New full-color-emitting phosphor, Eu$^{2+}$-doped Na$_{2-x}$Al$_2-x$Si$_x$O$_4$ (0 ≤ x ≤ 1), obtained using phase transitions for solid-state white lighting†

Ji Yeon Han,$^a$ Won Bin Im,$^b$ Donghyuk Kim,$^a$ Sang Hoon Cheong,$^a$ Ga-yeon Lee$^a$ and Duk Young Jeon$^{a,a}$

Received 28th October 2011, Accepted 27th December 2011
DOI: 10.1039/c2jm15501j

A new color-tunable Eu$^{2+}$-doped sodium aluminium silicate, Na$_{2-x-y}$Al$_2-x$Si$_x$O$_4$;yEu$^{2+}$ (0 ≤ x ≤ 1), phosphor system was investigated as a novel candidate for phosphor-converted white light-emitting diode (LED) applications and successfully synthesized by wet chemical methods based on the hydrolysis of tetraethyl orthosilicate (TEOS). Different crystal structures and emission spectra were obtained by varying the ratio of Al to Si in the phosphor Na$_{2-x}$Al$_2-x$Si$_x$O$_4$ with x value ranging from 0.25 to 0.55. The Na$_{2-x}$Al$_2-x$Si$_x$O$_4$;yEu$^{2+}$ phosphor system emitted a maximum intensity at 470–600 nm when using a 395 nm excitation wavelength, and the emission was strongly affected by the crystal structures determined by the x value. Substitution of Eu$^{2+}$ affected the center wavelength and emission intensity due to changes in the crystal-field effect, which was strongly dependent on the crystal structure. The LED device exhibited an excellent color-rendering index $R_g$ of 93 at a correlated color temperature of 4258 K with CIE color coordinates of (0.3629, 0.3427) under a 20 mA forward-bias current. Based on these results, we are currently evaluating the potential application of Na$_{2-x}$Al$_2-x$Si$_x$O$_4$;yEu$^{2+}$ as a white-emitting UV-convertible phosphor.

1. Introduction

White light-emitting diodes (LEDs) have been used more frequently as illumination light sources over the past several years because white LEDs can provide significant power savings, long lifetime (>100 000 h), high luminous efficiency, and environmental friendliness.1,2 An LED-based light is fabricated using the combination of a blue-emitting LED chip with a yellow-emitting Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (YAG:Ce$^{3+}$) phosphor; this combination is widely used due to an unsurpassed efficiency (>30 lm W$^{-1}$).3,4 Although a blue-emitting LED chip with a yellow-emitting YAG:Ce$^{3+}$ phosphor has a high efficiency, it has a poor color-rendering index because YAG:Ce$^{3+}$ phosphors have a relatively weak emission in the red spectral region, and it is difficult to obtain good color rendering as measured by the index ($R_g$).5,6 Furthermore, phosphors, with the exception of YAG:Ce$^{3+}$, have a weak or no absorption band in the range of 440–460 nm. Recently, the use of near-ultraviolet LEDs (near-UV LEDs), a new class of white LEDs, combined with multi-component phosphors has been attempted to overcome these drawbacks, and there have been extensive efforts to develop new phosphors for near-UV-pumped LED applications.5–10 Near-UV-pumped LEDs with multi-component phosphors can offer superior color uniformity, a high color-rendering index ($R_g$ > 90), and excellent light quality. In this article, we report a new Eu$^{2+}$-doped phosphor, Na$_{2-x}$Al$_2-x$Si$_x$O$_4$;Eu$^{2+}$ (0 ≤ x ≤ 1), that is potentially applicable to white LEDs. The crystal structure of Na$_{2-x}$Al$_2-x$Si$_x$O$_4$ is highly similar to that of the cristobalite-like structure of silicon dioxide, which is an important industrial material because of its excellent mechanical properties, such as a high chemical and thermal stability. The persistence of cristobalite outside of its thermodynamic stability range occurs because the transition from the α-phase to the β-phase requires breaking up and reforming the silica framework. In addition, the tetrahedral units of the framework structures are usually very stiff but are rather loosely joined at the shared corner atoms with a constant bond-bending force at the corners. A rich variety of structures results from the many different ways in which tetrahedra can be linked to form corner-sharing arrays. The structure of Na$_{2-x}$Al$_2-x$Si$_x$O$_4$ is similar to that of β-cristobalite, which is described as a “stuffed” cristobalite, and the stuffed cristobalite can be derived from β-cristobalite by partial cross-substitution of Si$^{4+}$ with Al$^{3+}$; β-cristobalite is subsequently stabilized by trapping Na$^+$ cations in the interstices of the (Si,Al)-O$_4$ network. The charge imbalance caused by the substitution of Al$^{3+}$ for Si$^{4+}$ induces crystal distortion, and a crystal structure transition occurs. The synthetic composition Na$_{2-x}$Al$_2-x$Si$_x$O$_4$ is well known as a sodium aluminate-carnegieite system with five...
different structure types based on distortions of the ideal β-cristobalite structure type.\textsuperscript{11,12} The distorted β-cristobalite type of structures has a continuous channel parallel to the c direction and two large interstitial sites at 1/2,1/2,1/2 and 3/4,3/4,3/4 in the Na\textsuperscript{+} channel.\textsuperscript{11} In this study, these interstitial Na\textsuperscript{+} sites have been used as activator sites for Eu\textsuperscript{2+} cations to provide luminescence. Eu\textsuperscript{2+}-doped silicate generally shows superior absorption in the spectral region of 250–400 nm, and because the 4f–5d transition of the Eu\textsuperscript{2+} ion is sensitive to the crystal field and covalency, the Eu\textsuperscript{2+}-doped silicate has strong absorption in the UV-to-visible spectral region and exhibits broad emission bands from blue to red.\textsuperscript{13,14} Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12} is expected to be a good candidate as a host material due to its strong absorption in the UV/blue light spectral region, its long wavelength emissions, and material design flexibility based on the simplicity of changing the (Si,Al)-O\textsubscript{4} network.

In this study, the structure and optical properties of a new color-tunable phosphor system, Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+}, were investigated. To the best of our knowledge, there has been no reported study on the Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12} stoichiometry of complex compositions, such as Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+}, using this method. In this study, the Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+} phosphor was synthesized successfully. In addition, the emission color of synthesized Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+} (0 ≤ x ≤ 1) phosphors can be easily tailored from blue to orange via tuning of the x value. This paper also reports the dependency of the emission properties of the Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+} (0 ≤ x ≤ 1) phosphors upon the Eu concentration. Finally, we succeeded in fabricating white-emitting UV LEDs and thoroughly examined their optical properties.

2. Experimental

2.1 Sample preparation

Powder samples of Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+} (0 ≤ x ≤ 1) were prepared by the solution method using proper amounts of aluminium nitrate nonahydrate (Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O ≥ 98%, Aldrich), sodium nitrate (NaNO\textsubscript{3} ≥ 99.99%, Aldrich), tetraethyl orthosilicate (TEOS; Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}, 99.999%; Aldrich), and europium(III) chloride hexahydrate (EuCl\textsubscript{3}·6H\textsubscript{2}O, 99.99%; Aldrich) as starting materials. All materials were dissolved in water (solution A) with the exception of TEOS, which was mixed with ethanol (solution B). After solutions A and B were prepared, they were thoroughly mixed together. Subsequently, a transparent mixture solution was obtained that had a pH < 2. The mixtures were dehydrated in an oven at 120 °C until the solvent dried completely. The dried powders were then annealed at 1300 °C in a reducing atmosphere of H\textsubscript{2}/N\textsubscript{2} (5%/95%) for 3 h. During a preliminary study, we observed that annealing at temperatures >1300 °C led to a significant loss of Na. The solution method was based on TEOS hydrolysis. TEOS is generally used as an Si source according to the following reaction equation:\textsuperscript{15}

\[
\text{Si(OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{C}_2\text{H}_3\text{OH}
\]

in ethanol at pH < 2.

2.2 Characterization

Room-temperature photoluminescence (PL) spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer PL system equipped with a xenon lamp (500 W) as an excitation source scanning the wavelength of 400–800 nm. X-Ray diffraction (XRD) data were obtained over a range of 10° ≤ 2θ ≤ 120° at 0.02° steps using a Cu-Kα radiation source (Philips X’Pert). Crystal structure refinement employed the Rietveld method as implemented in the General Structure Analysis System (GSAS) software suite.\textsuperscript{16} For time-resolved PL measurements, frequency-tripled Ti:sapphire laser pulses (~100 fs; Mira 900) were used to excite the phosphor at a wavelength of 390 nm, and a commercial time-correlated single-photon counting system was used for detection.

2.3 Fabrication of white LEDs

In the white LED fabrication, near-UV LED chips (λ\textsubscript{max} = 395 nm) were combined with Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+} phosphors, a blue-emitting BaMgAl\textsubscript{10}O\textsubscript{17}:Eu\textsuperscript{2+} phosphor, and green-emitting Ba\textsubscript{2}SiO\textsubscript{4}:Eu\textsuperscript{2+} phosphors. Optical properties, such as the luminescence spectra, color-rendering index (R\textsubscript{a}), and Commission International de l’Eclairage (CIE) color coordinates of the white LEDs, were characterized using an Xe lamp (500 W) with a DARS\textsubscript{A} PRO 5100 PL system (PSI Scientific Co. Ltd., Korea) and evaluated under varied forward biases of constant currents in which the light output was collected and measured using an integrating sphere.

3. Results and discussion

3.1 XRD refinement and crystal structure

Fig. 1 shows the composition phase diagram of the Eu\textsuperscript{2+}-doped sodium aluminate–carnegieite Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+} (0 ≤ x ≤ 1) system. An orthorhombic-type structure was obtained from Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+} at x = 0.25. At x = 0.35, tetragonal phase was observed, whereas a cubic β-cristobalite-type structure was observed at x = 0.55.\textsuperscript{11,12,17} In the Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+} phosphor system, it is assumed that Eu\textsuperscript{2+} (r = 0.117 nm when coordinate number (CN) = 6 and r = 0.100 nm when CN = 7) ions occupied the Na\textsuperscript{+} (r = 0.102 nm when CN = 6) sites because both the Al\textsuperscript{3+} (r = 0.039 nm) and the Si\textsuperscript{4+} (r = 0.026 nm) sites are too small to take the Eu\textsuperscript{2+} ions.\textsuperscript{18} To control the x values in the Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12}:Eu\textsuperscript{2+} system, the ratio of Al or Na to the Si content was controlled. Table 1 gives the results of the preparation

![Fig. 1 Composition phase diagram of Na\textsubscript{2}–Al\textsubscript{2}–Si\textsubscript{4}O\textsubscript{12} (0 ≤ x ≤ 1).](image-url)
with different mole ratios of NaNO₃ or Al(NO₃)₃ : TEOS (as a Si source). The initial phase was Na₁.₄₅Al₁.₄₅Si₀.₅₅O₄ with a 2 : 1 ratio of NaNO₃ or Al(NO₃)₃ to TEOS. When the ratio of the NaNO₃ or Al(NO₃)₃ to TEOS was varied from 0.8 : 1 to 5.6 : 1, the Na₂₋ₓAlₓ₋ₓSiₓO₄ structure from orthorhombic (x = 0.25) to orthorhombic (x = 0.45) to tetragonal (x = 0.35) and orthorhombic Na₁.₇₅Al₁.₇₅Si₀.₂₅O₄ (x = 0.25) mixture phases were observed. Finally, a phase of orthorhombic Na₁.₅₅Al₁.₅₅Si₀.₅₅O₄ (x = 0.25) was obtained when the Al content was 4.4-fold higher than the Si content. We demonstrated that crystal distortions of the Na₂₋ₓAlₓ₋ₓSiₓO₄:Eu²⁺ phosphor systems are generated by the different ratios of Al to Si. The crystal structure of the Na₂₋ₓAlₓ₋ₓSiₓO₄:Eu²⁺ phosphor system was strongly dependent on the x value, which was controlled by the Al and Na contents in the Na₂₋ₓAlₓ₋ₓSiₓO₄:Eu²⁺ system and induced the crystal distortion. Increasing Al and Na contents resulted in a decreased x value, which led to a change in the crystal structure from orthorhombic (x = 0.85) to cubic (x = 0.55) to orthorhombic (x = 0.45) to tetragonal (x = 0.35) and finally to orthorhombic (x = 0.25). In this study, the three phases—cubic, tetragonal, and orthorhombic—were represented by the Na₂₋ₓAlₓ₋ₓSiₓO₄:Eu²⁺ phosphor systems.

To obtain the crystal properties of the Na₂₋ₓAlₓ₋ₓSiₓO₄ with varied x values, a Rietveld refinement using X-ray powder diffraction was performed. Fig. 2 shows the Rietveld refinement of the XRD profiles of a Na₂₋ₓAlₓ₋ₓSiₓO₄ sample series (x = 0.25, 0.35, and 0.55). Based on the Rietveld refinement results, negligible amounts of impurity phases were identified in the samples. Initial structural models to approximate the actual Na₂₋ₓAlₓ₋ₓSiₓO₄ structure were constructed using previously reported crystallographic data. The final weighted R factors (Rwp) of the samples were successfully converged at a satisfactory level, and the refined structural parameters of Na₂₋ₓAlₓ₋ₓSiₓO₄ are listed in Table 2.

Fig. 3 displays the unit cell of the Na₂₋ₓAlₓ₋ₓSiₓO₄:Eu²⁺ representation with various x values. The parent structure of all of the sodium aluminate–carnegieite samples is a partially stuffed C9 structure with an ideal cubic lattice parameter, in which some proportion of the 12-coordinate interstitial sites is filled with Na⁺ to balance the negative charge created by the substitution of Si.

### Table 1 Products formed with different concentrations of excess Na and Al ions in the reaction mixture

<table>
<thead>
<tr>
<th>Serial no.</th>
<th>Reaction mixture</th>
<th>Product</th>
<th>Crystal structure</th>
<th>JCPDS #</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.8 : 0.8 : 1</td>
<td>1 : 1 : 1</td>
<td>Low-carnegieite</td>
<td>78-1588</td>
</tr>
<tr>
<td>2</td>
<td>1.4 : 1.4 : 1</td>
<td>1 : 1 : 1 + 1.15 : 1.15 : 0.85</td>
<td>Low-carnegieite + orthorhombic</td>
<td>78-1588 + 49-0007</td>
</tr>
<tr>
<td>3</td>
<td>2 : 2 : 1</td>
<td>1.45 : 1.45 : 0.55</td>
<td>Cubic</td>
<td>49-0002</td>
</tr>
<tr>
<td>4</td>
<td>2.6 : 2.6 : 1</td>
<td>1.45 : 1.45 : 0.55 + 1.55 : 1.55 : 0.45</td>
<td>Cubic + orthorhombic</td>
<td>49-0006</td>
</tr>
<tr>
<td>5</td>
<td>3.2 : 3.2 : 1</td>
<td>1.65 : 1.65 : 0.35</td>
<td>Tetragonal</td>
<td>49-0005</td>
</tr>
<tr>
<td>6</td>
<td>3.8 : 3.8 : 1</td>
<td>1.75 : 1.75 : 0.25</td>
<td>Orthorhombic</td>
<td>49-0004</td>
</tr>
<tr>
<td>7</td>
<td>4.4 : 4.4 : 1</td>
<td>1.75 : 1.75 : 0.25</td>
<td>Orthorhombic</td>
<td>49-0004</td>
</tr>
<tr>
<td>8</td>
<td>5 : 5 : 1</td>
<td>1.75 : 1.75 : 0.25</td>
<td>Orthorhombic</td>
<td>49-0004</td>
</tr>
<tr>
<td>9</td>
<td>5.6 : 5.6 : 1</td>
<td>1.75 : 1.75 : 0.25</td>
<td>Orthorhombic</td>
<td>49-0004</td>
</tr>
</tbody>
</table>

### Table 2 Rietveld refinement and crystal property data of Na₂₋ₓAlₓ₋ₓSiₓO₄ phosphors

<table>
<thead>
<tr>
<th>Formula</th>
<th>x = 0.25</th>
<th>x = 0.35</th>
<th>x = 0.55</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation type</td>
<td>CuKα</td>
<td>CuKα</td>
<td>CuKα</td>
</tr>
<tr>
<td>2θ range (degree)</td>
<td>10–120</td>
<td>10–120</td>
<td>10–120</td>
</tr>
<tr>
<td>T/K</td>
<td>295</td>
<td>295</td>
<td>295</td>
</tr>
<tr>
<td>Symmetry</td>
<td>Orthorhombic</td>
<td>Tetragonal</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbc̅</td>
<td>P4₁2₁2</td>
<td>P2₁</td>
</tr>
<tr>
<td>a/Å</td>
<td>10.451(2)</td>
<td>10.385(1)</td>
<td>14.577(5)</td>
</tr>
<tr>
<td>b/Å</td>
<td>14.291(6)</td>
<td>7.178(5)</td>
<td>—</td>
</tr>
<tr>
<td>c/Å</td>
<td>5.2186(3)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Rp</td>
<td>4.95%</td>
<td>4.79%</td>
<td>5.52%</td>
</tr>
<tr>
<td>Rwp</td>
<td>6.85%</td>
<td>7.10%</td>
<td>3.85%</td>
</tr>
<tr>
<td>X²</td>
<td>9.518</td>
<td>11.36</td>
<td>7.16</td>
</tr>
</tbody>
</table>

*The numbers in parentheses are the estimated standard deviations of the last significant figure.*
with Al in the tetrahedral framework. The O-atom sites are always fully occupied, whereas the average occupancies of the framework metal and Na sites are dependent upon the Na2/Al2-SiO4:Eu2+ composition. The ideal C9-type parent structures for the x = 0.25, 0.35, and 0.55 phases have cubic unit-cell parameters of 8.038, 8.008, and 7.964 Å, respectively. The stuffed C9 structure shows remarkably diverse chemistry attributable to the intrinsic flexibility of the Al-O-Si linkages.

### 3.2 Photoluminescence properties

Variations in the excitation (PLE) and emission (PL) spectra of the three Na2-xAl2-xSiO4:Eu2+ phosphor systems depending on the x value are shown in Fig. 4a and b, respectively. In the PLE spectra, the excitation peaks of the Na2-xAl2-xSiO4:Eu2+ phosphor systems were recorded at 250–500 nm. The excitation band corresponds to the transition from the 4f ground state to the 4f5d excited state of an Eu2+ ion. Fig. 4b shows the dominant emission wavelengths of Na2-xAl2-xSiO4:Eu2+ at various x values, which demonstrates that full-color emission was realized via changing of the x value in the three phosphor systems. The asymmetric emission spectra show that the Eu2+ ions have more than one emission center in the lattice. Consequently, it was deconvoluted into Gaussian components indicating different symmetry sites of the Eu2+ ion.

![Fig. 3 Unit cell representation of Na2-xAl2-xSiO4:Eu2+ phosphors along the [010] axis according to x values 0.25, 0.35, and 0.55. The red, yellow, and blue spheres represent Al or Si, Na, and O atoms, respectively.](image)

**Fig. 3** Unit cell representation of Na2-xAl2-xSiO4:Eu2+ phosphors along the [010] axis according to x values 0.25, 0.35, and 0.55. The red, yellow, and blue spheres represent Al or Si, Na, and O atoms, respectively.

By Gaussian deconvolution, the emission spectra of the Na2-xAl2-xSiO4:Eu2+ at various x values can be decomposed into 4, 3, and 8 Gaussian profiles with peaks centered at 467 nm (21 413 cm⁻¹), 503 nm (19 880 cm⁻¹), 566 nm (17 667 cm⁻¹), and 635 nm (15 748 cm⁻¹) (Fig. 4a, black dotted lines) and 580 nm (17 241 cm⁻¹), 670 nm (14 925 cm⁻¹), and 760 nm (13 157 cm⁻¹) (Fig. 4b, red dotted lines) and 500 nm (20 000 cm⁻¹), 524 nm (19 083 cm⁻¹), 544 nm (18 382 cm⁻¹), 565 nm (17 699 cm⁻¹), 590 nm (16 949 cm⁻¹), 614 nm (16 286 cm⁻¹), 640 nm (15 625 cm⁻¹), and 667 nm (14 992 cm⁻¹) (Fig. 4c, blue dotted lines), respectively. These peaks can be ascribed to different emission sites, which could be identified as the different coordination environments (Table S1†) of the Na⁺ ions being occupied by Eu²⁺ ions (ESI†). Variations in the excitation and emission spectra were attributed to changes in the environment surrounding the Eu²⁺ ions originated from different symmetry sites. The 4f⁰ → 4f⁵d transition of Eu²⁺ is strongly dependent on the host lattice because the outermost 5d orbit is highly sensitive to its crystal-field surroundings. Upon excitation at a wavelength of 395 nm, the internal quantum efficiencies of phosphors were found to be 2%, 6.5%, and 10.2% for x = 0.25, 0.35, and 0.55, respectively, as shown in Table 3. The various emission bands at 470–600 nm, which had wider full widths at half maximum (FWHM) than at 120 nm, were observed at different x values of 0.25–0.55. This finding implies that the incorporation of Na2-xAl2-xSiO4:Eu2+ into white LEDs may provide an improved color-rendering index.

![Fig. 4 Normalized PL spectra: (a) excitation and (b) emission of Na2-xAl2-xSiO4:Eu2+ phosphor systems as a function of the x value.](image)

**Fig. 4** Normalized PL spectra: (a) excitation and (b) emission of Na2-xAl2-xSiO4:Eu2+ phosphor systems as a function of the x value.

**Table 3** Spectral parameters for the Na2-xAl2-xSiO4:Eu2+ phosphor systems, quantum efficiency (QY), peak position of PL (Pem), and emission width (FWHMem)

<table>
<thead>
<tr>
<th>x Value</th>
<th>QY (%)</th>
<th>Pem/nm</th>
<th>FWHMem/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>10.2</td>
<td>550</td>
<td>155</td>
</tr>
<tr>
<td>0.35</td>
<td>6.5</td>
<td>600</td>
<td>180</td>
</tr>
<tr>
<td>0.25</td>
<td>2</td>
<td>470</td>
<td>175</td>
</tr>
</tbody>
</table>
emission behavior of these three phosphor systems with different \( x \) values is due to the different local structures around the Eu\(^{2+}\) ions. When Eu\(^{2+}\) substituted for singly charged Na\(^+\), the charge-compensating positive ion vacancy is necessary and it is expected to be located at one of the nearest Na\(^+\) sites around the Eu\(^{2+}\) ion. The position of vacancy strongly depends on the nearest-neighbor Na\(^+\) site and induces three different site symmetries, tetragonal \( C_{4v} \), trigonal \( C_{3v} \), and orthorhombic \( C_{2v} \) for the Eu\(^{2+}\) ion. As the crystal structure of the phosphor system changes, the local surroundings of the Eu\(^{2+}\)-substituted sites are significantly changed due to bond-length changes between the activator cation and the ligand anion. The different crystal structures cause changes to the local surroundings of the Eu\(^{2+}\)-substituted sites, namely a different crystal field. Crystal field splitting \( (D_q) \) is expressed as follows:\(^{22}\)

\[
D_q = \frac{1}{6} Z e^2 \frac{r^4}{R^6}
\]

(1)

where \( D_q \) is a measure of the energy level separation, \( Z \) is the valence charge of the anion ligand, \( e \) is the electron charge, \( r \) is the radius of the \( d \)-wave function, and \( R \) is the bonding length between the activator cation and the ligand anion. When Na\(^+\) is substituted by the larger Eu\(^{2+}\) ion, the distance between Eu\(^{2+}\) and O\(^{2-}\) becomes shorter, and the magnitude of the crystal field increases; as a result, the \( 5d \) band of Eu\(^{2+}\) is decreased, and the emission wavelength is red-shifted with increasing Eu\(^{2+}\) concentrations in all of the Na\(_{2-x}\)Al\(_x\)Si\(_2\)O\(_4\):Eu\(^{2+}\) phosphor systems regardless of the \( x \) value. As shown in Fig. 5e, the optimum Eu\(^{2+}\) concentrations of the \( x = 0.25, 0.35, \) and 0.55 systems were found to be 0.01, 0.05, and 0.05, respectively, and their optimized emission intensities were observed at those points. A continuously increased emission intensity (up to 0.05 mol) was seen for the \( x = 0.35 \) system due to phase transition.

The decrease in emission intensity beyond a critical concentration of Eu\(^{2+}\) can be explained by concentration quenching. This is mainly caused by the energy transfer among Eu\(^{2+}\) ions in the Na\(_{2-x}\)Al\(_x\)Si\(_2\)O\(_4\) lattice, which results in non-radiative energy, and the non-radiative transition increases with increasing Eu\(^{2+}\) content.\(^{23}\) A plausible reason for the different concentration-quenching behaviors may be the symmetry-related energy transfer behavior. The concentration-quenching behaviors also suggest that the Eu\(^{2+}\) ions in the \( x = 0.25 \) phosphor system are located in a heavily distorted cation environment relative to Eu\(^{2+}\) in the \( x = 0.55 \) phosphor system. The characteristic of concentration quenching of Na\(_{2-x}\)Al\(_x\)Si\(_2\)O\(_4\):Eu\(^{2+}\) phosphors can be confirmed through the observed dependence of the fluorescence decay curves on the \( x \) values. A long decay time is characteristic of most symmetrical surroundings, whereas a shorter decay time can be observed when site distortion occurs.\(^{24,25}\) It might be presumed that the distorted crystal has a higher number density of defect impurities that act as quenching sites. With increasing quenching sites, nonradiative transition is dominant and shows decreased radiative decay time according to the relationship

\[
\frac{1}{\tau_{\text{measured}}} = \frac{1}{\tau_{\text{radiative}}} + \frac{1}{\tau_{\text{nonradiative}}}
\]

The decay processes for Na\(_{2-x}\)Al\(_x\)Si\(_2\)O\(_4\):Eu\(^{2+}\) phosphors were also investigated and are shown in Fig. 6. The corresponding luminescent decay times monitored at 390 nm excitation can be fitted well with a second-order exponential decay curve using the following equation:\(^{26,27}\)

\[
I = A_1 \exp (-t/\tau_1) + A_2 \exp (-t/\tau_2)
\]

(2)

where \( I \) is the luminescence intensity, \( A_1 \) and \( A_2 \) are constants, \( \tau \) is the time, and \( \tau_1 \) and \( \tau_2 \) are the respective short and long lifetimes for the exponential components. Using these parameters, the average decay time (\( \bar{\tau} \)) can be determined using the following formula:\(^{28}\)

\[
\bar{\tau} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)
\]

(3)

The average decay times of the \( x = 0.25 \) (orthorhombic) and \( x = 0.35 \) (tetragonal) systems are 0.17 and 0.20 \( \mu \)s, respectively, whereas that of the \( x = 0.55 \) (cubic) system is 0.57 \( \mu \)s. The lattice distortion increased with decreasing \( x \), and the progressive substitution of Al with Si was seen in the tetrahedral framework sites.\(^{19}\) When the \( x \) value decreased, the Na\(_{2-x}\)Al\(_x\)Si\(_2\)O\(_4\):Eu\(^{2+}\)
phosphor systems showed further lattice distortion, which led to many Eu\(^{2+}\) ions occupying lower-symmetry sites, thereby accelerating the decay curve speed and reducing the decay time.

The substituting Eu\(^{2+}\) ion is accompanied by a charge-compensating cation vacancy in one of the adjacent Na\(^{+}\) ion sites in the Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphor system. The charge-compensating vacancy is required to be located close to the impurity to form a stable Eu\(^{2+}\)-vacancy dipole. The site symmetry is C\(_{2v}\) for the orthorhombic structure, C\(_{4v}\) for the tetragonal structure, and C\(_{4v}\) and O\(_h\) for the cubic structures. The C\(_{2v}\) symmetry of the substituting Eu\(^{2+}\) has a stronger coupling with the vacancy than the coupling of Eu\(^{2+}\) with the other site symmetries because of the shortened distance between the vacancy and the substituting Eu\(^{2+}\).\(^{29-31}\) The shortened distance between the vacancy and the Eu\(^{2+}\) resulted in shorter decay times in the x = 0.25 system. The different site symmetries present in the Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphor systems showed different crystal field splittings. As a result, the emission intensities for Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphor is important.

Temperature-dependence of relative emission intensities of all phosphor samples decrease with increasing temperature in the range of 25–175 °C. A decay of 48% for x = 0.25 (470 nm), 41% for x = 0.35 (580 nm), and 21% for x = 0.55 (550 nm), respectively, at 150 °C was observed. The inset displays the activation energy (\(\Delta E\)) of Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphors with various x values showed different crystal field splittings. As a result, the shifted central wavelength of the PL emission toward a longer wavelength with various Eu\(^{2+}\) concentrations induced full-color emission in the Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) (Fig. 7).

3.3 Thermal quenching properties

For the application of white-LEDs, the thermal stability of phosphor is important. Temperature-dependence of relative emission intensities for Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphors with various x values under 389 nm excitation is compared in Fig. 8. The relative emission intensities of all phosphor samples decrease with increasing temperature in the range of 25–175 °C. A decay of 48% for x = 0.25 (470 nm), 41% for x = 0.35 (580 nm), and 21% for x = 0.55 (550 nm), respectively, at 150 °C was observed. The inset displays the activation energy (\(\Delta E\)) of Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphors with various x values. The temperature dependence of the emission intensity is described by a modified Arrhenius equation as follows:\(^{32}\)

\[
I_T = \frac{I_0}{1 + A \exp(-\Delta E/kT)}
\]

where \(I_0\) is the initial emission intensity, \(I_T\) is the intensity at different temperatures, \(\Delta E\) is the activation energy of thermal quenching, \(A\) is a constant for a certain host, and \(k\) is the Boltzmann constant (8.617 \times 10^{-5} \text{ eV K}^{-1}). The \(\Delta E\) values were obtained to be 0.1895 eV for x = 0.25, 0.1981 eV for x = 0.35, and 0.2915 eV for x = 0.55, respectively.

The Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphor with x = 0.25 shows higher thermal stability than those of Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphors with x = 0.35 and 0.55 commodity.

3.4 Electroluminescence (EL) and fabrication of WLEDs

To create LEDs with a high color-rendering index, three types of white LEDs were fabricated using various phosphor combinations together with near-UV-LEDs (\(\lambda_{em} = 395\) nm). The white LEDs used a combination of the Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphor obtained in this study with blue-emitting BaMaAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) and green-emitting Ba\(_2\)SiO\(_4\):Eu\(^{2+}\) phosphors.

Fig. 9 shows the electroluminescence (EL) of the white LED devices under different forward-bias currents in the range of 20–60 mA. The EL spectra and CIE color coordinates are reported for the following combinations: (a) only BaMaAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) mixed in the x = 0.35 system; (b) only BaMaAl\(_{10}\)O\(_{17}\):Eu\(^{2+}\) and Ba\(_2\)SiO\(_4\):Eu\(^{2+}\) mixed with the yellow-emitting Na\(_{1.45}\)Al\(_{45}\)Si\(_{0.55}\)O\(_{4}\):0.05Eu\(^{2+}\) phosphor; and (c) the blue-emitting Na\(_{1.75}\)Al\(_{1.75}\)Si\(_{0.25}\)O\(_{4}\):0.01Eu\(^{2+}\) phosphor mixed with orange-emitting Na\(_{1.65}\)Al\(_{1.65}\)Si\(_{0.35}\)O\(_{4}\):0.05Eu\(^{2+}\) phosphor (Fig. 9). As shown in Fig. 9a–c, each phosphor has a broad emission band in the wide wavelength region. Each emission band was clearly located at approximately 450 nm (B), 510 nm (G), 570 nm (x = 0.55), 460 nm (x = 0.25), and 600 nm (x = 0.35). The EL intensity increased continuously as the applied forward bias current increased. This finding indicates that the Na\(_{2-x}\)Al\(_{2-x}\)Si\(_{O_2}\)Eu\(^{2+}\) phosphor-based white LED device does not show spectral saturation. The measured optical properties of these white LED devices are also summarized in Table 4. All of the white LED devices from the composite phosphors showed higher \(R_a\) values, i.e., (A) \(R_a = 88–90\), (B) \(R_a = 94\), and (C) \(R_a = 91–93\), than those prepared with YAG:Ce\(^{3+}\) in a similar manner. In particular, the blue-emitting phosphor with x = 0.25 mixed with the orange-emitting phosphor with x = 0.35 and the white LEDs (combination C) operated at 20 mA showed a correlated color temperature (CCT) of 4258 K and an excellent \(R_a\) of 93. The \(R_a\) value is close to that of blue, green, and yellow, i.e., the three components of white LEDs (combination B),
although a better color temperature was obtained from blue- and orange-emitting two-component-based white LEDs.

Furthermore, CIE chromaticity coordinates in the ranges of CIE $x = 0.36$ and CIE $y = 0.33-0.34$ were observed. The $R_a$ value is similar to the $R_a$ value of combination B, which combined blue, green, and yellow phosphors. Although the $R_a$ values of the white LEDs combining only Na$_{2-x}$Al$_2_x$Si$_2$O$_4$:Eu$^{2+}$ phosphor systems (combination C) were changed from 93 at 20 mA to 91 at 60 mA, the $R_a$ value is still higher than that of the commercial YAG:Ce$^{3+}$-based white LED. It is anticipated that the Na$_{2-x}$Al$_2_x$Si$_2$O$_4$:Eu$^{2+}$ phosphor will be considered a promising candidate for UV-LED-based white LED applications.

4. Conclusion

In conclusion, the color-changeable new composition Eu$^{2+}$-doped Na$_{2-x}$Al$_2_x$Si$_2$O$_4$ was successfully synthesized using a wet chemical reaction based on TEOS hydrolysis, and its stoichiometry, specifically the $x$ value, could be controlled easily due to the synthesis method. The three different $x$ value-dependent crystal structures were obtained by controlling the ratio of Al or Na to the Si content in that system. Furthermore, the structural distortion of the Na$_{2-x}$Al$_2_x$Si$_2$O$_4$:Eu$^{2+}$ phosphor was strongly dependent on the $x$ value, and the structural distortion induced a transition from a cubic to an orthorhombic phase. Variations in the $x$ value in the Na$_{2-x}$Al$_2_x$Si$_2$O$_4$:Eu$^{2+}$ phosphor caused a change in the PLE and PL spectra, starting with crystal distortion in the host lattice. White LEDs were successfully obtained through the application of Na$_{2-x}$Al$_2_x$Si$_2$O$_4$:Eu$^{2+}$ and orange-emitting Na$_{1.55}$Al$_{1.75}$Si$_{0.25}$O$_4$:Eu$^{2+}$, and a CIE chromaticity coordinate in the range of $x = 0.25-0.35$ and $y = 0.33-0.35$, 5.132–5.527 was observed. Combination C, in particular, which consisted of blue-emitting Na$_{1.75}$Al$_{1.75}$Si$_{0.25}$O$_4$:Eu$^{2+}$ and orange-emitting Na$_{1.65}$Al$_{1.65}$Si$_{0.35}$O$_4$:Eu$^{2+}$, showed a higher $R_a$ value of 0.93 and a lower correlated CCT of ~425 K. Thus, the present phosphor could be a promising candidate as a color-tunable phosphor for white LEDs with high $R_a$ and low CCT values.

Notes and references

25 J. Liu, Y. Wang, X. Yu and J. Li, J. Lumin., 2010, 130, 2171.