in Sr$_2$Al$_{2-x}$Si$_{1+y}$O$_{7-x}$N$_x$. The temperature dependence of photoluminescence indicates that Sr$_2$Al$_{2-x}$Si$_{1+y}$O$_{7-x}$N$_x$:Eu$^{2+}$ shows strong thermal quenching due to the dominant nonradiative process at room temperature.

Keywords: Crystal structure; Electronic structure; Luminescence; Phosphor; Distrontium dialuminum silicate trioxide; Oxynitride

1. Introduction

Wavelength-conversion phosphors play a key role in the development of high-efficiency white LEDs [1–3]. Among the LED phosphors, rare-earth-doped nitride/oxynitride-based luminescent materials are the best candidates, not only because of their high absorption and high conversion efficiency in the UV/blue region, but also because of their excellent thermal and chemical stability. With the rapid development of brighter white LEDs for general illumination applications, the use of nitride/oxynitride phosphors has shown impressive progress in just a few years [4–12].

Oxynitride materials can be obtained by two opposite substitution approaches, i.e., starting from nitride [13,14] and oxide [15] compounds. $\alpha$-Sialon is a good example of the first approach, in which Si–N is partially replaced by Al–O in the Si$_3$N$_4$ lattice [13,14]. Eu$^{2+}$-doped Ca-$\alpha$-sialon shows bright yellow-orange emission upon excitation by blue light [6,7]. In general, starting from a nitride compound is easier than starting from an oxide compound because the nitrogen atom is more flexible in its formation of various chemical bonds with metal and nonmetal atoms (Si, Al, etc.), with two- and three-, and even four-fold coordination [16] in which oxygen can easily occupy a suitable N site in the structure. In oxide lattices, however, the oxygen atom can only bond in two-fold coordination [17]. Thus, starting from an oxide, it is difficult to achieve a “real” oxynitride with high nitrogen solubility. In contrast to the limited number of nitride/oxynitride phosphor...
materials, there are a large number of oxide phosphors that have already been well developed [18,19]. If an appropriate amount of nitrogen and other related atoms such as Si and Al can be incorporated into these oxide lattices by a single- or cross-substitution, apart from the framework, the local structure around the cations will also be modified. Accordingly, it is expected that the luminescence properties can be improved or tailored for specific applications. In particular, with the abundant resources of oxide compounds, the formation of oxynitrides from oxides by chemical substitution offers a highly promising approach for obtaining novel properties in rare-earth-doped materials.

Within the melilite group of alkaline earth silicates, Sr2Al2SiO7 [20] is isotypic with gehlenite Ca2Al2SiO7 [21] and crystallizes in a tetragonal sheet structure with space group P-421m (No. 113). The sheet of Sr2Al2SiO7 consists and crystallizes in a tetragonal sheet structure with space group P-421m (No. 113). The sheet of Sr2Al2SiO7 forms an oxynitride significantly lower due to its sheet structure. As a result, the Si–N pair can be incorporated into Sr2Al2SiO7 to replace the Al–O pair and form an oxynitride lattice.

With respect to the luminescence properties, in contrast to extensive studies on rare-earth-doped alkaline-earth alumimates and silicates [18,19], the investigation of Eu2+-doped Sr2Al2SiO7 has been limited. Long-lasting phosphorescence has been found in Eu2+- or Ce3+-doped Sr2Al2SiO7, and the phosphorescence as a function of temperature and time has been discussed [23]. Under UV excitation, Sr2Al2SiO7:Eu2+ produces broadband luminescence with a peak at 520 nm, and its lifetime is about 1.7 μs. Unfortunately, no detailed information on the excitation and emission spectra, nor on the Eu concentration and its effect have been reported.

In the present study, we first investigate the crystal and electronic structures of undoped Sr2Al2SiO7 by a combination of the Rietveld refinement of powder X-ray diffraction data and first-principles calculations to obtain a better understanding of the optical properties of Eu-doped Sr2Al2SiO7. Second, using Si1-xN4 as a source material, we replace Al–O with Si–N in the host lattice of Sr2Al2SiO7 to form Sr2Al2SiO7:N. Furthermore, the temperature dependence of the photoluminescence of Sr2Al2SiO7:Eu2+ is discussed.

2. Experimental

2.1. Synthesis of Sr2Al2−xSi1+xO7−xN4:Eu2+

Undoped Sr2Al2SiO7 and Eu2+-doped Sr2Al2−xSi1+xO7−xN4 (x = 0–1.0) were prepared by a solid-state reaction. Appropriate amounts of the starting materials of SrCO3 (Aldrich, purity 99%), Al2O3 (Sumitomo Chemical Co., Ltd., AKP-30), SiO2 (Kojundo Chemical Co., Ltd., SIO07PB, 99.9%), Si1-xN4 (Ube, SN-E10) and Eu2O3 (Shinetsu Chemical Co., Ltd., purity >99.9%) were weighed and mixed in hexane solution using a ball mill with Si1-xN4 balls. Considering the necessity of reducing Eu2O3 to EuO, a small amount of additional Si1-xN4 was used [24]. After drying, the mixture was loaded into a BN boat and fired in a horizontal tube furnace at 1300–1400 °C for 5 h under N2–H2 (5%) atmosphere.

2.2. Characterization

The structural data were collected using an X-ray powder diffractometer (Rigaku, RINT Ultima-III) with a graphite monochromator using Cu-Kα radiation (λ = 1.54056 Å), operating at 40 kV and 40 mA. A step-scan model was used from 10° to 100° with a step size of 0.02° and a count time of 6 s per step. The X-ray powder diffraction data were refined by the Rietveld method using the GSAS package [25,26].

The photoluminescence spectra were measured at room temperature using a fluorescence spectrophotometer (Hitachi F-4500) with a 150 W Xenon short-arc lamp as a light source. The diffuse reflectance spectrum was recorded using a UV–vis spectrophotometer (JASCO, V-560) and a BaSO4 white plate as the standard reference. The temperature dependence of luminescence spectra was obtained from room temperature to 250 °C using a multichannel spectrophotometer (MCPD-7000) with a 200 W Xe lamp as an excitation source.

2.3. First-principles calculation method

The calculations of the total energy and electronic structure of Sr2Al2SiO7 were carried out using the ABINIT code [27] on the basis of density functional theory. The exchange-correlation functional generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof pseudopotential was used, with Sr (5s2), Al (3s23p1), Si (3s23p2) and O (2s22p4) levels treated as valence states. The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 40 Ha. Integrals over the Brillouin zone (BZ) were approximated by sums on a 4×4×4 mesh of special k-points. The structural data of Sr2Al2SiO7 obtained from the present study by the Rietveld refinement of the X-ray powder diffraction data were used in the calculations.
3. Results and discussion

3.1. Crystal and electronic structures of Sr$_2$Al$_2$SiO$_7$

Using Ca$_2$Al$_2$SiO$_7$ as an analogue, the distribution of Al/Si was proposed for Sr$_2$Al$_2$SiO$_7$, in which Al is partially ordered in the 2a site, while the other Al occupies the 4e site with an Al/Si ratio of 1:1 [20] on the basis of bond-strength sum calculations. Therefore, it is necessary to determine the Al/Si distribution from an energetic viewpoint by first-principles simulation, because X-ray powder diffraction analysis cannot distinguish the Al and Si atoms due to their similar scattering factors. Accordingly, calculations were performed on two models: (1) Al on 2a and Al$_{1/2}$Si$_{1/2}$ on 4e (i.e., partial ordering), and (2) Si on 2a and Al on 4e (full ordering). For model (1), a 1a x 1b x 2c supercell was built in which Al and Si are separately arranged into two sublattices along the c-axis. The total energy and the optimized lattice parameters after structural relaxation, along with the experimental values, are summarized in Table 1. The calculated lattice parameters are in good agreement with the experimental values, with deviations of less than 1% for both models. However, the total energy indicates that the partially ordered Al/Si model is energetically favorable for the distribution of Al/Si in Sr$_2$Al$_2$SiO$_7$ (with a lower total energy of about 0.01 Ha or 0.27 eV), in agreement with previously determined structure [20].

Fig. 1 shows the band structure along a high-symmetry path through the first BZ, and the corresponding total electronic density of states (DOS) of Sr$_2$Al$_2$SiO$_7$ based on the optimized supercell model. The electronic band structure demonstrates that Sr$_2$Al$_2$SiO$_7$ has an indirect band gap in spite of its “fat band” characteristics at the top.

Table 1
Lattice parameters and total energies of Sr$_2$Al$_2$SiO$_7$ for two models by first-principles calculations, as compared with experimental values from the Rietveld refinement of X-ray powder diffraction

|                      | Partial ordering model | Full ordering model | Experimental   |
|----------------------|------------------------|---------------------|----------------|
| Space group          | P-421m (No. 113)       |                     |                |
| a (Å)                | 7.8661                 | 7.7838              | 7.8251(1)      |
| b (Å)                | 7.8661                 | 7.7838              | 7.8251(1)      |
| c (Å)                | 5.3599                 | 5.3481              | 5.2700(1)      |
| Z                    | 2                      | 2                   | 2              |
| V (Å$^3$)            | 327.12                 | 324.03              | 322.69(1)      |
| Total energy (Ha/eV) | $-247.21/-6726.94$     | $-247.20/-6726.66$  |                |

Fig. 1. Electronic band structure and density of states of Sr$_2$Al$_2$SiO$_7$. 

![Electronic band structure and density of states of Sr$_2$Al$_2$SiO$_7$.](image)
of the valence band. The bottom of the conduction band is located at Γ in the BZ, while the top of the valence band is at M. Therefore, Sr₂Al₂SiO₇ is calculated to be an insulator with an energy gap of about 4.07 eV, which is somewhat smaller than the experimental result (≈5.3 eV, see sections below) obtained from the diffuse reflectance spectra of undoped Sr₂Al₂SiO₇, due to the fact that the result of the GGA calculation is normally lower than the experimental band gap by about 30–50%. On the basis of the band gap data obtained from the calculation and experiment, Sr₂Al₂SiO₇ appears to be a suitable luminescence host, in which, for example, the 5d→4f transitions of Eu²⁺ can be expected to occur between the valence and conduction bands without interference from them.

3.2. Structural properties of Sr₂₋ₓEuₓAl₂₋ₓSi₁₊ₓO₇₋ₓNₓ

As discussed above, the distribution of Al/Si in Sr₂Al₂SiO₇ is partial ordering. When Si–N is introduced to partially replace Al–O, the distributions of Al/Si and O/N are also problematic issues (i.e., the ordering of Al/Si and O/N), not only for X-ray diffraction analysis but also for first-principles calculations. By X-ray powder diffraction analysis, all the possible structural models were considered in the course of the refinement, producing very

![Graphs showing the relationship between x and lattice parameters and distance (Sr, Eu)-(O, N) in Sr₁.₉₆Eu₀.₀₄Al₂₋ₓSi₁₊ₓO₇₋ₓNₓ.](image-url)
similar results. For the accurate determination of the distributions of Al/Si and N/O in Sr₂Al₂SiO₇, further study by neutron diffraction is needed. Consequently, for the Rietveld refinement, we assume that the introduced Si randomly occupies the Al (2a) and Al/Si (4e) sites, and the N atom randomly occupies the three individual O (2c, 4e and 8f) sites. In addition, Eu²⁺ is placed on the Sr site (4e).

Fig. 2 shows the relationship between the lattice parameters and the x value in Sr₂Al₂₋ₓSiₓ+₁₋ₓOₓ₋₂₋ₓNₓ₋₂₋ₓEuₓ⁺ (2 mol%). The lattice parameters a, c and the unit cell volume markedly decrease with the incorporation of Si–N into Sr₂Al₂SiO₇:Eu⁺, indicating that Al–O can be replaced by Si–N in the lattice of Sr₂Al₂SiO₇. Because the bond length of Si–N (1.74 Å) is only slightly shorter than that of Al–O (1.75 Å) [28], it was expected that the overall lattice volume would undergo no significant structural changes. However, in fact, a large shrinkage of the unit cell volume indicates that the introduced Si indeed occupies both the 2a (Al1) and 4e (Al2/Si2) sites. Since the average distances of Al1–O and Al2/Si2–O are about 1.756(4) and 1.7069(12) Å, respectively, in Sr₂Al₂SiO₇, the silicon-and-oxygen-rich (Si, Al)–(O, N) bond, which can significantly decrease the bond length, can be regarded as being closer to the Si–O bond in length (1.57–1.7 Å) [17]. Additionally, because nitrogen tends to coordinate with a high-valence cation, namely Si⁴⁺, a model in which both Si and N are randomly distributed on the Al and O sites is a reasonable assumption. The decreasing tendency of the lattice parameters stops at x = 0.6, and remains constant afterwards (see Fig. 2), indicating that the maximum solubility of Si–N is about x = 0.6. Indeed, when x > 0.6, an unknown secondary phase is observed from the X-ray diffraction patterns. In contrast to the changes in the lattice parameters with x, the average interatomic distance of (Sr, Eu)–(O, N) shows a slight increase of 0.3% caused by the presence of nitrogen in the oxygen sites. As expected, with increasing Eu concentration in Sr₂₋ₓEuₓAl₂₋ₓO₁₋ₓN₄₋ₓ O₇₋ₓNₓ, the lattice parameters do not exhibit a significant decrease because of the similar ionic sizes of Eu²⁺ (~1.25 Å, CN = 8) and Sr²⁺ (~1.26 Å, CN = 8) [29], as shown in Fig. 3. Correspondingly, the change in the average interatomic distance of EuSr–O/N is also very limited from y = 0.001 to y = 0.03 for x = 0.4.

As a typical example, the Rietveld refinement of the X-ray powder diffraction pattern for x = 0.4 and y = 0.02 is shown in Fig. 4 and the structural data are listed in Table 2. As mentioned before, the sheet structure of Sr₂Al₂SiO₇ with its low rigidity partially allows Si and N into its lattice to replace Al and O, respectively, forming layers of (Si, Al)–(O, N)₄ tetrahedra (Fig. 5). In addition, the chemical

![Figure 4](image-url)
bonding of EuSr–O/N becomes more covalent due to the presence of nitrogen, which also changes the local structure around EuSr, as shown in Fig. 5(b).

3.3. Luminescence properties of Sr$_2$–$\gamma$Eu$_\gamma$Al$_2$–$\chi$Si$_1$+$\chi$O$_{7–\chi}$N$_\chi$

3.3.1. Effect of the incorporation of Si–N

Fig. 6 shows the reflection spectra of Sr$_{1.96}$Eu$_{0.04}$Al$_2$–$\chi$Si$_{1+\chi}$O$_{7–\chi}$N$_\chi$–doped Sr$_{2}$Al$_2$SiO$_7$:Eu$^{2+}$ (2 mol%). Owing to the lack of an excitation band at about 464 nm for Sr$_2$Al$_2$SiO$_7$:Eu$^{2+}$ (2 mol%), this unusual long-wavelength excitation band is strongly related to the incorporation of Si–N, because the intensity of this excitation band can be enhanced by increasing $\chi$. Meanwhile, the position of the excitation bands cannot be changed significantly at a fixed Eu concentration. For the excitation band at 325 nm, however, a slight blue shift can be seen with increasing $\chi$, which is associated with the enlargement of the EuSr–(O, N) bonds. Sr$_{2}$Al$_2$SiO$_7$:Eu$^{2+}$ (2 mol%) gives a very broad emission band centered at about 531 nm with a highly symmetric Gaussian-type profile, while for Sr$_{1.96}$Eu$_{0.04}$Al$_2$–$\chi$Si$_{1+\chi}$O$_{7–\chi}$N$_\chi$ ($\chi$ = 0.2–0.6) there are two clear emission bands of Eu$^{2+}$ centered at about 486 and 560 nm. The integrated emission intensity does not change significantly over $\chi$ and reaches a maximum at $\chi$ = 0.4. Moreover, the position of the emission bands can be further shifted to a longer wavelength from 557 to 564 nm by increasing $\chi$ up to $\chi$ = 0.6, which closely matches the solubility limit at $\chi$ = 0.6 for Si–N. The red shift of the very broad absorption band of Eu$^{2+}$ from UV to $\sim$480 nm, with a sharp absorption edge corresponding to a body color of greenish–yellow. Clearly, the absorption intensity slightly increases and the onset of the absorption band shifts to a longer wavelength from 478 to 485 nm with increasing amount of Si–N (i.e., $\chi$).

Table 2

Crystal data for Sr$_{2–\gamma}$Eu$_\gamma$Al$_2$–$\chi$Si$_{1+\chi}$O$_{7–\chi}$N$_\chi$ ($\chi$ = 0.4, $\gamma$ = 0.02)

| Atom | Wyck. | x/a | y/b | z/c | U$_i$/U$_c$ (100 Å$^2$) | SOF |
|------|-------|-----|-----|-----|------------------------|-----|
| Sr1 | 4e    | 0.3393(1) | 0.1670(1) | 0.5112(2) | 0.73 | 0.99 |
| Eu1 | 4e    | 0.3393(1) | 0.1670(1) | 0.5112(2) | 0.73 | 0.01 |
| Al1 | 2a    | 0.0000 | 0.0000 | 0.0000 | 0.44 | 0.80 |
| Si1 | 2a    | 0.0000 | 0.0000 | 0.0000 | 0.44 | 0.20 |
| Al2 | 4e    | 0.1417(1) | 0.3583(2) | 0.9629(5) | 0.38 | 0.40 |
| Si2 | 4e    | 0.1417(1) | 0.3583(2) | 0.9629(5) | 0.38 | 0.60 |
| O1 | 2c    | 0.5000 | 0.0000 | 0.1567(15) | 1.22 | 0.94 |
| N1 | 2c    | 0.5000 | 0.0000 | 0.1567(15) | 1.22 | 0.06 |
| O2 | 4e    | 0.1477(5) | 0.3523(5) | 0.2679(9) | 0.50 | 0.94 |
| N2 | 4e    | 0.1477(5) | 0.3523(5) | 0.2679(9) | 0.50 | 0.06 |
| O3 | 8f    | 0.0858(5) | 0.1688(5) | 0.8213(6) | 0.06 | 0.94 |
| N3 | 8f    | 0.0858(5) | 0.1688(5) | 0.8213(6) | 0.06 | 0.06 |

Fig. 5. Projection of the crystal structure of Sr$_{1.96}$Eu$_{0.04}$Al$_2$–$\chi$Si$_{1+\chi}$O$_{7–\chi}$N$_\chi$ ($\chi$ = 0.4) viewed along (001) direction (a) and the local coordination around the Sr/Eu atom (b). Black spheres represent the O/N atoms and the data show the bond lengths of Sr/Eu–O/N (in Å).
emission band of Eu$^{2+}$ can be explained well by the increase in crystal-field splitting ($\Delta_{C24}^{16}$ and 17.2k cm$^{-1}$ for $x = 0$ and 0.6, respectively, estimated from the excitation bands of Eu$_2^+$) and the increase in covalency due to the introduction of nitrogen. Variation of the emission bands yields similar excitation spectral profiles with different intensities at 325 and 460 nm. In Sr$_2$Al$_2$SiO$_7$, only one crystallographic site is available for Sr, which has already been confirmed by the presence of a single emission band of Sr$_2$Al$_2$SiO$_7$:Eu$^{2+}$ (2 mol%). Furthermore, no second phase can be observed in Sr$_{1.96}$Eu$_0.04$Al$_2$Si$_1$N$_x$ ($x = 0.2–0.6$). Therefore, the long-wavelength emission band may be related to energy transfer between the Eu ions and/or reabsorption of Eu, i.e., a transition between the crystal-field components of the 5d state in a single Eu$^{2+}$ ion.

3.3.2. Effect of Eu concentration

The reflection spectra of Sr$_{y}$Eu$_{y}$Al$_2$Si$_1$O$_7$ vary with $x$ ($\lambda_{ex} = 325$ nm, and $\lambda_{em} = 530$ and 560 nm for $x = 0$ and $x = 0.2–0.6$, respectively).

The absorption edge of undoped Sr$_2$Al$_2$SiO$_7$ is estimated to be at 226 nm (optical band gap $\sim 5.3$ eV). Similar to the case of Sr$_{1.96}$Eu$_0.04$Al$_2$Si$_1$N$_x$, with an increase in Eu concentration (i.e., $y = 0.001–0.03$), the absorption intensity of Eu$^{2+}$ markedly increases over the range of 200–500 nm and the onset of the absorption band shifts from 465 to 488 nm for Sr$_2$Eu$_{y}$Al$_1$Si$_1$O$_{6.6}$N$_{0.4}$. Fig. 9 shows the effect of Eu concentration on the PL luminescence of Sr$_{1+y}$Eu$_y$Al$_{1.6}$Si$_{1.4}$O$_{6.6}$N$_{0.4}$. At low Eu concentrations ($y \leq 0.005$), the strongest excitation band is at about 317 nm, with two weak subbands at about 273 and 405 nm. The dominant emission band of Eu$^{2+}$ is located at about 486 nm (namely, the intrinsic emission band from the 5d$^{-4}$f transition), with a shoulder at about 560 nm (Fig. 9), while, for $y > 0.005$, the profile of the excitation spectra changes as the Eu concentration increases. In agreement with the reflection spectra, the dominant excitation band shows a slight red shift from 317 to 325 nm. Moreover, the first excitation band ($\sim 273$ nm) shifts to a higher energy ($\sim 258$ nm); in contrast, the tail of the excitation spectra extends to a longer wavelength, giving an additional excitation band at around 460 nm. As a consequence, the emission shoulder at around 560 nm surpasses the intrinsic emission at 460 nm to become the dominant emission, which also shows a red shift with an increase in Eu content (Fig. 9). From the results shown in Figs. 7 and 9, we might conclude that, besides the effect of the introduction of Si–N due to an increase in the crystal-field strength and the covalency around Eu$^{2+}$, the long-wavelength excitation band at around 460 nm together with the emission band at about 560 nm are also related to Eu concentration due to
energy transfer and/or the transitions between the different energy levels of the 5d crystal-field components of Eu$^{2+}$. At high Eu concentrations, the local structure of EuSr–(O, N)$_8$ (see Fig. 5(b)) is modified by incorporating N into O, which results in greater crystal-field splitting of the 5d state of Eu$^{2+}$, creating more opportunities for a transition from high to low crystal-field components of Eu$^{2+}$. This can be better understood from Fig. 9(a), where large overlap between the excitation band at 460 nm and the intrinsic emission band at 486 nm is observed, particularly for Sr$_2$Eu$_{y}$Al$_{1.6}$Si$_{1.4}$O$_{6.6}$N$_{0.4}$ ($y = 0.02$). Although a higher Eu concentration can increase absorption and provide more possibilities for the energy transfer between different Eu$^{2+}$ ions, which is particularly favorable for the improvement of the excitation intensity at a lower energy (e.g., in the blue-light range), a large amount of Eu$^{2+}$ could also easily result in concentration quenching. The integrated emission intensity against the Eu$^{2+}$ concentration is plotted in Fig. 9(b). It is found that the emission intensity of Eu$^{2+}$ reaches a maximum at $y = 0.01$ (i.e., Eu$^{2+}$/Sr$_{100}$O$_{8}$:Eu$^{2+}$). When $y > 0.01$, the intensity shows an almost linear decrease with increasing Eu concentration. Clearly, the luminescence is very sensitive to Eu concentration and is rapidly quenched above $y = 0.01$.

3.3.3. Effect of the temperature

Despite the fact that Sr$_2$Al$_{2-x}$Si$_{1+x}$O$_7$N$_x$:Eu$^{2+}$ emits blue–green to greenish–yellow light with an excitation band at 460 nm, which is attractive for LED applications, the luminescence intensity of Eu$^{2+}$ is relatively low at room...
temperature. Because the optical band gap ($\sim 5.3$ eV) is sufficiently wide to accommodate the wanted $5d \rightarrow 4f$ transition of $\text{Eu}^{2+}$ between the conduction and valence bands of $\text{Sr}_2\text{Al}_2\text{Si}_{1+y}\text{O}_{7-x}\text{N}_x$, two possible reasons could account for the low efficiency. First, the highest $5d$ level of $\text{Eu}^{2+}$ could partially overlap with the bottom of the conduction band of the host lattice, resulting in autoionization and leading to lower quantum efficiency. In general, the band gap might decrease with the addition of Si–N into the oxide compounds [30,31], i.e., $\text{Sr}_2\text{Al}_2\text{SiO}_7$. As a result, the efficiency of $\text{Sr}_2\text{Al}_2\text{Si}_{1+y}\text{O}_{7-x}\text{N}_x;\text{Eu}^{2+}$ should also show a decrease with increasing $x$ due to a higher probability of autoionization. However, this is not the case for the present study because the emission intensity does not significantly change with $x$ ($x = 0.2–0.6$). Therefore, the occurrence of autoionization can be excluded. Thus, the main reason for the low efficiency is the thermal relaxation in the luminescent center of $\text{Eu}^{2+}$. The temperature dependence of the luminescence intensity with varying $x$ and $y$ is shown in Fig. 10. The relative emission intensity of $\text{Sr}_{1.96}\text{Eu}_{0.04}\text{Al}_2\text{Si}_{1+y}\text{O}_{7-x}\text{N}_x$ decreases rapidly and linearly with increasing temperature from room temperature to 250 $^\circ$C for $x = 0–0.6$ (Fig. 10(a)). It appears that the thermal stability of $\text{Eu}^{2+}$ slightly improves below 125 $^\circ$C for high $x$ values. With respect to the effect of Eu concentration on the thermal $\text{Eu}^{2+}$ luminescence, two markedly different behaviors can be seen in Fig. 10(b). In the low-temperature region (room temperature—75 $^\circ$C), the relative emission intensity is comparable for different Eu concentrations, and slightly higher for $y = 0.02$. At high temperatures ($>75$ $^\circ$C), a high Eu concentration results in strong thermal quenching, leading to a rapid reduction in the emission intensity. It is clear seen from Fig. 11 that, at low Eu concentrations, the emission of $\text{Eu}^{2+}$ is dominated by the intrinsic emission at 468 nm (namely, $5d \rightarrow 4f$), which is relatively stable against temperature. In addition, the position of the emission band shifts due to the expansion of the lattice at high temperatures, resulting in the decreasing covalence of $\text{Eu}_{\text{Sr}}$(O, N) and increasing the Stokes shift. At lower Eu concentrations, the Stokes shift may be a dominant factor because the change in the covalency of $\text{Eu}_{\text{Sr}}$(O, N) can be neglected. Therefore, the emission band shows a red shift with increasing temperature, as shown in Fig. 11. At high Eu concentrations, the emission of $\text{Eu}^{2+}$ is mainly due to the energy transfer of $\text{Eu}^{2+}$. However, at high temperatures, the probability of the energy transfer is decreased by the increased Eu–Eu distance. Accordingly, the emission originating from the energy transfer of $\text{Eu}^{2+}$ shows a more rapid decrease than the intrinsic emission. The low luminescence efficiency at room temperature indicates that the nonradiative process is stronger than the radiative process and dominates the luminescence properties of $\text{Sr}_{2-\gamma}\text{Eu}_\gamma\text{Al}_2\text{Si}_{1+y}\text{O}_{7-x}\text{N}_x$ due to the nonradiative recombination centers.

4. Conclusions

The partial ordering of Al and Si in $\text{Sr}_2\text{Al}_2\text{SiO}_7$ has been confirmed by first-principles calculations based on density functional theory. The electronic structure shows that $\text{Sr}_2\text{Al}_2\text{SiO}_7$ has an indirect band gap of about 4.07 eV, in good agreement with the optical band gap ($\sim 5.3$ eV)
determined by the diffuse reflection spectrum. Si–N can be introduced into Sr$_2$Al$_2$SiO$_7$ to replace Al–O with a solubility limit of about $x = 0.6$. Because of the presence of nitrogen, the shrunk lattice becomes more rigid and the covalency of the EuSr–(O, N) bond is increased. Sr$_2$Al$_{2-x}$Si$_{1+x}$O$_7$N$_x$:Eu$^{2+}$ shows a broadband emission band from 480 to 565 nm depending on both Eu concentration and $x$. With increasing $x$, the emission band of Eu$^{2+}$ shows a significant red shift. For high Eu concentrations ($x > 0.01$), a new excitation band appears at around 460 nm. The dominant emission band alternatively changes from an intrinsic emission band (~486 nm) associated with the 5d$\rightarrow$4f transition of Eu$^{2+}$ to another emission band (~560 nm) originating from energy transfer of the Eu ions and/or an electron transition at different crystal-field components of the 5d state within a single Eu$^{2+}$ ion. The emission intensity shows a significant linear decrease with increasing temperature (25–250 $^\circ$C), particularly for the emission band at around 560 nm. In addition, a high Eu concentration reduces the thermal stability of Sr$_2$Al$_{2-x}$Si$_{1+x}$O$_7$N$_x$:Eu$^{2+}$.

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