Photoluminescence properties of red-emitting Mn2+-activated CaAlSiN3 phosphor for white-LEDs
Zhang, Z.; Delsing, A.C.A.; Notten, P.H.L.; Zhao, Jingtai; Dorenbos, P.; Hintzen, H.T.J.M.

Published in:
ECS Journal of Solid State Science and Technology

DOI:
10.1149/2.017304jss

Published: 01/01/2013

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 11. Dec. 2018
Photoluminescence Properties of Red-Emitting Mn\(^{2+}\)-Activated CaAlSiN\(_3\) Phosphor for White-LEDs

Zhijun Zhang,a,b Anneke C. A. Delsing,a Peter H. L. Notten,a,* Jingtao Zhao,b Pieter Dorenbos,c and Hubertus T. Hintzena,b

a Energy Materials and Devices, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands
b Key Laboratory of Transparent Opto-Functional Inorganic Materials of Chinese Academy of Sciences, Shanghai Institute of Ceramics, Shanghai 200050, China
c Luminescent Materials Research Group, Delft University of Technology, 2629 JB Delft, The Netherlands

Multinary nitrides and oxynitrides have attracted more attentions in recent years. They have been extensively investigated as host lattices for phosphors when activated by rare-earth ions, such as Mn\(^{3+}\), Ce\(^{3+}\) (M\(^{3+}\) = Ca, Sr, Ba), Mg\(^{2+}\)Si\(_{N}\)O\(_2\) : Eu\(^{2+}\), Ce\(^{3+}\) (M\(^{3+}\) = Ca, Sr, Ba), 34 Mg\(^{2+}\)Al\(_{N}\)O\(_2\) : Eu\(^{2+}\), Ce\(^{3+}\) (M\(^{3+}\) = Ca, Sr, Ba).20 These nitrides and oxynitrides have many advantages including strong absorption from UV to blue, high quantum efficiency, chemical stability as well as excellent thermal characteristics, allowing them to be widely used as efficient conversion phosphors for white-LEDs.

Rare-earth ions with 4f - 5d transitions (e.g. Eu\(^{2+}\), Ce\(^{3+}\)) show long wavelength absorption and emission in nitride, due to the high covalency and large crystal splitting effect of nitrogen anion.21 The nitrides and oxynitrides activated by these rare-earth ions have been demonstrated to be promising efficient conversion phosphors for white-LEDs.22 More recently, interests also have been focused on the luminescence properties of transition metals, such as Mn\(^{2+}\).23-25

The wavelength position of the emission band of Mn\(^{2+}\), as a typical transition ion, also depends strongly on the host lattice, including the strength of the ligand field and the coordination number (CN). In general, Mn\(^{2+}\) usually gives a green emission when it is located on a lattice with weak crystal-field, whereas it shows an orange to deep red emission on a strong crystal-field site. On the other hand, the coordination number also has a great effect on the emission color: the Mn\(^{2+}\) ions emit green light when it is tetrahedrally coordinated (CN = 4) in the lattice whereas it emits red light in octahedral coordination (CN = 6).26 Mn\(^{2+}\)-doped inorganic phosphors have been used as phosphors for white-LEDs, e.g. Ba\(_2\)Zn\(_2\)Si\(_4\)O\(_9\) : Mn\(^{2+}\) (Red),27,28 fluorescent lamps, such as Ba\(_2\)Al\(_2\)O\(_3\) : Mn\(^{2+}\) (Green)28 and Zn\(_2\)Si\(_2\)O\(_6\) : Mn\(^{2+}\) (Green),29 and cathode-ray tubes (CRT), e.g. ZnS : Mn\(^{2+}\) (Orange).30,31 Zn\(_2\)(PO\(_4\))\(_2\) : Mn\(^{2+}\) (Red).24,25 There are few reports with regard to the luminescence properties of Mn\(^{2+}\) in nitride host lattices except some publications on \(\text{M}^\text{IV}\)Si\(_2\)N\(_2\) : Mn\(^{2+}\) (M\(^{4+}\) = Mg, Zn, Ca), 23-24 M\(^{2+}\)Si\(_3\)N\(_4\) : Mn\(^{2+}\) (M\(^{2+}\) = Ca, Sr, Ba), 24 MgSi\(_2\)N\(_4\) : Mn\(^{2+}\), 25 ZnGe\(_2\)N\(_4\) : Mn\(^{2+}\), 25,26 \(\gamma\)-AlON : Mn\(^{2+}\), Mg\(^{2+}\).37 However, Mn\(^{2+}\)-doped Mg\(_2\)Si\(_4\)N\(_2\) show weak absorption in the range of 350–470 nm due to the forbidden d - d transitions of Mn\(^{2+}\). As for the white-LEDs applications this absorption has to be increased by use of suitable sensitizer ions, such as Ce\(^{3+}\), Mn\(^{2+}\), Mn\(^{3+}\), Mg\(_2\)Si\(_4\)N\(_2\).38

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\(^{3+}\).10,39 CaAlSiN\(_3\) is isostructural with Al\(_3\)Si\(_2\)N\(_2\) (A = Li, Na) and crystalizes in \(\text{Cmc2}_1\) space group.3 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 \(\text{M}_\text{IV}^\text{4+}\)N\(_4\) (M\(^{4+}\) = Al, Si) rings.40 CaAlSiN\(_3\) : Eu\(^{3+}\) and CaAlSiN\(_3\) : Ce\(^{3+}\) exhibit efficient red and yellow-orange emission respectively under blue irradiation.10,39 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.41

Experimental

Starting Materials.— Ca\(_2\)Si\(_2\)O\(_2\)N\(_2\) (Alfa, 98%, powder), AlN (Tokuyama Chemical Co., Ltd., F-grade), \(\alpha\)-Si\(_3\)N\(_2\) (Permascand, 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\(^{2+}\) powders were prepared by solid-state reaction method at high temperature. Appropriate amounts of starting materials were 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 excitation and emission slits were set at 15 nm. The emission spectra were 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 :

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.
CN linear regimes can be discriminated: for high Mn$^{2+}$ concentration agrees with that of MnAlSiN$_3$, i.e., the result of the absorption by Mn$^{2+}$ replacement can be charge compensated by Al$^{3+}$ ions and surrounding ligand and decreases from the $4^A_1$ ($^2S$) ground state to the $4^A_1$ ($^4S$) excited states. In contrast to the undoped sample, the daylight color of Mn$^{2+}$-doped CaAlSiN$_3$ shows gray-white to light red color, varying with Mn$^{2+}$ concentration as a result of the absorption by Mn$^{2+}$ ion the visible range of 350–600 nm.

Additionally, the absorption edge of CaAlSiN$_3$:Mn$^{2+}$ shifts to longer wavelength, corresponding to the decrease in the optical bandgap with increasing Mn$^{2+}$ concentration. According to the band and electronic structure calculation results, the bottom of the conduction band (CB) of CaAlSiN$_3$ 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 CaAlSiN$_3$ 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 CaAlSiN$_3$:Mn$^{2+}$ with increasing Mn$^{2+}$ concentration can be ascribed to the spin-exchange interaction between the Mn$^{2+}$ 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 Mn$^{2+}$ in CaAlSiN$_3$. In general, it is well known that the 3$d^7$ multiplet energies of Mn$^{2+}$ in the host lattice strongly depends on the crystal field and the covalent interaction with the host lattice because the 3$d$ electrons of the transition metal Mn$^{2+}$ ions are outermost electrons, thus, the emission spectrum of Mn$^{2+}$ (3$d^7$) 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-3$d$ shell transition of transition metal ions in host lattice. According to the Tanabe-Sugano diagram for the 3$d^7$ electron configuration of Mn$^{2+}$, the energies of the $^4E$ ($^2G$), $^4A_1$ ($^2G$) and $^4E$ ($^2D$) excited state relative to the $^4A_1$ ($^2S$) 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 Mn$^{2+}$ 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 Mn$^{2+}$ ion exhibits a $^4S$ ground state and the first excited state is a $^4G$ state, the Tanabe-Sugano diagrams predict that the energy differences between the $^4T_1$ ($^2G$) and $^4T_2$ ($^2G$) excited states and the $^4A_1$ ($^2S$) ground state of Mn$^{2+}$ ions are extremely sensitive to the crystal-field strength $Dq$ and decreases with increase of crystal field strength $Dq$. The emission wavelength of Mn$^{2+}$ strongly depends on the crystal field strength of the host lattice. Mn$^{2+}$ usually gives a green emission when it is located on a lattice site with weak crystal field, whereas it exhibits an orange to deep red emission on a strong crystal field site.
in the CaAlSiN₃ host lattice.⁶⁴,⁶⁵ 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₋ₓMnₓAlₓSiN₃ (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 Eu³⁺ and yellow-orange emission band from Ce³⁺ are observed in CaAlSiN₃.⁵⁰,⁵¹ 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 Al¹⁺ sites (MnAl) can be substituted by Mn³⁺, which occurs in some other cases.⁶,⁵² Thus, Mn³⁺ ions will be located in a tetrahedrally and pentahedrally nitrogen coordinated site. According to the crystal structure of CaAlSiN₃, Al¹⁺ 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 2.493 Å. As a consequence, the crystal field strength is larger for Mn²⁺ at the Al¹⁺ 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 Al¹⁺ site (MnAl), and the other emission band at higher energy (18,250 cm⁻¹ or 548 nm) originates from the Mn²⁺ locating at the Ca²⁺ 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.⁸⁹,⁹⁰ 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 Al¹⁺ site and Ca²⁺ site, respectively. The excitation band of Mn²⁺ consists of several overlapping transitions due to the disordered Al/Si 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 ⁴A₁ (⁴S) to ⁴T₁ (⁴G), ⁴T₂ (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

![Figure 6. Excitation and emission spectra of Ca₁₋ₓMnₓAlₓSiN₃ (x = 0.05).](image)

![Figure 7. Luminescence spectra of Ca₁₋ₓMnₓAlₓSiN₃ (x = 0.05) with deconvoluted Gaussian subbands for emission spectra.](image)

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

<table>
<thead>
<tr>
<th>Phosphors</th>
<th>CaAlSiN₃:Mn²⁺</th>
<th>ZnSiN₂:Mn²⁺</th>
<th>ZaGeN₂:Mn²⁺</th>
<th>MgSiN₂:Mn²⁺</th>
<th>Ca₂Si₅N₈:Mn²⁺</th>
<th>Sr₂Si₅N₈:Mn²⁺</th>
<th>Ba₂Si₅N₈:Mn²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Cmc₂₁</td>
<td>Pna₂₁</td>
<td>Pna₂₁</td>
<td>Pna₂₁</td>
<td>Cc</td>
<td>Pnn₂₁</td>
<td>Pnn₂₁</td>
</tr>
<tr>
<td>Body color</td>
<td>Light red</td>
<td>Gray-white</td>
<td>Gray-white</td>
<td>Gray-white</td>
<td>Gray-white</td>
<td>Gray-white</td>
<td>Gray-white</td>
</tr>
<tr>
<td>Host absorption edge (nm)</td>
<td>240</td>
<td>250</td>
<td>376</td>
<td>287</td>
<td>250</td>
<td>265</td>
<td>270</td>
</tr>
<tr>
<td>Excitation bands (nm)</td>
<td>275, 334,</td>
<td>260, 390,</td>
<td>327, 425</td>
<td>360, 380,</td>
<td>250, 307,</td>
<td>250, 263,</td>
<td>248, 261,</td>
</tr>
<tr>
<td></td>
<td>381, 451</td>
<td>470, 490</td>
<td></td>
<td>430, 465</td>
<td>396, 435</td>
<td>405, 427,</td>
<td>436, 405,</td>
</tr>
<tr>
<td>Emission bands (nm)</td>
<td>548, 627</td>
<td>620</td>
<td>610</td>
<td>625, 692</td>
<td>599</td>
<td>606</td>
<td>567</td>
</tr>
<tr>
<td>FWHM (nm)</td>
<td>100</td>
<td>–</td>
<td>130</td>
<td>70</td>
<td>70</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Ref.</td>
<td>This work</td>
<td>32</td>
<td>36</td>
<td>35</td>
<td>34</td>
<td>34</td>
<td>34</td>
</tr>
</tbody>
</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$_{Ca}^{2+}$, 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 change of the ratio between the emission intensity of 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$_{Ca}^{2+}$, 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
intensity is half to the initial intensity at room temperature) for CaAlSiN$_3$: Mn$^{2+}$ (5 at%) is above 200 C, which is much better than that of commercial YAG: Ce$^{3+}$ phosphor. In addition, the emission intensity of CaAlSiN$_3$: Mn$^{2+}$ (5 at%) can reach up to about 30% to that of the commercial red-emitting phosphor CaAlSiN$_3$: Eu$^{2+}$ (LP-N640) for excitation with blue light (450 nm) at room temperature, as shown in the inset of Figure 10.

Conclusions

Mn$^{2+}$-activated CaAlSiN$_3$ phosphors have been prepared by a solid-state reaction successfully and the solubility of Mn$^{2+}$ in host lattice as well as their photoluminescence properties were investigated. CaAlSiN$_3$: Mn$^{2+}$ exhibits a broad band emission in the wavelength range of 475–750 nm. There are two obvious overlapping Mn$^{2+}$ emission bands with peak centers at 548 and 627 nm, which are attributed to the Mn$^{2+}$ locating at the Ca site (Mn$_{Ca}$) and AI site (Mn$_{Al}$), respectively. The effect of the Mn$^{2+}$ concentration in CaAlSiN$_3$ on the luminescence properties was investigated and explained on the basis of the presence of the two Mn$^{2+}$ sites, combined with preferential site occupation and energy transfer depending on the Mn$^{2+}$ concentration. CaAlSiN$_3$: Mn$^{2+}$ 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.

Acknowledgment

The authors gratefully acknowledge financial support from the European Union, the Freistaat Thueringen, the Leuchtsstoffwerk Breitungen GmbH (Germany) under contract 2008FE0070 and the National Natural Science Foundation of China under grant No. 11104298. And we thank Dr. Sven Rösler for the temperature dependent luminescence measurement. The authors also gratefully acknowledge Prof. Dr. Yuying Huang and Dr. Xing Gao (SSRF, China) for helpful technical assistance of XANES experiments.

References