Luminescence properties of Eu2+-doped MAI2-xSixO4-xNx (M = Ca, Sr, Ba) conversion phosphor for white LED applications
Li, Y.; de With, G.; Hintzen, H.T.J.M.

Published in:
Journal of the Electrochemical Society

DOI:
10.1149/1.2167950

Published: 01/01/2006

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):
Undoped and Eu-doped MAI$_2$Si$_x$O$_{4-x}$N$_x$ (M = Ca, Sr, Ba) were synthesized by a solid-state reaction method at 1300–1400°C under nitrogen-hydrogen atmosphere. The solubility of (SiN)$_2^+$ in MAI$_2$O$_4$ was determined. Nitrogen can be incorporated into MAI$_2$O$_4$ by replacement of (AlO)$_2^+$ by (SiN)$_2^+$, whose amount of solubility depends on the M cation. The solubility of (SiN)$_2^+$ is very low in CaAl$_2$O$_4$ and SrAl$_2$O$_4$ lattices (x ≈ 0.025 and 0.045, respectively), whereas a large amount of (SiN)$_2^+$ can be incorporated into BaAl$_2$O$_4$ (x = 0.6). Incorporation of (SiN)$_2^+$ hardly modifies the luminescence properties of Eu$^{2+}$-doped MAI$_2$O$_4$ (M = Ca, Sr) because of limited solubility of (SiN)$_2^+$, showing the blue and green emission almost at constant wavelength of 440 and 515 nm, respectively. Eu$^{2+}$-doped BaAl$_2$Si$_x$O$_{4-x}$N$_x$ exhibits a broad green emission band with a maximum in the range of 500–526 nm, depending on the concentration of (SiN)$_2^+$ and Eu$^{2+}$. In addition, both excitation and emission bands of Eu$^{2+}$ show a significant red shift as nitrogen is incorporated. BaAl$_2$Si$_x$O$_{4-x}$N$_x$Eu$^{2+}$ can be efficiently excited in the range of 390–440 nm radiation, which makes this material attractive as conversion phosphor for white light-emitting diode (LED) lighting applications.

© 2006 The Electrochemical Society. [DOI: 10.1149/1.2167950] All rights reserved.

Undoped and Eu-doped MAI$_2$Si$_x$O$_{4-x}$N$_x$ (M = Ca, Sr, Ba) were synthesized by a solid-state reaction method at 1300–1400°C under nitrogen-hydrogen atmosphere. The solubility of (SiN)$_2^+$ in MAI$_2$O$_4$ was determined. Nitrogen can be incorporated into MAI$_2$O$_4$ by replacement of (AlO)$_2^+$ by (SiN)$_2^+$, whose amount of solubility depends on the M cation. The solubility of (SiN)$_2^+$ is very low in CaAl$_2$O$_4$ and SrAl$_2$O$_4$ lattices (x ≈ 0.025 and 0.045, respectively), whereas a large amount of (SiN)$_2^+$ can be incorporated into BaAl$_2$O$_4$ (x = 0.6). Incorporation of (SiN)$_2^+$ hardly modifies the luminescence properties of Eu$^{2+}$-doped MAI$_2$O$_4$ (M = Ca, Sr) because of limited solubility of (SiN)$_2^+$, showing the blue and green emission almost at constant wavelength of 440 and 515 nm, respectively. Eu$^{2+}$-doped BaAl$_2$Si$_x$O$_{4-x}$N$_x$ exhibits a broad green emission band with a maximum in the range of 500–526 nm, depending on the concentration of (SiN)$_2^+$ and Eu$^{2+}$. In addition, both excitation and emission bands of Eu$^{2+}$ show a significant red shift as nitrogen is incorporated. BaAl$_2$Si$_x$O$_{4-x}$N$_x$Eu$^{2+}$ can be efficiently excited in the range of 390–440 nm radiation, which makes this material attractive as conversion phosphor for white light-emitting diode (LED) lighting applications.

© 2006 The Electrochemical Society. [DOI: 10.1149/1.2167950] All rights reserved.

As an important class of phosphors, Eu$^{2+}$-doped MAI$_2$O$_4$ (M = Ca, Sr, Ba), has been widely used as persistent luminescent materials because of their high efficiency, chemical stability, and long-lasting high-lumiance afterglow characteristics. These phosphors also have been proposed for plasma display panel (PDP) and optoelectronic applications. Under ultraviolet and cathode-ray excitation these phosphors show a strong blue (M = Ca), green (M = Sr), and blue-green (M = Ba) fluorescence.

In MAI$_2$O$_4$ (M = Ca, Sr, Ba), the three-dimensional framework is built-up by a motif of six rings formed by corner-sharing AlO$_4$ tetrahedra. The tetrahedral framework is isosctructural, with the SiO$_2$ polymorph having the tridymite structure. The various MAI$_2$O$_4$ structures differ in the arrangement and number of crystallographic sites of the divalent cations within the channels formed by the AlO$_4$ rings. CaAl$_2$O$_4$ has a monoclinic structure in space group P2$_1$/n. In this structure there are three Ca sites: two of them are sixfold and the third is ninefold coordinated, with the oxygen atoms in a different channel. However, for the larger M cations, SrAl$_2$O$_4$ and BaAl$_2$O$_4$ crystallize in a monoclinic and a hexagonal system with the space group P2$_1$ and P6$_3$, respectively. Both Sr and Ba ions occupy two crystallographic sites, which are located in the channels of the AlO$_4$ rings, each with ninefold coordination with the oxygen anions.

Although extensive investigations have been done on Eu$^{2+}$-doped alkaline earth aluminates MAI$_2$O$_4$ (M = Ca, Sr, Ba), in previous studies considerable attention has been paid to improve the performance of these phosphors by partial substitution of the M ion (for example, replacement of Ca with Sr and vice versa) and/or by doping activator ions (for example, Eu$^{2+}$ with Dy$^{3+}$). These effects can enhance the efficiency, optimize emission color range, and extend persistence time. However, it is only possible to tailor the excitation and absorption bands in the UV range. As a consequence, for obtaining an efficient emission these phosphor materials have to be excited in the UV region (e.g., below ~350 nm). Therefore, with respect to white light-emitting diode (LED) applications, the excitation bands of Eu$^{2+}$-doped MAI$_2$O$_4$ (M = Ca, Sr, Ba) phosphors do not match with the UV-blue emission (~370–460 nm) from InGaN-based LEDs. For use as wavelength conversion phosphors for white-light LEDs, usually a strong absorption in the UV-blue range (i.e., 370–460 nm) and highly efficient conversion from absorbed blue into green, yellow, and red light are required. Hence, in order to make MAI$_2$O$_4$:Eu$^{2+}$ (M = Ca, Sr, Ba) phosphors meet these requirements, apart from the above-mentioned routes other novel approaches have to be adopted. Recently, Eu$^{2+}$-doped alkaline-earth-silicon-nitride and oxinitride have shown an unusual long wavelength emission with excitation in the visible range (370–460 nm). Therefore, if silicon and oxygen atoms can be incorporated into MAI$_2$O$_4$, e.g., (AlO)$_2^+$ replacement by (SiN)$_2^+$ [which is an opposite routine to convert nitride into oxinitride, for example, (SiN)$_2^+$ → (AlO)$_2^+$ replacement in Si$_3$N$_4$ → SiAlON$_2$ and Y$_2$Si$_3$N$_4$ → Y$_2$Si$_3$Al$_2$O$_3$N$_{4-x}$] or Eu$^{2+}$ on the phase formation and crystal structure was studied by X-ray powder diffraction combined with Rietveld refinement. Finally, the luminescence of Eu$^{2+}$-doped MAI$_2$-Si$_x$O$_{4-x}$N$_x$ (M = Ca, Sr, Ba) and the dependence of luminescence properties on Eu$^{2+}$ concentration in BaAl$_2$Si$_x$O$_{4-x}$N$_x$ were also investigated.

**Experimental**

Starting materials.— MO$_3$ (M=Ca, Sr, Ba) (Merck, >99.99%), SiO$_2$ (Degussa Aerosil OX50), γ-Al$_2$O$_3$ (AKPG), >99.995, α-Si$_3$N$_4$ (SKW Trostberg, α content 23.3%, O content 0.7 wt %) and Eu$_2$O$_3$ (Rhône-Poulenc, 99.99%) were employed as the raw materials. Oxygen presence in the Si$_3$N$_4$ starting powder was not considered in the synthesis procedures.

**Synthesis of undoped and Eu$^{2+}$-doped MAI$_2$-Si$_x$O$_{4-x}$N$_x$ (M = Ca, Sr, Ba).**—Si$_3$N$_4$ was used as the source of (SiN)$_2^+$ using the following reaction

\[
\text{MO}_3 + (2x)\times2\text{Al}_2\text{O}_3 + x\times4\text{Si}_3\text{N}_4 + x\times4\text{SiO}_2 \\
\rightarrow \text{MAI}_2\text{Si}_x\text{O}_{4-x}\text{N}_x + \text{CO}_2
\]

[1]

The raw materials were homogeneously wet-mixed in the appropriate amounts by a planetary ball mill for 4–5 h in isopropanol with

Y. Q. Li, G. de With, and H. T. Hintzen

Laboratory of Materials and Interface Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, 5600 MB, Eindhoven, The Netherlands

**Luminescence Properties of Eu$^{2+}$-Doped MAI$_2$Si$_x$O$_{4-x}$N$_x$ (M = Ca, Sr, Ba) Conversion Phosphor for White LED Applications**

Y. Q. Li, G. de With, and H. T. Hintzen


0013-4651/2006/153(4)/G278/5/$20.00 © The Electrochemical Society
agate balls in an agate container. After mixing the mixture was dried in a stove and ground in an agate mortar. Subsequently, the powders were fired in Mo or alumina crucibles at 1300–1400°C for 8–12 h in a reducing atmosphere of N₂–H₂ (10%) in a horizontal tube furnace two times with an intermediate grinding between the firing steps. The same processes were adopted for obtaining Eu-doped materials.

**Characterization.**—The obtained samples were analyzed by X-ray powder diffraction on a Rigaku D/Max-γB diffractometer operating at 40 kV, 30 mA with Bragg–Brentano geometry (flat graphite monochromator, scintillation counter) using Cu Kα radiation. Phase formation was checked by a routine scan (2°/min). The lattice parameters were determined in the 2θ range of 10–120° with a step size of 0.01° 2θ and a counting time of 6 s per step. In order to correlate the changes of the local structures with the luminescence properties, the structure of BaAl₂₋ₓSiₓO₄₋ₓNₓ was refined by the Rietveld method using structural parameters of BaAl₂O₄ as the starting model, assuming both Si⁴⁺ and N⁻³ random distributing over the Al³⁺ and O²⁻ sites, respectively, in BaAl₂O₄. For the Rietveld refinement XRD data were recorded with a step-scan mode using silicon powder as an internal standard with a step size of 0.01° 2θ and a counting time of 6 s per step. The Rietveld refinement was performed using the program GSAS. The refined parameters include the scale factor, zero shift, background, lattice parameters, peak profile parameters, fractional coordinates of individual atoms, and isotropic displacement parameters.

The photoluminescence spectra were determined at room temperature on the powder samples by a Perkin-Elmer LS-50B luminescence spectrometer with a Xenon discharge lamp as excitation source. The radiation was detected by a red sensitive photomultiplier R928. The spectra were obtained in the range of 200–700 nm with a scanning speed of 100 nm/min and excitation and emission slit widths of 2.5 nm. Excitation spectra were automatically corrected for the variation in the lamp intensity by a second photomultiplier and a beam splitter, and all the emission spectra were corrected by taking into account the combined effect of the spectral response of the R928 detector and the monochromator by using the measured spectra of a calibrated W-lamp as the light source. Diffuse reflectance spectra were recorded in the range of 230–700 nm, with BaSO₄ white powder (100%) and black felt (3%) as the references.

**Results and Discussion**

**Effect of (Sin)⁺ substitution for (AlO)⁺ in MA₁₋ₓOₓ (M = Ca, Sr, Ba) on phase formation and structure.**—When nitrogen is incorporated in MA₁₋ₓOₓ, (AlO)⁺ is expected to be replaced by the (Sin)⁺ pair to form hybrid (Al,Si)⁺–(O,N)₄ tetrahedra in the framework. As proof, the lattice parameters are expected to decrease, corresponding to the unit cell volume shrinkage because of shorter Si–N distances (~1.65 to 1.75 Å) compared to N–O distances (~1.70 to 1.78 Å) in MA₁₋ₓOₓ. With the ionic radius of M decreasing from Ba to Ca, it is found that the incorporation of nitrogen according to Reaction 1 becomes more difficult. As a consequence, the maximum solubility of (Sin)⁺ in MA₁₋ₓOₓ significantly decreases from Ba to Sr and Ca compounds. In the case of Ca₁₋ₓAlₓOₓ and Sr₁₋ₓAlₓOₓ, the solubility of (Sin)⁺ is almost negligible. The obtained lattice parameters of MA₁₋ₓSiₓO₄₋ₓNₓ, as a function of x, demonstrate that the maximum solubility of (Sin)⁺ in Ca₁₋ₓAlₓOₓ and Sr₁₋ₓAlₓOₓ lattice is only x = 0.025 (i.e., 1.25 mol %) and x = 0.045 (i.e., 2.25 mol %), respectively (Fig. 1). Accordingly, when the x value surpasses the maximum solubility, a secondary phase of Ca₁₋ₓAlₓSiₓO₄₋ₓNₓ or Sr₁₋ₓAlₓSiₓO₄₋ₓNₓ appears in the Ca₁₋ₓAlₓSiₓO₄₋ₓNₓ and Sr₁₋ₓAlₓSiₓO₄₋ₓNₓ system, respectively.

![Figure 1](image1.png)

**Figure 1.** Relationship between the unit cell volume and x values of (a) Ba₁₋ₓAlₓSiₓO₄₋ₓNₓ and (b) Sr₁₋ₓAlₓSiₓO₄₋ₓNₓ.

In contrast, the lattice parameters and in particular the unit cell volume of Ba₁₋ₓAlₓSiₓO₄₋ₓNₓ significantly decrease with increasing x value up to 0.6, indicating that (Sin)⁺ is effectively incorporated into Ba₁₋ₓAlₓOₓ lattice to a high extent (Fig. 2). For x values larger than 0.6, the unit cell volume remains almost constant and a distinct secondary phase of Ba₂SiO₄ is found; thus, the maximum solubility...
of (SiN)\(^{x}\) in BaAl\(_2\)O\(_4\) is about \(x = 0.6\) (Fig. 2). Consequently, the observed X-ray diffraction (XRD) pattern of BaAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\) perfectly matches with the calculated pattern based on BaAl\(_2\)O\(_4\) tridymite structure\(^8\) (Fig. 3). Although, as expected, both the \(a\) and \(c\) axes decrease with increasing \(x\) [i.e., (SiN)\(^{x}\) content, Fig. 2], the \(c/a\) ratio of BaAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\) is almost constant (~0.843).

The larger solubility of (SiN)\(^{x}\) in the BaAl\(_2\)O\(_4\) lattice may be related to the larger difference between the shortest (1.665 Å) and longest (1.808 Å) Al–O bonds of the Al\(_2\)O\(_4\) network (reflected by the large standard deviation of 0.042 Å for the Al–O distances) as induced by the larger ionic size of the Ba ion. These largely distorted (AlO\(_4\)) tetrahedra are probably very compatible with incorporation of a Si–N pair without changing its structure too much. In contrast, in CaAl\(_2\)O\(_4\) and SrAl\(_2\)O\(_4\) all the tetrahedral (AlO\(_4\)) units are very regular (i.e., the Al–O distances are very similar, with a very small standard deviation of 0.012 and 0.013 Å for the Ca and Sr compounds, respectively\(^9,10\)), resulting in strong distortions due to incorporation of SiN.

When (AlO)\(^{x}\) is replaced by (SiN)\(^{x}\) in BaAl\(_2\)O\(_4\), the average (Si–Al–O) distances, obtained by the Rietveld refinement, decreased for larger (SiN)\(^{x}\) amounts corresponding to an overall shrinkage of the lattice. For example, these distances (Si–Al–O) are 1.7534, 1.7529, and 1.7431 Å, respectively, for \(x = 0\), 0.1, and 0.3 in BaAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\). At the same time, however, the average Ba–O distances slightly increase (i.e., 2.918 Å vs 2.924 Å for \(x = 0\) and 0.3, respectively), indicating that Ba needs more space due to coordination with N (larger than O). It is worth noting that for a better understanding of the site preferences of Si (on the four available Al sites) and N (on the six available O sites) in BaAl\(_2\)O\(_4\), neutron diffraction experiments need to be performed due to the similar scattering factors of N\(^{15}\)/O\(^{15}\) and Al\(^{17}\)/Si\(^{17}\) for X-ray powder diffraction.

**Luminescence properties of Eu-doped MAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\) (M = Ca, Sr, Ba).**—The luminescence properties of Eu-doped MAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\), strongly depend on the type of the cation M, similar to the case of MAl\(_2\)O\(_4\)-Eu\(^{3+}\) (M = Ca, Sr, Ba)\(^9,15\). While the position of the Eu\(^{3+}\) excitation and emission bands is nearly independent of \(x\) for M = Ca and Sr, it strongly depends on \(x\) for M = Ba. Overview results of the obtained luminescence properties (i.e., excitation, emission, and Stokes shift) are listed in Table I. MAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\)-Eu\(^{3+}\) (M = Ca, Sr).—As described above, the solubility of (SiN)\(^{x}\) in CaAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\) and SrAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\) is very low (Table I), hence, it is expected that the excitation and emission spectra of the Eu-doped compounds have no significant change compared with those of Eu-doped MAl\(_2\)O\(_4\) (M = Ca, Sr). Both the excitation and emission behaviors are very similar, except for some minor differences like an enhanced shoulder at about 370 nm in the excitation spectrum for M = Ca and a slightly broadened emission band for M = Sr. Additionally, the maximal shift of the Eu\(^{3+}\) emission bands is less than 10 nm with increasing \(x\). Consequently, the Stokes shift shows a decrease in the range of the lattice. For example, these average (AlSiO)–(O,N) distances are 1.7534, 1.7529, and 1.7431 Å, respectively, for \(x = 0\), 0.1, and 0.3 in BaAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\). At the same time, however, the average Ba–O distances slightly increase (i.e., 2.918 Å vs 2.924 Å for \(x = 0\) and 0.3, respectively), indicating that Ba needs more space due to coordination with N (larger than O). It is worth noting that for a better understanding of the site preferences of Si (on the four available Al sites) and N (on the six available O sites) in BaAl\(_2\)O\(_4\), neutron diffraction experiments need to be performed due to the similar scattering factors of N\(^{15}\)/O\(^{15}\) and Al\(^{17}\)/Si\(^{17}\) for X-ray powder diffraction.

| Table I. Overview of structural parameters of undoped and luminescence data of 10 mol % Eu-doped MAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\) (M = Ca, Sr, Ba). |
|-----------------------------------------------|-----------------|-----------------|-----------------|
| MAl\(_2\)Si\(_{1-x}\)O\(_{4-x}\)N\(_x\) | M = Ca | M = Sr | M = Ba |
| **Maximum solubility of (SiN)\(^{x}\)** | **Structural parameters** | **Monoclinic P2\(_1\)/n** | **Monoclinic P2\(_1\)** | **Hexagonal P6\(_3\)** |
| **Max. x** | **a (Å)** | **b (Å)** | **c (Å)** | **V (Å\(^3\))** | **Excitation band (nm)** | **Emission band (nm)** | **Stokes shift (cm\(^{-1}\))** | **Crystal field splitting (cm\(^{-1}\))** |
| **x = 0.025** | 8.614(3) | 8.671(4) | 8.4435(8) | 8.4384(10) | 260, 329, 380 | 438 | 3500 | 13,360 |
| **x = 0.02** | 8.48(4) | 8.992(3) | 8.8184(9) | 8.8275(8) | 260, 340, 386 | 443 | 3600 | 13,600 |
| **x = 0.02** | 8.58(4) | 9.038(8) | 5.1575(7) | 5.1527(5) | 280, 340, 386 | 354 | 6500 | 14,000 |
| **x = 0.02** | 8.48(4) | 9.038(8) | 9.340(1) | 9.332(2) | 280, 340, 387 | 519 | 6600 | 14,000 |
| **x = 0.02** | 8.58(4) | 9.038(8) | 383.35(10) | 383.18(9) | 280, 340, 400 | 519 | 6600 | 14,000 |
| **x = 0.3** | 10.094(3) | 10.646(6) | 10.446(6) | 10.445(6) | 383.22(8) | 440 | 526 | 10,000 |
| **x = 0.3** | 9.09(4) | 10.664(6) | 826.85(8) | 826.85(8) | 440 | 526 | 3700 |

\(^a\) Stokes shift calculated from the energy difference between the lowest 5d excitation band and emission band of Eu\(^{3+}\).

\(^b\) Crystal-field splitting estimated from the energy difference between highest and lowest observed 5d excitation levels of Eu\(^{3+}\).
the Eu²⁺ emission band to a concomitant shift of the lowest excitation band due to an increase of the crystal field splitting of the 5d state of the Eu²⁺ ions as a consequence of the replacement of O²⁻ by N³⁻. Also, an increase of degree of covalent bonding induced by nitrogen contributes to this shift (Table I). For \( x > 0.3 \), the excitation bands show a slight blue-shift, especially for \( x > 0.5 \) (Fig. 5), which can be understood from the fact that the Eu-O/N distances become larger as the amount of (SiN)⁺ increases, resulting in a smaller crystal field splitting and counteracting the effect of the replacement of O²⁻ by N³⁻. The integrated emission intensity of \( \text{BaAl}_2Si_xO_{4-x}N_2:Eu \) (10 mol %) reaches a maximum at \( x = 0.3 \) for excitation in the range of 400–460 nm. When \( x \) is larger than 0.3, the emission intensity shows a significant decrease. The quantum efficiency of \( \text{BaAl}_2Si_xO_{4-x}N_2:Eu \) (10 mol %, \( x = 0.3 \)) is about 54%, with an excitation wavelength at 460 nm.

Besides the replacement of (AlO)⁺ by (SiN)⁺, as usual the Eu²⁺ concentration also shows a significant influence on the structure and luminescence properties of \( \text{BaAl}_2Si_xO_{4-x}N_2:Eu \). Figure 6 shows the lattice parameter changes of \( \text{BaAl}_2Si_xO_{4-x}N_2 \) (\( x = 0.3 \)) as a function of the Eu concentration. As expected, the lattice parameters decrease with increasing Eu concentration because the ionic radius
Figure 7. Reflection spectra of $\text{BaAl}_2\cdot\text{Si}_x\cdot\text{O}_{4-x}\cdot\text{N}_x$ ($x = 0, 0.3$) and $\text{Ba}_{3-x}\cdot\text{Eu}_{x}\cdot\text{Al}_2\cdot\text{Si}_3\cdot\text{O}_{12-x}\cdot\text{N}_x$-$\text{Eu}^{2+}$ ($x = 0.3, y = 0.01, 0.05, 0.10$ corresponding to 1, 5, and 10 mol % Eu).

Integrated emission intensity increases for higher Eu contents whereas it decreases for short excitation wavelength ($390$ nm) (see inset in Fig. 8).

Conclusions

The maximum solubility of (SiN)$x$ in MAI$_{2-x}$SiO$_{4-x}$N$_x$ with tridymite structure significantly decreases from Ba to Sr and Ca compounds. In CaAl$_2$O$_4$ and SrAl$_2$O$_4$, the solubility of (SiN)$x$ is very limited [i.e., $x = 0.025$ (1.25%) and $x = 0.045$ (2.25%), respectively], whereas the maximum solubility of (SiN)$x$ in BaAl$_2$O$_4$ lattice is about $x = 0.6$ (i.e., 30 mol %). As a consequence, the Eu$^{2+}$ emission is found at 440 and 515 nm for Eu-doped MAI$_{2-x}$SiO$_{4-x}$N$_x$ ($M =$ Ca, Sr), similar to the corresponding compounds without incorporation of nitrogen. BaAl$_2$SiO$_4$N$_x$-$\text{Eu}^{2+}$ exhibits a long-wavelength excitation band peaking at about 440 nm, corresponding to a green emission at about 500–526 nm ($x = 0.3$). Compared with BaAl$_2$O$_4$-$\text{Eu}^{2+}$ (excitation at about 388 nm and emission at about 500 nm), the red shift due to the incorporation of nitrogen can be understood from increased covalency and crystal field splitting. The luminescence properties of BaAl$_2$SiO$_4$N$_x$-$\text{Eu}^{2+}$ can be further modified by adjusting the amount of (SiN)$x$ and Eu concentration. Consequently, BaAl$_2$SiO$_4$N$_x$-$\text{Eu}^{2+}$ shows high potential as a green-emitting conversion phosphor for white-light LED applications.

Abbreviations

$\text{Eu}^{2+}$:europium
$\text{BaAl}_2\cdot\text{Si}_x\cdot\text{O}_{4-x}\cdot\text{N}_x$: boracite-type compounds
$\text{Eu}^{2+}$:europium
$\text{Ba}_{3-x}\cdot\text{Eu}_x\cdot\text{Al}_2\cdot\text{Si}_3\cdot\text{O}_{12-x}\cdot\text{N}_x$-$\text{Eu}^{2+}$: $\text{Eu}^{2+}$:europium
$\text{Ba}_{x}\cdot\text{Eu}_{y}\cdot\text{Al}_{1-x}\cdot\text{Si}_x\cdot\text{O}_{4-x}\cdot\text{N}_x$: $\text{Eu}^{2+}$:europium

References