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

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Recent research is focused on investigating the luminescence properties of Mn$^{2+}$ in CaAlSiN$_3$ and exploring its potential possibilities to be used as a new kind of LED conversion phosphor, which is up to now only claimed but not proved. 41

Experimental

Starting Materials.—Ca$_2$N$_2$ (Alfa, 98%, powder), AlN (Tokuyama Chemical Co., Ltd., F-grade), $\alpha$-Si$_3$N$_4$ (Permacast, 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 of 1 cm in diameter under 170 MPa, then fired at 1750 °C for 2 h in a molybdenum crucible under flowing N$_2$-H$_2$ (10%) atmosphere. After sintering, these samples were gradually cooled down to 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) (Bruker, D8 Endeavor X-ray Diffractometer) 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.
Figure 1. Crystal structure of CaAlSiN₃, and the coordination environment of Ca, Al/Si atoms, as well as Ca-N, Al/Si-N distances (Å) in CaAlSiN₃.

and a count time of 1 s. The XRD measurements were performed at room temperature in air. The cell parameters of CaAlSiN₃ : Mn²⁺ 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 mrad². 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 (BaSO₄, reflection ~ 100%) in the wavelength region of 230–700 nm. The reflection 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 CaAlSiN₃.—It can be observed from Figure 2 that the position of the K-edge of Mn in CaAlSiN₃ is similar to that of MnO (6540.6 eV), locating at lower energy than that of MnO₂ (6541.6 eV), which means that Mn in CaAlSiN₃ 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 Mn²⁺ sites and about the local structure of Mn²⁺ in CaAlSiN₃.

Phase formation and the solubility of Mn²⁺ in CaAlSiN₃.—According to the powder XRD patterns (Figure 3), the Mn-doped CaAlSiN₃ samples were obtained as nearly single phase material with CaAlSiN₃ structure (ICSD no: 161796). Like in the case of CaAlSiN₃ : Mn(OH)₂

Figure 2. The X-ray absorption near-edge structure (XANES) spectra of Mn²⁺ in CaAlSiN₃, and the standard samples MnO and MnO₂.

Figure 3. Powder X-ray diffraction patterns of Mn-doped CaAlSiN₃.
Co^{3+}, Li^{+} it is difficult to obtain undoped and Mn-doped CaAlSiN₃ samples as a single phase material according to the stoichiometric composition. It was found that Al/Si disorderly occupies the 8b site in the space group of Cmc₂₁ with a ratio of about 1/2 with a more appropriate formula CaAl₁₋₄Si₁₋₃N₅ (δ = 0.3 - 0.4) instead of 1/1 proposed for an ideal CaAlSiN₃, probably due to the incomplete reaction resulting in a significantly lower Al solubility in CaAlSiN₃. Thus, a small amount of AlN can be detected for undoped and Mn-doped CaAlSiN₃ samples.

The unit cell volume of Caₙ₋₁MnₓAlSiN₃ decreases with increasing Mn²⁺ concentration (Figure 4), as expected for Mn²⁺ (r = 0.75 Å, CN = 5, r = 0.83 Å, CN = 6) being smaller than Ca²⁺ (r = 1.00 Å, CN = 6). In agreement with Al²⁺ by Mn²⁺ replacement, the unit cell volume of Caₙ₋₁MnₓAlSiN₃ extrapolated for high Mn²⁺ to x = 1 concentration agrees with that of MnAlSiN₃ (JCPDS : 50-0749), the cell volume of MnAlSiN₃, i.e. x = 1.0, was calculated from D. P. Thompson. However, as a function of the Mn²⁺ concentration, two linear regimes can be discriminated: for high Mn²⁺ concentrations (x > 0.15) the dependence is stronger than for low Mn²⁺ concentrations (x < 0.15), with a bending point at about 15 at% Mn²⁺ (x = 0.15). The weaker dependence can be explained by assuming that at low Mn concentrations, Mn²⁺ not only occupies the Ca²⁺ position, but in addition also partly occupies the Al¹⁺ site with Mn²⁺ (r = 0.66 Å, CN = 4) larger than Al¹⁺ (r = 0.39 Å, CN = 4). The Al¹⁺ by Mn²⁺ replacement can be charge compensated by Al³⁺/Si¹⁺ replacement or N⁵⁻/O⁵⁻ replacement. Unfortunately, a Rietveld refinement of the XRD patterns with MnAlSiN₃ substituted on both the Ca²⁺ as well as Al¹⁺ 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 Mn²⁺-doped CaAlSiN₃ samples. For undoped CaAlSiN₃ 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 CaAlSiN₃ host lattice. The value of the bandgap is close to the results published. The intense reflection in the visible spectral range is in agreement with the observed gray-white daylight color of undoped CaAlSiN₃. For Mn²⁺-doped CaAlSiN₃, 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 3A₁ (6S) ground state of Mn²⁺ to its excited states. In contrast to the undoped sample, the daylight color of Mn²⁺-doped CaAlSiN₃ shows gray-white to light red color, varying with Mn²⁺ concentration as a result of the absorption by Mn²⁺ ion the visible range of 350–600 nm.

Additionally, the absorption edge of CaAlSiN₃ : Mn²⁺ shifts to longer wavelength, corresponding to the decrease in the optical bandgap with increasing Mn²⁺ concentration. According to the band and electronic structure calculation results, the bottom of the conduction band (CB) of CaAlSiN₃ is mainly composed of Ca 3d orbitals, and Al/Si 3s/3p orbitals are hybridized at higher energy, while the top of valence band (VB) are dominated by the 2p states of N atoms. Thus, the VB → CB inter-band transition of CaAlSiN₃ is corresponding to a transition from N 2p to Ca 3d and Al/Si 3s/3p energy levels. The red-shift of the optical bandgap of CaAlSiN₃ : Mn⁺ with increasing Mn²⁺ concentration can be ascribed to the spin-exchange interaction between the Mn²⁺ ions and the band electrons (the so-called s - d and p- d interactions), which gives rise to a negative and a positive correction to the energy of the conduction and valence bands, respectively, and leads to a redshift of the optical bandgap.

Photoluminescence properties of Mn²⁺ in CaAlSiN₃.— In general, it is well known that the 3d⁰ multiplet energetic of Mn²⁺ in the host lattice strongly depends on the crystal field and the covalent interaction with the host lattice because the 3d electrons of the transition metal Mn²⁺ ions are outermost electrons, thus, the emission spectrum of Mn²⁺ (3d⁰) consists of a broad band varying from green to red color. It is well known that Tanabe-Sugano diagrams are used in coordination chemistry to interpret the characteristics of UV-Vis spectra due to the intra-3d shell transition of transition metal ions in host lattice. According to the Tanabe-Sugano diagram for the 3d² electron configuration of Mn²⁺, the energies of the 4E (5G), 4A₁ (5G) and 3E (4D) excited state relative to the 4A₁ (6S) ground state are insensitive to the crystal-field strength Dq, and is determined only by the Racah parameter B. The Racah B depends greatly on the covalent interaction between Mn²⁺ ions and surrounding ligand and decreases from the free-ion value with increase of the covalent interaction (the nephelauxetic effect). On the other side, the Mn²⁺ ion exhibits a 5S ground state and the first excited state is a 4G state, the Tanabe-Sugano diagrams predict that the energy differences between the 4T₁ (5G) and 4T₂ (5G) excited states and the 4A₁ (5S) ground state of Mn²⁺ ions are extremely sensitive to the crystal-field strength Dq and decreases with increase of crystal field strength Dq. The emission wavelength of Mn²⁺ strongly depends on the crystal field strength of the host lattice. Mn²⁺ usually gives a green emission when it is located on a lattice site with weak crystal field, whereas it exhibits an orange to red emission on a strong crystal field site.

Figure 6 shows the excitation and emission spectra of Ca₁₋ₓMnₓAlSiN₃ (x = 0.05). Under 451 nm excitation, Ca₁₋ₓMnₓAlSiN₃ (x = 0.05) shows a broad emission band in the wavelength range of 500–800 nm. The observed band emission is ascribed to the 2T₁ (4G) → 6A₁ (6S) transition of Mn²⁺ incorporated
in the CaAlSiN₃ host lattice. ⁶A₁ (⁵S) is the ground level, and ⁴T₁ (⁴G) 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 Ca₁₋ₓMnₓAlSiN₃ (x = 0.05) under 334, 381 and 451 nm excitation (Figure 7). In the crystal structure of CaAlSiN₃, there is only one crystallographic site for the Ca atom, which is coordinated with five N atoms (Figure 1). For Eu²⁺ and Ce³⁺-doped CaAlSiN₃, only the Ca sites with strong crystal field strength are substituted by Eu²⁺ and Ce³⁺ ions. As a consequence, a red emission band from Eu²⁺ and yellow-orange emission band from Ce³⁺ are observed in CaAlSiN₃.⁵⁰ Thus, if only the Ca²⁺ sites are substituted by Mn²⁺ ions, it is expected that there will be only a single narrow symmetrical emission band in the luminescence spectra of Mn²⁺-doped CaAlSiN₃. 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 Mn²⁺ sites in CaAlSiN₃ which are ascribed to MnCa and MnAl, not only the Ca²⁺ sites (MnCa), but also Al³⁺ sites (MnAl) can be substituted by Mn²⁺, which occurs in some other cases.⁵¹,⁵² Thus, Mn²⁺ ions will be located in a tetrahedrally and pentahedrally nitrogen coordinated site. According to the crystal structure of CaAlSiN₃, Al³⁺ site is coordinated with four N atoms with the average Al - N distance 1.805 Å, which is much smaller than that of Ca²⁺, coordinated with five N atoms with the average Ca-N distance 2.4934 Å. As a consequence, the crystal field strength is larger for Mn²⁺ at the Al³⁺ site than at the Ca²⁺ site. Considering the Tanabe-Sugano diagram, the emission band at lower energy (15,950 cm⁻¹ or 627 nm) is assigned to the Mn²⁺ locating at the Al site (MnAl), and the other emission band at higher energy (18,250 cm⁻¹ or 548 nm) originates from the Mn²⁺ locating at the Ca site (MnCa).

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.⁴⁹,⁵³ However, it rules out the possibility that there exists efficient energy transfer from CaAlSiN₃ host lattice to Mn²⁺ 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 Mn²⁺ incorporated on the Al³⁺ site and Ca²⁺ site, respectively. The excitation band of Mn²⁺ consists of several overlapping transitions due to the disordered AlSi lattice occupation of the same crystallographic position in the CaAlSiN₃ lattice. These excitation subbands can be assigned to the transitions of Mn²⁺ at different sites (MnCa, MnAl) from ground state ⁴S to ⁴T₁ (⁴G), ⁴T₂ (⁴G), ⁴T₁ (⁴G), ⁴E (⁴G), ⁴T₂ (⁴D) and ⁴E (⁴D) excited states, respectively. Table 1 summarizes the characteristics of CaAlSiN₃ : Mn²⁺ (5%) phosphor and compares them with other typical Mn²⁺-doped nitride based phosphors.

Figure 8 shows excitation spectra of CaAlSiN₃ : Mn²⁺ with different Mn²⁺ doping concentrations. The position of the overall excitation bands in the spectra is nearly independent of the Mn²⁺ concentration, which is similar to that of Eu²⁺ and Ce³⁺ in CaAlSiN₃.⁹,¹⁰ However, the Mn²⁺ concentration exhibits a great effect on the luminescence intensities, as well as the profiles of the emission bands. With increasing Mn²⁺ concentration, the peak positions of the emission bands for

**Table 1. Characteristics of Mn²⁺-doped CaAlSiN₃ phosphor compared to typical Mn²⁺-doped nitride based phosphors at room temperature.**

<table>
<thead>
<tr>
<th>Phosphors</th>
<th>Crystal system</th>
<th>Body color</th>
<th>Host absorption edge (nm)</th>
<th>Excitation bands (nm)</th>
<th>Emission bands (nm)</th>
<th>FWHM (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaAlSiN₃ : Mn²⁺</td>
<td>Cmc2₁</td>
<td>Light red</td>
<td>240</td>
<td>275, 334, 381, 451</td>
<td>548, 627</td>
<td>100</td>
<td>32</td>
</tr>
<tr>
<td>ZnSiN₂ : Mn²⁺</td>
<td>Pna2₁</td>
<td>Gray-white</td>
<td>250</td>
<td>260, 390, 420, 470, 490</td>
<td>620</td>
<td>130</td>
<td>36</td>
</tr>
<tr>
<td>ZrGeN₂ : Mn²⁺</td>
<td>Pna2₁</td>
<td>Gray-white</td>
<td>376</td>
<td>327, 425</td>
<td>610</td>
<td>70</td>
<td>35</td>
</tr>
<tr>
<td>MgSiN₂ : Mn²⁺</td>
<td>Pna2₁</td>
<td>Gray-white</td>
<td>287</td>
<td>360, 380, 430, 465</td>
<td>625, 692</td>
<td>70</td>
<td>34</td>
</tr>
<tr>
<td>Ca₂Si₃N₈ : Mn²⁺</td>
<td>Cc</td>
<td>Gray-white</td>
<td>250</td>
<td>250, 307, 396, 426, 489</td>
<td>606</td>
<td>60</td>
<td>34</td>
</tr>
<tr>
<td>Sr₂Si₃N₈ : Mn²⁺</td>
<td>Pnn2₁</td>
<td>Gray-white</td>
<td>265</td>
<td>250, 263, 316, 405, 427, 488</td>
<td>567</td>
<td>60</td>
<td>34</td>
</tr>
<tr>
<td>Ba₂Si₃N₈ : Mn²⁺</td>
<td>Pnn2₁</td>
<td>Gray-white</td>
<td>270</td>
<td>248, 261, 290, 436, 405, 421, 486</td>
<td></td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>
The redshift of the overall emission bands under 331/383 nm is observed at low Mn2+ concentration (x < 0.05), then the overall emission bands exhibit a blueshift with increasing Mn2+ concentration (x > 0.05). The combination of the redshift of the individual Mn2+ centers (MnCa, MnAl) discussed before with the energy transfer from high-energy MnCa2+ to low-energy MnAl2+ is anticipated to eventually result 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 Ca2+ sites with Mn2+ for higher Mn-concentrations (x > 0.05), resulting in a higher intensity of the high energy Mn2+ emission center. Figure 9 shows the overall emission intensity of CaAlSiN3 : Mn2+ as a function of Mn2+ concentration under the excitation wavelength of 451 nm and 332 nm. The maximum emission intensity is observed for 5 at% Mn2+ doped CaAlSiN3. The overall emission intensity declines gradually as the concentration of Mn2+ exceeds 5 at% due to concentration quenching, which is mainly caused by the non-radiative energy transfer among Mn2+ 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 MnAl2+ (lower energy, 15,950 cm−1 or 627 nm) and MnCa2+ (higher energy, 18,250 cm−1 or 548 nm) is shown in the inset of Figure 9. When Mn2+ ions were incorporated into CaAlSiN3, at low concentration (0 < x ≤ 0.05), not only the Ca2+ site, but also the Al3+ site can be substituted by Mn2+. As a consequence, emission at lower energy from MnAl2+ increases, as well as emission at higher energy from MnCa2+ can be observed, besides, there exists energy transfer from MnCa2+ to MnAl2+ according to the excitation spectra. Thus, the ratio between the emission intensity of MnAl2+ and MnCa2+ increases from 0.5 at% Mn2+ to 5 at% Mn2+. As the concentration of Mn2+ exceeds 5 at% till 15 at%, the ratio declines intensively due to the related concentration quenching of MnAl2+, then it increases slightly with concentration of Mn2+ increasing from 15 at% to 30 at%, which can be ascribed to the related concentration quenching of MnCa2+ and less concentration quenching for MnAl2+ because most of Mn2+ ions will substitute Ca2+ ions instead of Al3+ at high Mn2+ concentration (>15 at%). This is in good agreement with a linear decrease of the unit cell volume with varying Mn2+ content (>15 at%).

Figure 10 shows the relative emission intensity of CaAlSiN3 : Mn2+ (5 at%) as a function of sample temperature, using commercial YAG : Ce3+ phosphor as a standard for comparison. The quenching temperature Tq (the temperature at which the relative emission
intensity is half to 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⁺ (LPN-640) 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 broadband 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 (Mn_{Ca}) and Al site (Mn_{Al}), respectively. The effect of the Mn²⁺ 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 Mn²⁺ concentration. CaAlSiN₃: Mn²⁺ 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