(Ba,Sr)Y₂Si₂Al₂O₂N₅ : Eu²⁺: a novel near-ultraviolet converting green phosphor for white light-emitting diodes

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A highly intense green-emitting phosphor BaY₂Si₂Al₂O₂N₅ : Eu²⁺ (BYN : Eu²⁺) peaking at 511 nm was synthesized by a solid state reaction. The structure refinement, luminescence properties of BYN : Eu²⁺ phosphors as well as their thermal quenching and the fabrication of white-light-emitting diodes (W-LEDs) were firstly investigated. By partially substituting Ba by Sr, namely (Ba,Sr)Y₂Si₂Al₂O₂N₅ : Eu²⁺ (BSYN : Eu²⁺), the emission peak was shifted to 565 nm, giving a yellow-orange color, due to the splitting of the 5d energy level. By utilizing a mixture of blue-emitting BaMgAl₁₀O₁₇ : Eu²⁺, green-emitting BYN : Eu²⁺ and red-emitting CaAlSiN₃ : Eu²⁺ phosphors as light converters, an intense white GaN-based n-UV-LED (380 nm) was fabricated to exhibit good color-rendering index R₈ of 84.5 at a correlated color temperature of 5089 K and CIE coordinates of (0.3425, 0.3478). Based on these results, we are currently evaluating the potential application of BYN : Eu²⁺ as a green-emitting near-UV convertible phosphor.

1 Introduction

In recent years, there has been a growing focus on research in the area of white light-emitting-diodes (W-LEDs) due to their merits of being environmentally friendly, highly efficient and having a longer lifetime. Hence, W-LEDs are expected to be a promising candidate to replace conventional incandescent and fluorescent lamps. Typically, white light can be obtained by blue LED chips and the yellow phosphor YAG : Ce³⁺ (YAG). However, the disadvantages of this combination are low color-rendering index and high color temperature due to the deficiency of red emission in the visible spectrum. During the past few years, the W-LEDs fabricated using near-ultraviolet (n-UV) LEDs (380–420 nm) coupled with red, green, and blue phosphors have attracted much attention. Hence, there is an urgent need to develop new n-UV excitable phosphors that can be effectively excited in the near ultraviolet range. Nitride/oxy-nitride hosts are good candidates as host structures due to several merits, such as high chemical stability and good thermal quenching, and exhibit intense luminescence for W-LEDs application when activated with Eu²⁺, such as in SrSi₃N₂O₅, Ca-z-sialon, β-sialon, Sr₂Si₃N₆, and CaAlSiN₃. The barium oxynitride BYN was first reported by Wilson et al. To the best of our knowledge, little research has been carried out into the luminescence properties of europium-doped BYN and its corresponding application in W-LEDs.

In this study, the luminescence properties, thermal stability and the applications in n-UV LED of green-emitting BYN : Eu²⁺ phosphors are reported. The present results demonstrate that BYN : Eu²⁺ and BSYN : Eu²⁺ phosphors exhibited tunable emission color and good thermal stability. The W-LEDs fabricated based on BYN : Eu²⁺ exhibit a good color-rendering index and high luminous efficiency. These results demonstrated that BYN : Eu²⁺ is a promising green-emitting phosphor for n-UV LED application.

2 Experimental

2.1 Materials and synthesis

Polycrystalline phosphors with compositions of (Ba₁₋ₓ₋₅SrₓEu₀ₓ)₂Y₂Si₂Al₂O₂N₅ described are prepared by a solid-state reaction. Briefly, the constituent raw materials BaCO₃ (Aldrich, 99.999%), SrCO₃ (Aldrich, 99.9+%), Y₂O₃ (Aldrich, 99.99%), AlN (Aldrich, 99.99%), n-Si₃N₄ (Aldrich, 99.99%), Eu₂O₃ (Aldrich, 99.99%) are weighed in stoichiometric proportions and ground in the glove box, then sintered under a reducing atmosphere at 1400 °C for 8 h. The products are then obtained by cooling down to room temperature in the furnace, grinding, and pulverizing for further measurements.

2.2 Materials characterization

The composition and phase purity of products were measured by powder X-ray diffraction (XRD) analysis with an X’Pert PRO
advanced automatic diffractometer with Cu-K\(\alpha\) radiation (\(\lambda = 1.5418\) Å) operated at 45 kV and 40 mA. The XRD data were collected in a 2\(\theta\) range from 10° to 80°. The powder XRD structure refinement was carried out in the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The structural refinement of the (Ba0.92Eu0.08)YSi2Al2O2N5 sample was performed by the GSAS program. The measurements of PL and photoluminescence excitation (PLE) spectra were performed by using a Spex Fluorolog-3 spectrofluorometer (Instruments S.A., N.J., U.S.A) equipped with a 450W Xe light source and double excitation monochromators.

3 Results and discussion

3.1 Crystal structure of hexagonal BaYSi2Al2O2N5

D. J. Wilson et al. reported the X-ray single crystal structure data of BaYSi2Al2O2N5.\textsuperscript{13} Because of the consideration of similar ionic radii and stronger luminescence, Yb atoms were replaced by Y atoms in this study. Fig. 1 shows experimental, calculated, and difference results in Rietveld refinement XRD patterns of Eu-doped BaYSi2Al2O2N5 at room temperature by GSAS program. The initial parameters of refinement for BYN : Eu\textsuperscript{2+} sample were referred from the single crystal data of BaYbSi2Al2O2N5. The (Ba0.92Eu0.08)YSi2Al2O2N5 synthesized in this study crystallized as a hexagonal structure with space group \(P6_3mc\). For (Ba0.92Eu0.08)YSi2Al2O2N5, the lattice constants were determined to be \(a = b = 6.11862(5)\) Å, \(c = 9.95227(2)\) Å, and the cell volume was obtained as 322.671(6) Å\(^3\). All atom positions, fraction factors and thermal vibration parameters were refined convergence and satisfied well the reflection condition, \(\chi^2 = 3.80\), \(R_p = 3.93\%\), \(R_{wp} = 5.52\%\) (Table 1). The simulation of the crystal structure of (Ba0.92Eu0.08)YSi2Al2O2N5 using Rietveld refinement is shown in Fig. 2. It consists of SiO\(_4\) and N\(_4\) tetrahedra, which were connected by Ba\textsuperscript{2+} ions. One Ba atom is coordinated by twelve nitrogen atoms with three kinds of distances: 3.07 Å × 6 (Ba-N2/O1), 3.14 Å × 3(Ba-N3/O3), 2.96 Å × 3(Ba-N3/O3). In other words, the average bond length of Eu–N was similar to that of the SrYSi2N5 structure.\textsuperscript{14} Because the coordination numbers of SrYSi2N5 and BaYbSi2Al2O2N5 are both twelve, the Eu–N bond length should be longer than that of other nitride phosphors.\textsuperscript{14,11}

3.2 Photoluminescence properties of BaYSi2Al2O2N5 : Eu\textsuperscript{2+}

Fig. 3 shows the reflectance spectra of the pure BYN host and europium-doped BYN phosphors. The absorption spectrum for the BYN host exhibited an absorption band from 300 nm to 200 nm, which was due to the host absorption. The absorption edge of the BYN host was determined to be 4.9 eV. The strong absorption in the near-UV range (300–500 nm) was observed for the BYN : 8%Eu\textsuperscript{2+} sample, which resulted mainly from the transition of Eu\textsuperscript{2+} that originates from the 4f\(^7\) ground state to the 4f\(^6\)5d excitation state. Fig. 4 shows the PLE/PL spectra of BYN : x%Eu\textsuperscript{2+} phosphors (x = 1, 2, 4, 8, 12, 16). These samples presented a green-emitting band peaking from 510 nm to 535 nm under the optimal excitation wavelength of 365 nm. The emission peaks of BYN : x%Eu phosphors shifted slightly to longer

![Image](Image 80x593 to 252x725)

Fig. 1 Rietveld refinement XRD patterns of Eu-doped BaYSi2Al2O2N5 at room temperature by GSAS program. (experimental – cross, calculated – line, difference – bottom).

![Image](Image 80x593 to 252x725)

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wavelength with increasing Eu$^{2+}$ concentration. The red shift was mainly ascribed to the lattice distortion resulting from the mismatch between larger Ba$^{2+}$ (CN = 12, $R_{Ba} = 1.61$ Å) and smaller Eu$^{2+}$ (CN = 12, $R_{Eu} = 1.45$ Å) radii. The lattice distortion thus caused some changes in the crystal field acting on the Eu$^{2+}$ ions, resulting in the red shift. The Stokes' shifts of BYN : $x$Eu$^{2+}$ phosphors shown in Table 2 were estimated to be 7715 cm$^{-1}$–8265 cm$^{-1}$. These values were slightly larger than those of other oxynitride phosphors, such as MSi$_2$O$_2$N$_2$2/3 : Eu$^{2+}$ for 1700–5100 cm$^{-1}$, published by Y. Q. Li's group. The difference may be due to the larger splitting of the 5d crystal field in the BYN : Eu$^{2+}$ host with higher covalence. The excitation bands, peaking at ~294, ~354 and ~426 nm, were observed to mainly arise from the absorption of the host (~294 nm) and 4f$^5$5d$^1$ multiplets of the Eu$^{2+}$ excited states (~354 nm and ~426 nm). The broad excitation band ranging from 300 to 450 nm was consistent with the reflectance spectrum of BYN : Eu shown in Fig. 3. The broad excitation range was ascribed to the highly covalent nature of Ba$^{2+}$–O(N) bonds and large crystal-field splitting. The value for the centre of gravity, the averaging of the observed excitation maxima of the excitation spectrum, was determined to be 27 000–28 000 cm$^{-1}$. The normalized PL intensity of BYN : Eu$^{2+}$ as a function of doped Eu$^{2+}$ content is also given in Table 2. The optimal doping concentration was observed to be 8 mol%, the PL intensity was found to decline dramatically when the content of Eu$^{2+}$ exceeds 8 mol% due to concentration quenching. The quantum efficiencies of composition-optimized BYN : Eu$^{2+}$ and the (Ba,Sr)$_2$SiO$_4$ : Eu$^{2+}$ commodity excited at 400 nm are determined to be 32.5% and 90.1%, respectively. The lower luminescence of BYN : 8%Eu$^{2+}$ could be further enhanced by process optimization. In order to further estimate the critical energy transfer distance ($R_c$) between these activators in the host, the following equation is valid since there is only one crystallographically distinct Ba$^{2+}$ site in the BYN lattice. As a result, the critical energy transfer distances between Eu$^{2+}$ ions in the phosphor can be calculated by the following equation:

$$R_c = 2 \left( \frac{3V}{4\pi x C N} \right)^{1/3}$$

where $x_c$ is the critical concentration, $N$ is the number of cation sites in the unit cell, and $V$ is the volume of the unit cell. In this case, $V = 322.671$ Å$^3$, $N = 2$ and the critical doping concentration of Eu$^{2+}$ in the BYN host was found to be 0.08. Therefore, $R_c$ of Eu$^{2+}$ was then determined to be 15.68 Å.

### 3.3 Crystal structure and luminescence properties of (Ba,Sr)YSi$_2$Al$_2$O$_2$N$_5$ : Eu$^{2+}$

Fig. 5 shows the XRD patterns of BaYSi$_2$Al$_2$O$_2$N$_5$ and SrYSi$_2$Al$_2$O$_2$N$_5$. The results of similar XRD patterns indicate that these two samples are isostructural. The dependence of the emission spectra of (Ba$_{1-x}$Sr$_x$)YSi$_2$Al$_2$O$_2$N$_5$ : 8%Eu$^{2+}$ on Sr composition is shown in Fig. 6. The upper inset of Fig. 6 displays the photos of the series of BSYN : Eu$^{2+}$ phosphors under UV-box excitation at 365 nm. The corresponding luminescence properties of (Ba,Sr)YSi$_2$Al$_2$O$_2$N$_5$ : Eu$^{2+}$ phosphors are given in Table 3. The emission hue of (Ba$_{1-x}$Sr$_x$)YSi$_2$Al$_2$O$_2$N$_5$ : Eu$^{2+}$ changed from green at 510 nm, yellow at 550 nm to orange at 565 nm with an increase in the $x$ value and the CIE coordinates of BSYN : Eu$^{2+}$ could tuned from (0.2923, 0.5771) to (0.4168, 0.5163). The obvious red shift phenomena could be explained by the increase in splitting of the 5d energy level due to the substitution of larger Ba atoms by smaller Sr atoms. With 0.15 mol% Sr substitution, the PL intensity of BSYN : Eu$^{2+}$ was slightly
enhanced by 112%, and decreased with the substitution content above 0.15 mol%. The dramatic drop of luminescence might be due to the mismatch of ionic radii of Ba and Sr, resulting in the shrinkage of the lattice with higher Sr content in the BYN lattice. The results demonstrate that the BYN:Eu2+ is a color tunable phosphor by changing the Ba/Sr ratio, which could be more flexible for the generation of white light by combination of other phosphors and LED chips.

### 3.4 Thermal quenching properties of BaYSi2Al2O2N5:Eu2+

For application in high power LEDs, the thermal stability of phosphors is one of the important issues to be considered. The temperature dependence of the PL spectra for the BYN:Eu2+ phosphor under excitation at 380 nm is shown in Fig. 7. The activation energy ($E_a$) can be expressed by

$$\ln \left( \frac{I}{T} \right) = \ln A - \frac{E_a}{kT}$$

where $I_o$ and $I$ are the luminescence intensities of BYN:Eu2+ at room temperature and testing temperature, respectively; $A$ is a constant; $k$ is the Boltzmann constant ($8.617 \times 10^{-5}$ eV K$^{-1}$). The $E_a$ was obtained to be 0.25 eV K$^{-1}$. The inset displays and compares the thermal quenching property of BYN:Eu2+ and the green-emitting (Ba,Sr)$_2$SiO$_4$ :Eu$^{2+}$ commodity. As shown in Fig. 7, we observed that the thermal stability of BYN:Eu2+ was similar to that of the green commodity phosphor.

### Table 2

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\lambda_{ex}/$nm</th>
<th>$\lambda_{em}/$nm</th>
<th>Stokes shift/cm$^{-1}$</th>
<th>Centre of gravity/cm$^{-1}$</th>
<th>$E_a$/cm$^{-1}$</th>
<th>Normalized PL intensity (%)</th>
<th>CIE ($x$, $y$)</th>
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<tr>
<td>0.01</td>
<td>294, 354, 426</td>
<td>510</td>
<td>7715</td>
<td>27 933</td>
<td>10 539</td>
<td>72</td>
<td>(0.2345, 0.5577)</td>
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<tr>
<td>0.02</td>
<td>291, 358, 425</td>
<td>512</td>
<td>7866</td>
<td>27 933</td>
<td>10 484</td>
<td>62</td>
<td>(0.2410, 0.5540)</td>
</tr>
<tr>
<td>0.04</td>
<td>291, 354, 425</td>
<td>515</td>
<td>8055</td>
<td>28 038</td>
<td>10 835</td>
<td>89</td>
<td>(0.2655, 0.5698)</td>
</tr>
<tr>
<td>0.08</td>
<td>289, 362, 429</td>
<td>519</td>
<td>8054</td>
<td>27 777</td>
<td>11 292</td>
<td>100</td>
<td>(0.2923, 0.5771)</td>
</tr>
<tr>
<td>0.12</td>
<td>289, 362, 433</td>
<td>527</td>
<td>8125</td>
<td>27 675</td>
<td>11 307</td>
<td>80</td>
<td>(0.3164, 0.5856)</td>
</tr>
<tr>
<td>0.16</td>
<td>291, 359, 433</td>
<td>533</td>
<td>8265</td>
<td>27 701</td>
<td>11 270</td>
<td>64</td>
<td>(0.3477, 0.5779)</td>
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### Table 3

<table>
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<tr>
<th>Sr</th>
<th>$\lambda_{em}$/nm</th>
<th>Normalized PL intensity (%)</th>
<th>CIE ($x$, $y$)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>519</td>
<td>100</td>
<td>(0.2923, 0.5771)</td>
</tr>
<tr>
<td>0.1</td>
<td>528</td>
<td>112</td>
<td>(0.3260, 0.5676)</td>
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<tr>
<td>0.2</td>
<td>533</td>
<td>106</td>
<td>(0.3418, 0.5863)</td>
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<tr>
<td>0.4</td>
<td>545</td>
<td>82</td>
<td>(0.3980, 0.5528)</td>
</tr>
<tr>
<td>0.6</td>
<td>550</td>
<td>56</td>
<td>(0.4075, 0.5290)</td>
</tr>
<tr>
<td>0.8</td>
<td>565</td>
<td>17</td>
<td>(0.4168, 0.5163)</td>
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</table>
three-phosphors-converted LED and single-phosphor-converted lamp LEDs shown in the inset exhibited highly intense luminescence, indicating that BYN : Eu\textsuperscript{2+} could be a potential and flexible n-UV-excitable green phosphor for applications in displays and illumination.

4 Conclusions

In summary, a green-emitting BaYSi\textsubscript{2}Al\textsubscript{2}O\textsubscript{2}N\textsubscript{5} : Eu\textsuperscript{2+} phosphor has been reported in this study. By introducing Sr atoms into the host, the emission hue was slightly changed from green to yellow to orange, due to the splitting of the crystal field. The optimal doping concentration of Eu\textsuperscript{2+} was 8 mol\%. The crystal distance of energy transfer was determined to be 15.68 Å. The electroluminescence spectra by combination of 380 nm chip and R/G/B phosphors indicate that the BaYSi\textsubscript{2}Al\textsubscript{2}O\textsubscript{2}N\textsubscript{5} : Eu\textsuperscript{2+} phosphor is a potential candidate for n-UV LED applications.

Acknowledgements

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