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Synthesis of the Phase Pure $\text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2:\text{Eu}^{2+}$ Green Phosphor and its Application in High Color Rendition White LEDs

Wanyuan Li, Rong-Jun Xie, Tianliang Zhou, Lihong Liu, Yuejin Zhu

Abstract

The promising green oxynitride phosphor, $\text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2:\text{Eu}^{2+}$, was synthesized at 1350 °C for 5 hours in a reducing $\text{N}_2/\text{H}_2$ (5%) atmosphere by using the solid-state reaction method. The phase purity was investigated by varying the nominal compositions, and the pure phase was achieved by carefully controlling the Si/Ba and O/Ba ratios. The phosphor displayed a broad excitation band covering from the ultraviolet (UV) to the blue spectral region, and showed a single symmetrical emission band peaking at 525 nm with a full width at half maximum (FWHM) of ~ 68 nm. The as-prepared green phosphor exhibited a small thermal quenching, remaining 90% of the initial emission intensity when measured at 200 °C. The internal and external quantum efficiencies measured under the 450 nm excitation were 68 and 38%, respectively. Color temperature-tunable white LEDs with high color rendering index of $Ra = 88-94$ were attained by combining the prepared green phosphor and a red phosphor $\text{Sr}_2\text{Si}_3\text{N}_6:\text{Eu}^{2+}$ with a blue LED chip.

1. Introduction

White light-emitting diodes (LEDs) are considered as next generation solid state lighting sources due to their high efficiency, long lifetime, robustness and environment friendly. Phosphor is one of key components in these devices. White LEDs, commercialized in 1996, are commonly fabricated by combining a blue GaInN LEDs with a yellow (Y, Gd)$_3$(Al, Ga)$_5$O$_{12}$:Ce$^{3+}$ (YAG:Ce) phosphor. The YAG:Ce phosphor shows a high luminescence efficiency and chemical stability. However, it is lack of enough red components in its spectrum, making the white LEDs only has a medium color rendering index ($Ra < 80$). To attain high color rendition white LEDs ($Ra > 80$), highly efficient green and red phosphors are generally required. Recently, rare earth-activated nitride/oxynitride luminescent materials have attracted much attention because of their excellent photoluminescent properties for white LEDs applications, which include Eu$^{2+}$-doped red $\text{M}_2\text{Si}_2\text{N}_4$ ($\text{M} = \text{Ba}, \text{Sr}$ and $\text{Ca}$), green $\beta$-$\text{SiAlON}$, MSi$_2$O$_3$N$_2$ ($\text{M} = \text{Ba}, \text{Sr}, \text{Ca}$), and $\text{Sr}_3\text{Al}_5\text{Si}_2\text{N}_{3x}\text{O}_{2x}$ ($x = 0$), as well as $\text{Ce}^{3+}$-activated yellow $\text{CaAlSiN}_3$, $\text{Y}_3\text{Si}_5\text{N}_x\text{O}_{12}$, $\text{La}_3\text{Si}_5\text{N}_x\text{O}_{12}$, and $\text{SrAlSi}_4\text{N}_7$. Differing from other counterparts, $\text{Ba}_3\text{Si}_6\text{O}_9\text{N}_4:\text{Eu}^{2+}$ exhibits strong thermal quenching and a low luminescence efficiency at room temperature.

A number of highly efficient green phosphors, including orthosilicate ($\text{Sr}_2\text{Si}_2\text{O}_4:\text{Eu}^{2+}$, $\text{Ba}_2\text{Si}_2\text{O}_4:\text{Eu}^{2+}$), thiogallate ($\text{MGa}_2\text{S}_4:\text{Eu}^{2+}$, $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) and yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$), have been developed for use in white LEDs. On the other hand, these phosphors (except $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$) are suffering from large thermal quenching and serious moisture sensitivity, making them hard to be used in highly reliable white LEDs. Recently, europium doped green phosphors in the system of $\text{Ba}_3\text{Si}_6\text{O}_{12-x}\text{N}_2:\text{Eu}^{2+}$ with $(x, y) = (6, 6), (9, 4), (12, 2), (15, 0)$ have attracted great attention due to the easy synthesis, high thermal quenching temperature (except $\text{Ba}_3\text{Si}_6\text{O}_9\text{N}_4$), and high quantum efficiency. Among these, $\text{Ba}_3\text{Si}_6\text{O}_{12-x}\text{N}_2:\text{Eu}^{2+}$ has been extensively investigated in terms of its structure, photoluminescence as well as mechanoluminescence. Differing from other counterparts, $\text{Ba}_3\text{Si}_6\text{O}_{12-x}\text{N}_2:\text{Eu}^{2+}$ exhibits strong thermal quenching and a low luminescence efficiency at room temperature.
temperature\textsuperscript{28,35}. The reason, suggested by Mikami et al., is that the lowest 5d states of Eu\textsuperscript{2+} are very close to the conduction bands of Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}, and thermally-activated photoionization occurs at room temperature. On the other hand, although it has a similar crystal structure with Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{10}N\textsubscript{4},\textsuperscript{36} Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+} shows smaller thermal quenching and higher luminance\textsuperscript{29}. Furthermore, it exhibits a narrow emission band and high color purity, which has the comparable phospholinescence properties to β-SiAlON:Eu\textsuperscript{2+}, and is thus potentially used for wide color gamut white LEDs.

The synthesis of Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+} often encounters problems of phase purity\textsuperscript{37-39} with orthosilicates formed as impurity phases that significantly decrease the thermal stability of the green phosphor. To achieve phase pure Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+}, some specific synthetic methods have been employed, for instance, high-temperature/high-pressure synthesis\textsuperscript{30} as well as using the Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2} precursor\textsuperscript{30}. However, these approaches are involved with either complicated facilities or multi-step processing. In this work, we attempted to obtain the high purity Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+} phosphor by simply controlling the Si/Ba and O/Ba ratios of the starting powders via the conventional solid state reaction method. The phospholinescence properties of the prepared phosphor were investigated in terms of photoluminescence spectra, quantum efficiency and thermal quenching. Finally, the application of the green phosphor to high color rendition white LEDs was demonstrated.

2. Experimental section

Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+} green phosphors were synthesized by using starting powders of BaCO\textsubscript{3} (Aladdin, AR), SiO\textsubscript{2} (Aladdin, >99%), Si\textsubscript{3}N\textsubscript{4} (UBE E-10, >96%), and Eu\textsubscript{2}O\textsubscript{3} (BAOTOU STEEL RARE-EARTH, >99%). The weighted raw powders were mixed in a mortar and hand packed into the BN crucibles, and then fired in a tube furnace under a reducing atmosphere N\textsubscript{2}/H\textsubscript{2} (5%). The powders were firstly heated to 900 °C at a heating rate of 10 °C min\textsuperscript{-1}, and then to 1350 °C at a rate of 6 °C min\textsuperscript{-1}. The holding time for all samples was 5 hours. After firing, the samples were cooled down to room temperature in the furnace.

The phase purity of Ba\textsubscript{3-x}Eu\textsubscript{x}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2} (x=0.05~0.3) was analyzed by X-ray powder diffraction (XRD, Advance D8, Bruker, Cu K\textsubscript{α}, λ=1.5418 Å), operating at 40 KV and 40 mA in the 2\textdegree range of 10°~70° with a step size of 0.02° and 0.2 s per step. Photoluminescence spectra were measured at room temperature on a fluorescence spectrophotometer (F-4600, Hitachi) with a 200W Xe-lamp as an excitation source. The thermal quenching was evaluated at the temperature range of 30-350 °C by using a fluorescence excitation and detection system (Firefly HR4000LED, Ocean Optics). The absorption and quantum efficiency of the prepared phosphor were measured using a Hamamatsu MPCD-7000 multichannel photo detector with a 200 W Xe-lamp as an excitation and the reflection spectrum of BaSiO\textsubscript{4} white standards was used for calibration. The morphology of Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+} was observed by scanning electron microscopy (FE-SEM, S-4800, Hitachi). To fabricate white LEDs, the prepared Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+} green phosphor was mixed with a commercial Sr\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu\textsuperscript{2+} red phosphor and epoxy, and the phosphor blend was then mounted on a blue LED chip (460 nm). The optical properties of white LEDs were investigated by a high accuracy array spectroradiometer (Haas-2000, Everfine) under forward-bias current of 20 mA at room temperature.

3. Results and discussion

3.1. Phase identification and microstructure

The target phosphor Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+} was prepared under the flowing N\textsubscript{2} - H\textsubscript{2} (5%) atmosphere through the following chemical reaction:

\[ 6\text{BaCO}_3 + 9\text{SiO}_2 + \text{Si}_3\text{N}_4 \xrightarrow{1350\degree C, H/\text{N}_2+} 2\text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2\text{Eu}^{2+} + 6\text{CO}_2 \]  

The XRD patterns of the samples with different Si/Ba ratios in the starting powders are given in Fig. 1. As seen, the sample with Si/Ba = 2.00, which was stoichiometrically weight out, revealed that most of the high intensity peaks match well with the reported data of Mikami et al.\textsuperscript{27}. It indicates that the Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2} phase was dominated. In addition, some weak diffraction peaks of impurities were detected, which can be identified as orthorhombic Ba\textsubscript{5}Si\textsubscript{8}O\textsubscript{21} and monoclinic Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}. Similar to Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2} consisting of corner sharing [SiO\textsubscript{4}] tetrahedra, both barium orthosilicates were structurally formed by corner-sharing [SiO\textsubscript{4}] tetrahedra, as shown in Fig. 2. By considering the formation temperature of barium orthosilicate\textsuperscript{28}, one can suppose that the Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2} phase forms via the dissolution-diffusion-precipitation stages: (i) the low-melting-point barium orthosilicates firstly emerge when the temperature is up to about 1000 ~ 1200 °C; (ii) when the temperature further rises to ~ 1350 °C, Si\textsubscript{3}N\textsubscript{4} starts to dissolve in the Ba-Si-O liquid phase, (iii) the target phase Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2} then precipitates from the nitrogen saturated liquid phase accompanying with the formation of barium orthosilicates.

Fig. 1 X-ray diffraction patterns of Ba\textsubscript{3-x}Eu\textsubscript{x}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2} with different ratio of Si/Ba

It is seen that the impurity orthosilicate phases (BaSi\textsubscript{2}O\textsubscript{5} and Ba\textsubscript{5}Si\textsubscript{8}O\textsubscript{21}) have the larger O/Ba ratios but smaller (or equal) Si/Ba ratios than Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}, as shown in Table I. This is indicative of deficiency of Si\textsubscript{3}N\textsubscript{4} in the raw materials, caused by the presence of the SiO\textsubscript{2} layer on the partially oxidized Si\textsubscript{3}N\textsubscript{4}. Therefore, in order to suppress the formation of orthosilicates, the excessive amount of Si\textsubscript{3}N\textsubscript{4} in the raw materials was used.

Experimental

The phase purity of Ba\textsubscript{3-x}EuxSi\textsubscript{6}O\textsubscript{12}N\textsubscript{2} (x=0.05~0.3) was analyzed by X-ray powder diffraction (XRD, Advance D8, Bruker, Cu K\textsubscript{α}, λ=1.5418 Å), operating at 40 KV and 40 mA in the 2\textdegree range of 10°~70° with a step size of 0.02° and 0.2 s per step. Photoluminescence spectra were measured at room temperature on a fluorescent spectrophotometer (F-4600, Hitachi) with a 200W Xe-lamp as an excitation source. The thermal quenching was evaluated at the temperature range of 30-350 °C by using a fluorescence excitation and detection system (Firefly HR4000LED, Ocean Optics). The absorption and quantum efficiency of the prepared phosphor were measured using a Hamamatsu MPCD-7000 multichannel photo detector with a 200 W Xe-lamp as an excitation and the reflection spectrum of BaSiO\textsubscript{4} white standards was used for calibration. The morphology of Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+} was observed by scanning electron microscopy (FE-SEM, S-4800, Hitachi). To fabricate white LEDs, the prepared Ba\textsubscript{3}Si\textsubscript{6}O\textsubscript{12}N\textsubscript{2}:Eu\textsuperscript{2+} green phosphor was mixed with a commercial Sr\textsubscript{2}Si\textsubscript{5}N\textsubscript{8}:Eu\textsuperscript{2+} red phosphor and epoxy, and the phosphor blend was then mounted on a blue LED chip (460 nm). The optical properties of white LEDs were investigated by a high accuracy array spectroradiometer (Haas-2000, Everfine) under forward-bias current of 20 mA at room temperature.
Si₃N₄ was added, resulting in higher Si/Ba ratios (>2). As seen in Fig. 1, the amount of both impurity phases reduces with increasing the Si/Ba ratio. Among the two orthosilicates, the content of Ba₅Si₈O₂₁ decreases faster than that of BaSi₂O₅, implying that the excessive Si₃N₄ addition leads to the increments of both the Si/Ba ratio and the amount of SiO₂.

**Table I** Ratios of Si/Ba and O/Ba in Ba₃Si₆O₁₂N₂ and impurity phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>Si/Ba</th>
<th>O/Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₃Si₆O₁₂N₂</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Ba₄Si₆O₁₆</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>Ba₅Si₈O₂₁</td>
<td>1.6</td>
<td>4.2</td>
</tr>
<tr>
<td>BaSiO₃</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>BaSi₂O₅</td>
<td>2</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 3 presents the excitation and emission spectra of Ba₂.₈₅Eu₀.₁₅Si₆O₁₂N₂ with varying Si/Ba ratios. As seen, the spectra show a great similarity except for the luminescence intensity, which are resulted from the same dominant phase Ba₃Eu₀.₁₅Si₆O₁₂N₂. The orthosilicates have no luminescence under the blue light irradiation³¹, ⁴¹, ⁴², they only have an influence in the luminescence intensity of the phosphor. The strongest luminescence is observed when the Si/Ba is equal to 2.08.

Next, as BaSiO₃ is an oxygen-rich phase, and has a higher O/Ba ratio than Ba₅Si₈O₂₁, the O/Ba ratio must be reduced to suppress the formation of BaSiO₃ (while keeping Si/Ba = 2.08). As shown in Fig. 4, the orthosilicate impurity phases turn to disappear with decreasing the O/Ba ratio. A phase pure Ba₃Si₆O₁₂N₂ is finally obtained at O/Ba = 3.52. On the other hand, another two orthosilicates (Ba₅Si₈O₂₁ and BaSi₂O₅) form at O/Ba ratios less than 3.4, both of which have lower Si/Ba and O/Ba ratios than Ba₃Si₆O₁₂N₂ (see Table I). It means that the low O/Ba ratio tends to produce Ba₅Si₈O₂₁ and BaSi₂O₅.

As shown above, the ratios of Si/Ba and O/Ba play an important role in the formation of the pure phase of Ba₃Si₆O₁₂N₂. The stoichiometric ratio of Si/Ba or O/Ba in the starting materials according to Ba₃Si₆O₁₂N₂ cannot lead to a pure phase because the SiO₂ layer on the Si₃N₄ surface is not considered or compensated during weighing out the starting materials. Ba₅Si₈O₂₁ and BaSi₂O₅ easily form with larger Si/Ba and O/Ba ratios in the starting powders, while Ba₄Si₆O₁₆ and BaSiO₃ appear with smaller Si/Ba and O/Ba ratios. The phase pure Ba₃Si₆O₁₂N₂ can be achieved by the careful control of the Si/Ba (2.08) and O/Ba (3.52) ratios through increasing and decreasing the content of Si₃N₄ and SiO₂, respectively.

Figure 5 shows the XRD patterns of Ba₃₋ₓEuₓSi₆O₁₂N₂ (x=0.05~0.3) phosphors with Si/Ba = 2.08 and O/Ba = 3.52. The doping of Eu does not generate any other impurity phases, indicating the accommodation of Eu in the lattice of Ba₃Si₆O₁₂N₂.
A typical SEM image of the as-prepared Eu²⁺-doped Ba₃Si₆O₁₂N₂ is shown in Fig. 6. The phosphor particles are slightly agglomerated, with the primary particle having a size of 3 μm in diameter.

Fig. 6 SEM image of Ba₂.₈₅Eu₀.₁₅Si₆O₁₂N₂ prepared at 1350 °C

### 3.2. Photoluminescence Properties

The Eu²⁺-doped Ba₃Si₆O₁₂N₂ phosphor shows a very broad excitation band with the right tail extending to 500 nm, as illustrated in Fig. 7, which absorbs UV or blue light strongly and matches well with the blue LED chips. Under 310, 360, 430, or the 460 nm excitation, the emission spectra are all symmetric band centered at 525 nm, which owns to the 4f⁶5d¹ → 4f⁷ transitions of Eu²⁺. The full width at half maximum (FWHM) is about 68 nm, which is very suitable for use as a green phosphor in backlight applications.

As seen in Fig. 8, the concentration quenching occurs at x = 0.25 for Ba₃-xSi₆O₁₂N₂:xEu²⁺ (x = 0.05~0.3). It is mainly attributed to the energy transfer among Eu²⁺. The probability of energy transfer is largely dependent on the distance between activator ions. With increasing the amount of doped Eu²⁺, the distance between Eu²⁺ ions shortens, which increases the probability of nonradiative energy transfer between Eu²⁺. As there is a small overlap between the excitation and emission spectra, the contribution of reabsorption to concentration quenching can be omitted. The critical distance for energy transfer can be roughly calculated by using Eq. (2)⁴⁴,

\[ R_c = \frac{2V}{3x(Z)^{1/3}} \]  

(2)

where \( x_c \) is the critical concentration of the activator ion, \( V \) the volume of the unit cell, and \( Z \) the cations number in the unit cell that can be occupied by activator ions. For Ba₃Si₆O₁₂N₂:Eu²⁺, Braun addressed that Eu²⁺, showed in Fig. 2, mainly occupied the Ba₁ site,³⁰ so \( Z = 1 \) instead of \( Z = 3 \). Taking \( x_c = 0.25, V = 316.935 Å³ \) into Eq. (2), the critical distance is then computed to be about 13.43 Å.

Figure 8 also shows the redshift of the emission spectrum with increasing the Eu²⁺ concentration. When the smaller Eu²⁺ ions (r = 1.10 Å) substitute larger Ba²⁺ (r = 1.34 Å) ones, the volume lattice shrinks, resulting in a strong crystal field strength. The redshift is thus ascribed to the enhanced crystal field splitting.
3.3. Thermal quenching

In general, small thermal quenching is required for LED phosphors, especially those used in high-power LEDs, which can minimize the changes in chromaticity and efficiency of white LEDs. Figure 9 shows the temperature-dependent emission spectrum of Ba$_{2.85}$Eu$_{0.15}$Si$_6$O$_{12}$N$_2$. The emission spectrum is blue-shifted as the temperature is raised, which is due to the thermally induced lift up of the lowest 5d energy levels. When the phosphor is heated up to 200 °C, the luminescence still remains 90% of the initial intensity measured at room temperature (see Fig.10). The thermal quenching of Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$ is much smaller than that of Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$ and YAG:Ce$^{3+}$.

Fig. 9 The emission spectra of Ba$_{2.85}$Eu$_{0.15}$Si$_6$O$_{12}$N$_2$ (Si/Ba=2.08 and O/Ba=3.4), excited at 460 nm at varying temperatures.

Thermal quenching can be interpreted by using the configurational coordinate diagram,$^1$, 46, as illustrated in Fig. 11. In the diagram, the X-axis represents the metal-ligand distance $R$, and the Y-axis is the energy $E$ of an absorbing center. The ground state and excited state energy levels quantized for harmonic oscillator are represented by parabola $U_0$ and $U'$, respectively. A crossing point X of parabola $U_0$ and $U'$ is indicated in the diagram, and it is at a higher energy level than point A' that is the excited state energy level of luminescent centers after being promoted by the absorbed energy. Generally, the luminescent centers go through nonradiative relaxation to the lowest vibrational level corresponding to point O'. At this moment, when temperature increases, the centers will be thermally activated from point O' to the junction point X. This means that the excited Eu$^{2+}$ ions easily reach the ground state through the phonon vibration rather than emitting photons. As a result, luminescence owing to the transition from point O' to point A is quenched. The probability of thermal quenching process is strongly dependent on the energy barrier $\Delta E_q$ between point O' and point X. A greater $\Delta E_q$ is the lower thermal quenching of the phosphor. The activation energy for thermal quenching $\Delta E_q$ can be calculated from the Arrhenius equation described by Eq. (3)$^47$.

$$I_T = \frac{I_0}{1 + c \exp(\frac{\Delta E_q}{kT})}$$

(3)

Where $I_0$ is the initial emission intensity, $I_T$ is the intensity at a given temperature $T$, $c$ is a constant, and $k$ is Boltzmann’s constant. The $\Delta E_q$ was calculated to be 0.257 eV by fitting the plot of $\ln(\frac{I_0}{I_T} - 1)$ vs $1/T$. The $\Delta E_q$ value for Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$ is larger than 0.202 and 0.2 eV for Sr- and Ca-$\alpha$-SiAlON:Eu$^{2+}$ phosphors, respectively.$^48$

Fig. 11 Configurational coordinate diagram showing the thermal quenching process

Fig. 12 Absorption, internal and external quantum efficiencies of Ba$_{3-k}$Eu$_k$Si$_6$O$_{12}$N$_2$ (x = 0.15)
3.4. Quantum Efficiency

The absorption efficiency ($\eta_a$), internal quantum efficiency ($\eta_i$) and external quantum efficiency ($\eta_o$) can be obtained by using Eqs. 4-6:49

$$
\eta_a = \frac{\int [E(\lambda) - R(\lambda)]d\lambda}{\int E(\lambda)d\lambda}
$$

(4)

$$
\eta_i = \frac{\int [P(\lambda) - R(\lambda)]d\lambda}{\int E(\lambda)d\lambda}
$$

(5)

$$
\eta_o = \frac{\int P(\lambda)d\lambda}{\int E(\lambda)d\lambda}
$$

(6)

where $E(\lambda)$, $R(\lambda)$, and $P(\lambda)$ are the intensity per unit wavelength in the spectra of excitation, reflectance, and emission of the phosphor, respectively. The absorption and quantum efficiency of Ba$_2$-xEuxSi$_6$O$_{12}$N$_2$ (x = 0.15) as a function of the exciting wavelength are shown in Fig. 12. Under the 450 nm excitation, the absorption, internal and external quantum efficiencies of the green phosphor are 56, 68 and 38%, respectively. These data are lower than those reported by Mikami et al., which could be further enhanced by optimizing the processing conditions and controlling the particle size, morphology, and crystallinity of the phosphor.

3.5. LED applications

White LED lamps were prepared by combining a blue LED chip with red Sr$_2$Si$_4$N$_4$:Eu$^{2+}$ and green Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$ phosphors. The emission spectra of white LEDs with varying correlated color temperatures (CCT), which are obtained by controlling the ratio of phosphors and silicone epoxy (P : G) and the ratio between green and red (P$_G$:P$_R$) phosphors, are given in Fig. 13. As seen, three primary emission bands are centered at 460 (LED chip), 530 (Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$) and 616 nm (Sr$_2$Si$_4$N$_4$:Eu$^{2+}$), respectively. Three emission bands constitute a spectrum that appears white to the naked eye. The optical properties of white LEDs are shown in Table II. As seen, high color rendition is obtained in this work. The average Ra values for white LEDs with varying CCT lie between 88 and 94. Moreover, the R9 values are also quite high, which is acceptable for general lighting. The average luminous efficiency (lm/W) of the white LEDs is 60.6 ~ 75.5 lm/w, which is higher than that of cold cathode fluorescent lamps (50 lm/W, Ra=50 ~ 88). This indicates that the green-emitting Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$ phosphor is very suitable for use in high color rendering white LEDs that replace traditional fluorescent tubes or incandescent bulbs for general illumination.

Conclusions

In this work, Eu-doped Ba$_3$Si$_6$O$_{12}$N$_2$ green phosphors (Ba$_2$-xEuxSi$_6$O$_{12}$N$_2$ (x = 0.05~0.3)) were synthesized by the solid-state reaction at 1350°C for 5 hours under a reducing atmosphere of N$_2$/H$_2$ (5%). The pure phase of Ba$_3$Si$_6$O$_{12}$N$_2$ was obtained by carefully controlling the Si/Ba and O/Ba ratios. The prepared Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$ phosphor showed a symmetrical emission band centered at ~525 nm, and a broad excitation band covering the UV to blue light region. Compared to Ba$_2$SiO$_4$:Eu$^{2+}$ and Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ green phosphors, Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$ exhibited a smaller thermal quenching. High color rendering white LEDs can be achieved by using Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$ and a red phosphor, indicating Ba$_3$Si$_6$O$_{12}$N$_2$:Eu$^{2+}$ is a promising green phosphor for white LEDs.

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Notes and references

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References

A phase pure green $\text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2:\text{Eu}^{2+}$ phosphor (left) was successfully synthesized by controlling the Si/Ba and O/Ba of the starting materials, and it has great potentials to prepare high CRI ($R_a>90$) white LEDs (right).