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Photoluminescence Properties of Red-Emitting Mn$^{2+}$-Activated CaAlSiN$_3$ Phosphor for White-LEDs

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Abstract

Mn$^{2+}$-doped CaAlSiN$_3$ phosphors have been prepared by a solid-state reaction method at high temperature and the solubility of Mn$^{2+}$ in the host lattice as well as their photoluminescence properties were investigated. In CaAlSiN$_3$, not only Ca$^{2+}$ sites, but also Al$^{3+}$ sites can be substituted by Mn$^{2+}$ ions. CaAlSiN$_3$: Mn$^{2+}$ absorbs blue light in the spectral range of 440–460 nm, and exhibits a broad band emission in the wavelength range of 475–750 nm, which can be ascribed to the $T_1 (^4G) \rightarrow {}^4A_1 ({}^5S)$ transition of Mn$^{2+}$ located at two different sites in CaAlSiN$_3$. The emission bands at lower energy (15,950 cm$^{-1}$ or 627 nm) and higher energy (18,250 cm$^{-1}$ or 548 nm) are assigned to the Mn$^{2+}$ locating at the Al site (Mn$\text{Al}$) and Ca site (Mn$\text{Ca}$), respectively with energy transfer from Mn$\text{Ca}$ to Mn$\text{Al}$. In addition, the integral luminescence intensity only decreases to about 94% at 150°C of the value at 50°C, which is of great interest for the applications of white-LEDs.

Introduction

Recently, a new quaternary nitride system, CaAlSiN$_3$ has drawn much attention for its applications in the white-LEDs when doped with Eu$^{3+}$ or Ce$^{3+}$. CaAlSiN$_3$ is isostructural with ASi$_2$N$_3$ (A = Li, Na) and crystallizes in Crn$_2$ space group. The Ca atom is located at the channels built up by the six-membered rings of (Al/Si)N$_4$ tetrahedra and directly coordinated with five nitrogen atoms cross over the unit cell (Figure 1). The Al and Si atoms are randomly distributed on the same tetrahedral sites and connected with nitrogen atoms to form the vertex-linked MV$^6$N$_{18}$ (MV = Ca, Sr, Ba) rings. CaAlSiN$_3$: Eu$^{3+}$ and CaAlSiN$_3$: Ce$^{3+}$ exhibit efficient red and yellow-orange emission respectively under blue irradiation. In the present work, we focus on investigating the luminescence properties of Mn$^{2+}$ in CaAlSiN$_3$ and explore its potential possibilities to be used as a new kind of LED conversion phosphor, which is up to now only claimed but not proofed.

Experimental

Starting Materials.—Ca$_3$N$_2$ (Alfa, 98%, powder), AlN (Tokuyama Chemical Co., Ltd., F-grade), α-Si$_3$N$_4$ (Permacand, P95H, α-content, 93.2%, oxygen content: ~1.5%) and Mn powder (Alfa, > 99%) are used as the as-received raw materials.

Syntheses of Mn$^{2+}$-doped CaAlSiN$_3$.—CaAlSiN$_3$: Mn$^{2+}$ powder was prepared by a solid-state reaction method at high temperature. Appropriate amounts of starting materials were firstly weighed out, thoroughly mixed and ground in an agate mortar. The powder mixtures were fired in molybdenum crucibles at 1600°C for 2 h in a horizontal tube furnace under N$_2$–H$_2$ (10%) atmosphere. After firing, the samples were gradually cooled down in the furnace. Subsequently, the resulting powder was reground and pressed into pellets after sintering, these samples were gradually cooled down in room temperature in the furnace. There was no apparent reaction of the prepared samples with the Mo crucibles. All processes were handled in a dry glove box flushed with dry nitrogen because of air and water sensitivity of some starting materials.

X-ray diffraction data collection and analysis.—All measurements were performed on finely ground samples, which were analyzed by X-ray powder diffraction (XRD) using Cu K$_\alpha$ radiation at 40 kV and 40 mA with a graphite monochromator. The 2θ ranges of all the data sets are from 10 to 80° using step scan with a step size of 0.02° in 2θ

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Figure 1. Crystal structure of CaAlSiN$_3$, and the coordination environment of Ca, Al/Si atoms, as well as Ca-N, Al/Si-N distances (Å) in CaAlSiN$_3$.

and a count time of 1 s. The XRD measurements were performed at room temperature in air. The cell parameters of CaAlSiN$_3$:Mn$^{2+}$ were determined from the X-ray powder diffraction patterns using the indexing program Fullprof.$^{42}$

X-ray absorption near-edge structure (XANES).—Mn K-edge of X-ray absorption near-edge structure (XANES) spectra at about 6540 eV were recorded at room temperature at Shanghai Synchrotron Radiation Facility (SSRF, China) in transmission modes. The X-ray light source was from the BL14W1 beam line at the SSRF. The electron energy in the storage ring was 3.5 GeV, with a current of 200 mA and the emission angle of the light was 1.5 × 0.1 mrad$^{2}$. The beam size can be focused to 0.3 mm × 0.3 mm. The scanning range was from 6500 to 6650 eV. The energy steps were 0.2 eV (from 6500 to 6650 eV), which was appropriate for obtaining a clear Mn K-edge XANES spectrum. The information on the valence state and local structure of the element of interest can be obtained from the XANES spectra based on the energy, shape and fine structure of the edges.

Optical measurements.—The diffuse reflectance, emission and excitation spectra of the samples were measured at room temperature by a Perkin Elmer LS 50B spectrophotometer equipped with a Xe flash lamp. The reflection spectra were calibrated with the reflection of black felt (reflection 3%) and white barium sulfate (BaSO$_4$, reflection ~ 100%) in the wavelength region of 230–700 nm. The excitation and emission slits were set at 15 nm. The emission spectra were corrected by dividing the measured emission intensity by the ratio of the observed spectrum of a calibrated W-lamp and its known spectrum from 300 to 900 nm. Excitation spectra were automatically corrected for the variation in the lamp intensity (and thus for the spectral dependence of the excitation energy) by a second photomultiplier and a beam-splitter. All luminescence spectra were measured with a scan speed of 400 nm/min at room temperature in air. The temperature dependent emission measurement was carried out by the special equipment made by University of Jena under excitation with 450 nm from room temperature to 200°C with a heating rate of 8°C/min, and the temperature was hold for 5 min before starting the measurement.

Results and Discussion

Valency State of Mn in CaAlSiN$_3$.—It can be observed from Figure 2 that the position of the K-edge of Mn in CaAlSiN$_3$ is similar to that of MnO (6540.6 eV), locating at lower energy than that of MnO$_2$ (6541.6 eV), which means that Mn in CaAlSiN$_3$ is found in the divalent state. However, the signal of the extended X-ray absorption fine structural (EXAFS) data is too weak to get information about the number of Mn$^{2+}$ sites and about the local structure of Mn$^{2+}$ in CaAlSiN$_3$.

Phase formation and the solubility of Mn$^{2+}$ in CaAlSiN$_3$.—According to the powder XRD patterns (Figure 3), the Mn-doped CaAlSiN$_3$ samples were obtained as nearly single phase material with CaAlSiN$_3$ structure (ICSD no: 161796). Like in the case of CaAlSiN$_3$ :
It is difficult to obtain undoped and Mn-doped CaAlSiN\textsubscript{3} samples as a single phase material according to the stoichiometric composition. It was found that Al/Si disorderly occupies the 8\textit{b} site in the space group of \textit{Cmc}\textsubscript{2}1 with a ratio of about 1/2 with a more appropriate formula Ca\textsubscript{Al}\textsubscript{1-x}Si\textsubscript{x}N\textsubscript{3} (\(\delta = 0.3\) - 0.4) instead of 1/1 proposed for an ideal CaAlSiN\textsubscript{3}. This is probably due to the incomplete reaction resulting in a significantly lower Al solubility in CaAlSiN\textsubscript{3}. Thus, a small amount of AlN can be detected for undoped and Mn-doped CaAlSiN\textsubscript{3} samples.

The unit cell volume of Ca\textsubscript{1-x}Mn\textsubscript{x}AlSiN\textsubscript{3} decreases with increasing Mn\textsuperscript{2+} concentration (Figure 4), as expected for Mn\textsuperscript{2+} (\(r = 0.75\) Å, CN = 5, \(r = 0.83\) Å, CN = 6) being smaller than Ca\textsuperscript{2+} (\(r = 1.00\) Å, CN = 6). In agreement with Al\textsuperscript{3+} by Mn\textsuperscript{2+} replacement, the unit cell volume of Ca\textsubscript{1-x}Mn\textsubscript{x}AlSiN\textsubscript{3} extrapolated for high Mn\textsuperscript{2+} to \(x = 1\) concentration agrees with that of MnAlSiN\textsubscript{3} (JCPDS : 50-0749), the cell volume of MnAlSiN\textsubscript{3}, i.e. \(x = 1.0\), was calculated from D. P. Thompson\textsuperscript{19}). However, as a function of the Mn\textsuperscript{3+} concentration, two linear regimes can be discriminated: for high Mn\textsuperscript{2+} concentrations (\(x > 0.15\)) the dependence is stronger than for low Mn\textsuperscript{2+} concentrations (\(x < 0.15\)), with a bending point at about 15 at\% Mn\textsuperscript{2+} (\(x = 0.15\)). The weaker dependence can be explained by assuming that at low Mn concentrations, Mn\textsuperscript{2+} not only occupies the Ca\textsuperscript{2+} position, but in addition also partly occupies the Al\textsuperscript{3+} site with Mn\textsuperscript{2+} (\(r = 0.66\) Å, CN = 4) larger than Al\textsuperscript{3+} (\(r = 0.39\) Å, CN = 4). The Al\textsuperscript{3+} by Mn\textsuperscript{2+} replacement can be charge compensated by Al\textsuperscript{3+}/Si\textsuperscript{4+} replacement or N\textsuperscript{3+}/O\textsuperscript{2-} replacement. Unfortunately, a Rietveld refinement of the XRD patterns with Mn\textsuperscript{2+} substituted on both the Ca\textsuperscript{2+} as well as Al\textsuperscript{3+} sites or XANES/EXAFS measurements did not allow us to confirm this interpretation, which however is fully supported by luminescence measurements, as discussed in the next section.

**Diffuse reflection spectra.**—Figure 5 shows the diffuse reflection spectra of undoped and Mn\textsuperscript{2+}-doped CaAlSiN\textsubscript{3} samples. For undoped CaAlSiN\textsubscript{3} show a drastic drop in reflection in the ultraviolet (UV) range around 300 nm with an estimated bandgap at about 240 nm (5.2 eV), essentially corresponding to the valence-to-conduction band transitions of CaAlSiN\textsubscript{3} host lattice. The value of the bandgap is close to the results published.\textsuperscript{10,30} The intense reflection in the visible spectral range is in agreement with the observed gray-white daylight color of undoped CaAlSiN\textsubscript{3}. For Mn\textsuperscript{2+}-doped CaAlSiN\textsubscript{3}, there are several weak absorption bands can be observed in the wavelength range of 350–600 nm, which can be attributed to the transitions from the \(4\text{A}_{1} (\text{e}^{S})\) ground state of Mn\textsuperscript{3+} to its excited states. In contrast to the undoped sample, the daylight color of Mn\textsuperscript{2+}-doped CaAlSiN\textsubscript{3} shows gray-white to light red color, varying with Mn\textsuperscript{2+} concentration as a result of the absorption by Mn\textsuperscript{2+} ion the visible range of 350–600 nm.
in the CaAlSiN$_3$ host lattice. $^6$A$_1$ ($^5$S) is the ground level, and $^4$T$_1$ ($^4$G) is the lowest excitation level the energy of which decreases with the increase of the crystal field. Moreover, two obvious overlapping emission sub-bands in the wavelength range of 450–800 nm could be distinguished in the emission spectra of Ca$_{1-x}$Mn$_x$AlSiN$_3$ ($x = 0.05$) under 334, 381 and 451 nm excitation (Figure 7). In the crystal structure of CaAlSiN$_3$, there is only one crystallographic site for the Ca atom, which is coordinated with five N atoms (Figure 1). For Eu$^{3+}$ and Ce$^{3+}$-doped CaAlSiN$_3$, only the Ca sites with strong crystal field strength are substituted by Eu$^{3+}$ and Ce$^{3+}$ ions. As a consequence, a red emission band from Eu$^{3+}$ and yellow-orange emission band from Ce$^{3+}$ are observed in CaAlSiN$_3$. Thus, if only the Ca$^{2+}$ sites are substituted by Mn$^{2+}$ ions, it is expected that there will be only a single narrow symmetrical emission band in the luminescence spectra of Mn$^{2+}$-doped CaAlSiN$_3$. As already mentioned above, however, the emission band is nonsymmetrical, and can be further deconvoluted into two Gaussian subbands with peaks at about 548 nm (18,250 cm$^{-1}$, green emission) and about 627 nm (15,950 cm$^{-1}$, red emission), respectively (Figure 7). This indicates that there are two different Mn$^{2+}$ sites in CaAlSiN$_3$ which are ascribed to Mn$_{Ca}$ and Mn$_{Al}$, not only the Ca$^{2+}$ sites (Mn$_{Ca}$), but also Al$^{3+}$ sites (Mn$_{Al}$) can be substituted by Mn$^{2+}$, which occurs in some other cases. Thus, Mn$^{2+}$ ions will be located in a tetrahedrally and pentahedrally nitrogen coordinated site. According to the crystal structure of CaAlSiN$_3$, Al$^{3+}$ site is coordinated with four N atoms with the average Al - N distance 1.8050 Å, which is much smaller than that of Ca$^{2+}$, coordinated with five N atoms with the average Ca-N distance 2.4934 Å. As a consequence, the crystal field strength is larger for Mn$^{2+}$ at the Al$^{3+}$ site than at the Ca$^{2+}$ site. Considering the Tanabe-Sugano diagram, the emission band at lower energy (15,950 cm$^{-1}$ or 627 nm) is assigned to the Mn$^{2+}$ locating at the Al site (Mn$_{Al}$), and the other emission band at higher energy (18,250 cm$^{-1}$ or 548 nm) originates from the Mn$^{2+}$ locating at the Ca site (Mn$_{Ca}$).

There are four principle excitation bands extending over a broad range of wavelengths by monitoring the emission wavelengths of 548 and 627 nm, as shown in Figure 6, which is consistent with the diffuse reflectance spectra. Definitely, the weak excitation band below 275 nm originates from host lattice excitation, which is in agreement with the results published. However, it rules out the possibility that there exists efficient energy transfer from CaAlSiN$_3$, host lattice to Mn$^{2+}$ ions due to the weak excitation band from host lattice. There is big difference in the excitation spectra by monitoring the different emission wavelengths: two excitation maxima at 334/451 nm (in the wavelength range of 275–600 nm) and 334/381 nm (in the wavelength range of 275–500 nm) can be observed by monitoring the peak wavelength at 627 and 548 nm, related to Mn$^{2+}$ incorporated on the Al$^{3+}$ and Ca$^{2+}$ site, respectively. The excitation band of Mn$^{2+}$ consists of several overlapping transitions due to the disordered AlSi occupation of the same crystallographic position in the CaAlSiN$_3$ lattice. These excitation subbands can be assigned to the transitions of Mn$^{2+}$ at different sites (Mn$_{Ca}$, Mn$_{Al}$) from ground state $^5$D$_{0}$ ($^5$S) to $^7$T$_{1}$ ($^4$G), $^7$T$_{2}$ ($^4$G), $^7$A$_1$ ($^4$G), $^7$E ($^4$G), $^7$F$_{2}$ ($^4$D) and $^7$E ($^4$D) excited states, respectively. Table 1 summarizes the characteristics of CaAlSiN$_3$ : Mn$^{2+}$ (5%) phosphor and compares them with other typical Mn$^{2+}$-doped nitride based phosphors.

Figure 8 shows excitation spectra of CaAlSiN$_3$: Mn$^{2+}$ with different Mn$^{2+}$ doping concentrations. The position of the overall excitation bands in the spectra is nearly independent of the Mn$^{2+}$ concentration, which is similar to that of Eu$^{3+}$ and Ce$^{3+}$ in CaAlSiN$_3$. However, the Mn$^{2+}$ concentration exhibits a great effect on the luminescence intensities, as well as the profiles of the emission bands. With increasing Mn$^{2+}$ concentration, the peak positions of the emission bands for

![Figure 6](image-url)

**Figure 6.** Excitation and emission spectra of Ca$_{1-x}$Mn$_x$AlSiN$_3$ ($x = 0.05$).

![Figure 7](image-url)

**Figure 7.** Luminescence spectra of Ca$_{1-x}$Mn$_x$AlSiN$_3$ ($x = 0.05$) with deconvoluted Gaussian subbands for emission spectra.

### Table 1. Characteristics of Mn$^{2+}$-doped CaAlSiN$_3$ phosphor as compared to typical Mn$^{2+}$-doped nitride based phosphors at room temperature.

<table>
<thead>
<tr>
<th>Phosphors</th>
<th>CaAlSiN$_3$:Mn$^{2+}$</th>
<th>ZnSiN$_2$:Mn$^{2+}$</th>
<th>ZrGeN$_2$:Mn$^{2+}$</th>
<th>MgSiN$_2$:Mn$^{2+}$</th>
<th>Ca$_2$Si$_3$N$_8$:Mn$^{2+}$</th>
<th>Sr$_2$Si$_3$N$_8$:Mn$^{2+}$</th>
<th>Ba$_2$Si$_3$N$_8$:Mn$^{2+}$</th>
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</thead>
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<tr>
<td>Crystal system</td>
<td>Cmc$_2$</td>
<td>Pna$_2$</td>
<td>Pna$_2$</td>
<td>Pna$_2$</td>
<td>Pna$_2$</td>
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<tr>
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<td>Gray-white</td>
<td>Gray-white</td>
<td>Gray-white</td>
<td>Gray-white</td>
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<tr>
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<td>376</td>
<td>287</td>
<td>250</td>
<td>265</td>
<td>270</td>
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<td>edge (nm)</td>
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<tr>
<td>Emission bands</td>
<td>548, 627</td>
<td>620</td>
<td>610</td>
<td>625, 692</td>
<td>599</td>
<td>606</td>
<td>567</td>
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<td>(nm)</td>
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<td>FWHM (nm)</td>
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<td>–</td>
<td>130</td>
<td>70</td>
<td>70</td>
<td>60</td>
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</table>
Mn$_{Ca}^{2+}$ and Mn$_{Al}^{2+}$ sites show a redshift according to the results of fitting the overall emission bands. The redshift of the emission bands of the individual Mn$^{2+}$ centers (Mn$_{Ca}$, Mn$_{Al}$) is ascribed to the shrinkage of the host lattice with increasing Mn$^{2+}$ concentration resulting in a larger crystal field strength, and consequently a lower emission energy according to the Tanabe-Sugano diagram. The position of the overall emission band shows a slight redshift (less than 7 nm) under 451 nm excitation. However, a redshift of the overall emission bands under 331/383 nm is observed at low Mn$^{2+}$ concentration ($x < 0.05$), then the overall emission bands exhibit a blueshift with increasing Mn$^{2+}$ concentration ($x > 0.05$). The combination of the redshift of the individual Mn$^{2+}$ centers (Mn$_{Ca}$, Mn$_{Al}$) discussed before with the energy transfer from high-energy Mn$_{Ca}^{2+}$ to low-energy Mn$_{Al}^{2+}$ is anticipated to eventually results in the redshift of the overall emission band. The observed blueshift of the overall emission band cannot be explained with the above mentioned effects and therefore is attributed to preferential site occupation of the Ca$^{2+}$ sites with Mn$^{2+}$ for higher Mn-concentrations ($x > 0.05$), resulting in a higher intensity of the high energy Mn$^{2+}$ emission center. Figure 9 shows the overall emission intensity of CaAlSiN$_3$ : Mn$^{2+}$ as a function of Mn$^{2+}$ concentration under the excitation wavelength of 451 nm and 332 nm. The maximum emission intensity is observed for 5 at% Mn$^{2+}$ doped CaAlSiN$_3$. The overall emission intensity declines gradually as the concentration of Mn$^{2+}$ exceeds 5 at% due to concentration quenching, which is mainly caused by the non-radiative energy transfer among Mn$^{2+}$ ions, which usually occurs as a result of exchange interaction or a multipole - multipole interaction.

The change of the ratio between the emission intensity of the luminescence from Mn$_{Ca}^{2+}$ (lower energy, 15,950 cm$^{-1}$ or 627 nm) and Mn$_{Al}^{2+}$ (higher energy, 18,250 cm$^{-1}$ or 548 nm) is shown in the inset of Figure 9. When Mn$^{2+}$ ions were incorporated into CaAlSiN$_3$, at low concentration ($0 < x < 0.05$), not only the Ca$^{2+}$ site, but also the Al$^{3+}$ site can be substituted by Mn$^{2+}$. As a consequence, emission at lower energy from Mn$_{Al}^{2+}$, as well as emission at higher energy from Mn$_{Ca}^{2+}$ can be observed, besides, there exists energy transfer from Mn$_{Ca}^{2+}$ to Mn$_{Al}^{2+}$ according to the excitation spectra. Thus, the ratio between the emission intensity of Mn$_{Al}^{2+}$ and Mn$_{Ca}^{2+}$ increases from 0.5 at% Mn$^{2+}$ to 5 at% Mn$^{2+}$. As the concentration of Mn$^{2+}$ exceeds 5 at% till 15 at%, the ratio declines intensively due to the related concentration quenching of Mn$_{Al}^{2+}$, then it increases slightly with concentration of Mn$^{2+}$ increasing from 15 at% to 30 at%, which can be ascribed to the related concentration quenching of Mn$_{Ca}^{2+}$ and less concentration quenching for Mn$_{Al}^{2+}$ because most of Mn$^{2+}$ ions will substitute Ca$^{2+}$ ions instead of Al$^{3+}$ at high Mn$^{2+}$ concentration (>15 at%). This is in good agreement with a linear decrease of the unit cell volume with varying Mn$^{2+}$ content (>15 at%).

Figure 10 shows the relative emission intensity of CaAlSiN$_3$ : Mn$^{2+}$ (5 at%) as a function of sample temperature, using commercial YAG : Ce$^{3+}$ phosphor as a standard for comparison. The quenching temperature $T_q$ (the temperature at which the relative emission intensity is observed for 5 at% Mn$^{2+}$ doped CaAlSiN$_3$). The inset shows the relative emission intensity of CaAlSiN$_3$ : Mn$^{2+}$ (5 at%) compared to the commercial red-emitting phosphor CaAlSiN$_3$ : Eu$^{3+}$ (LP-N640) under the same conditions.
intensity is half the initial intensity at room temperature) for CaAlSiN₃: Mn²⁺ (5 at%) is above 200 °C, which is much better than that of commercial YAG: Ce³⁺ phosphor. In addition, the emission intensity of CaAlSiN₃: Mn²⁺ (5 at%) can reach up to about 30% to that of the commercial red-emitting phosphor CaAlSiN₃: Eu²⁺-(LP-N640) for excitation with blue light (450 nm) at room temperature, as shown in the inset of Figure 10.

Conclusions

Mn²⁺-activated CaAlSiN₃ phosphors have been prepared by a solid-state reaction successfully and the solubility of Mn²⁺ in host lattice as well as their photoluminescence properties were investigated. CaAlSiN₃ : Mn²⁺ exhibits a broad band emission in the wavelength range of 475–750 nm. There are two obvious overlapping Mn²⁺ emission bands with peak centers at 548 and 627 nm, which are attributed to the Mn²⁺ locating at the Ca site (MnCa) and Al site (MnAl), respectively. The effect of the Mn³⁺ concentration in CaAlSiN₃ on the luminescence properties was investigated and explained on the basis of the presence of the two Mn²⁺ sites, combined with preferential site occupation and energy transfer depending on the Mn³⁺ concentration. CaAlSiN₃ : Mn³⁺ materials are attractive LED phosphors due to the absorption in the blue range of the spectrum (440–460 nm), efficient luminescence with emission bands in the red part of the spectrum (590–670 nm) and a high thermal quenching temperature in air.

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References