Photoluminescence properties of $\beta$-SiAlON : Yb$^{2+}$, a novel green-emitting phosphor for white light-emitting diodes

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Abstract
We have synthesized Yb$^{2+}$-activated Si$_{6-z}$Al$_z$O$_z$N$_{8-z}$ (0.05 $\leq$ $z$ $\leq$ 2.3, 0.03 mol% $\leq$ Yb$^{2+}$ $\leq$ 0.7 mol%) green phosphors by solid-state reaction at 1900 °C for 2 h under a nitrogen pressure of 1.0 MPa. Phase purity, photoluminescence and its thermal quenching were investigated. A single phase was obtained for all values of $z$ and Yb$^{2+}$ concentration. A distinct emission band was observed at 540 nm originating from the 5d–4f electronic transition in Yb$^{2+}$ under 480 nm excitation. The photoluminescence properties mainly depended on the Yb$^{2+}$ concentration and chemical composition of the matrix. The resultant phosphor showed high thermal stability, that is, the emission intensity at 150 °C was about 82% of that measured at room temperature. The experimental results indicate that $\beta$-SiAlON : Yb$^{2+}$ is a potential green phosphor for white light-emitting diodes (LEDs), which use blue LEDs as the primary light source.

Keywords: phosphor, green-emitting, white LEDs, oxynitride, beta-sialon

1. Introduction
Oxynitride or nitride phosphors doped with rare-earth elements often exhibit longer excitation and emission wavelengths than their oxide counterparts, owing to large crystal-field splitting and strong nephelauxetic effect resulting from the coordination of rare-earth ions to nitrogen [1–7]. Besides, the oxynitride and nitride phosphors are expected to have high thermal and chemical stabilities because their matrices are built on stiff frameworks consisting of Si–N or Al–N tetrahedra [8–10]. Therefore, these phosphors have emerged as an important family of luminescent materials and optimal candidates for white light-emitting diodes (LEDs). Examples include $\alpha$-SiAlON : Eu$^{2+}$ [11], LaSi$_3$N$_5$ : Ce$^{3+}$ [8], CaAlSiN$_3$ : Ce$^{3+}$ [12], $M_2$Si$_2$N$_8$ : Eu$^{2+}$ (M = Ca, Sr, Ba) [4], MSi$_2$O$_2$N$_2$ : Eu$^{2+}$ (M = Ca, Sr, Ba) and $\beta$-SiAlON : Eu$^{2+}$ [13]. White LEDs based on such oxynitride or nitride phosphors showed good color rendering properties and high luminous efficiency. $\beta$-SiAlON (Si$_{6-z}$Al$_z$O$_z$N$_{8-z}$, where $z$ represents the number of Al–O pairs substituting for Si–N pairs, 0 $\leq$ $z$ $\leq$ 4) [14, 15] is structurally derived from $\beta$-Si$_3$N$_4$ by equivalent substitution of Al–O for Si–N; it has a hexagonal crystal structure with a continuous channel parallel to the c axis and the P6$_3$ or P6$_3$/m space group. Since it is not necessary for $\beta$-SiAlON to accommodate the metal ions for charge compensation, rare-earth ions have been confirmed to locate in the continuous channel by electron microscopy [16]. Recently, interesting photoluminescence
(PL) properties have been reported in \( \alpha \)-SiAlONs doped with various rare-earth ions (i.e., Eu\(^{2+}\), Yb\(^{2+}\), Ce\(^{3+}\), Tb\(^{4+}\), Sm\(^{2+}\) or Pr\(^{3+}\)), which provide more options for the use in white LEDs [7, 11], [17–19]. Doping these rare-earth ions into \( \beta \)-SiAlON host lattice also can obtain optimal PL properties. Through extensive investigation of Eu\(^{2+}\)-activated \( \beta \)-SiAlON, a green-emitting phosphor has been developed, which is superior to commercial green–yellow phosphors YAG : Ce\(^{3+}\) and ZnS : Cu, Al [13–15], [20, 21]. Similar to Eu\(^{2+}\), Yb\(^{2+}\) commonly exhibits 4f–5d fluorescence. Xie et al [17] reported strong green emission in Yb\(^{2+}\)-doped \( \alpha \)-SiAlON arising from the 4f\(^{14}\)-4f\(^{13}\)5d interconfigurational transitions of Yb\(^{2+}\). In contrast to Yb\(^{2+}\)-doped fluorides, sulfates and phosphates [22–24], this longer-wavelength emission is contributed by the nitrogen-rich location of Yb\(^{2+}\) that leads to the combination of strong crystal-field splitting of the 5d states of Yb\(^{2+}\) and high covalent bonding (nephelauxetic effect) between Yb\(^{2+}\) and (O, N). Previous studies on Ce\(^{3+}\)-doped \( \alpha \)-SiAlON and \( \beta \)-SiAlON [25, 26] found that the latter phosphor has a larger crystal-field splitting and a smaller Stokes shift than the former one. Therefore, Yb\(^{2+}\)-doped \( \beta \)-SiAlON is expected to display interesting PL properties for its application in phosphor-conversion devices, since Yb\(^{2+}\) ions are accommodated in the continuous channel parallel to the c-axis and are coordinated to 6 nitrogen atoms.

In this work, we have prepared \( \beta \)-SiAlON : Yb\(^{2+}\) materials by gas-pressure sintering technique. The effects of the host crystal compositions and Yb\(^{2+}\) concentration on the phase purity and PL properties, as well as thermal quenching behavior, and quantum efficiency of the prepared phosphors were characterized.

2. Experimental details

\( \text{Si}_3\text{N}_4 \) (SN-E10, Ube Industries, Tokyo, Japan), AlN (TAIMICRON, Type F, Tokyo, Japan), \( \text{Al}_2\text{O}_3 \) (TAIMICRON, Daimemi Chemicals Co. Ltd, Tokyo, Japan) and \( \text{Yb}_2\text{O}_3 \) (Shin-Etsu Chemical Co. Ltd, Tokyo, Japan) were used as raw materials. The powders with a total weight of 2 g were thoroughly mixed in a mortar by hand to result in the composition \( \text{Yb}_2\text{Si}_{10-x}\text{Al}_{1+5y}\text{O}_{3+5x}\text{N}_{3-x} \) (0.05 \( \leq x \leq 2.3 \), 0.0003 \( \leq x \leq 0.007 \)). The mixture was sintered by gas-pressure sintering technique, at a constant heating rate of 600 °C h\(^{-1}\), from room temperature to 800 °C, in a vacuum of 10\(^{-2}\) Pa, in a gas-pressure sintering furnace (FVPHR-R-10, FRET-40, Fujiedepa Kogyo Co. Ltd, Osaka, Japan) equipped with a graphite heater. At 800 °C, nitrogen gas (99.9999% purity) was introduced into the chamber, and the temperature was raised to 1900 °C. The samples were held at 1900 °C for 2 h under a nitrogen gas pressure of 1.0 MPa. After firing, power was shut off, and the samples were naturally cooled in the furnace.

Phase purity was characterized by x-ray powder diffraction (XRD, Rigaku RINT2000 operated at 40 kV and 40 mA), using Cu Ka radiation (\( \lambda = 1.5406 \) Å). A step size of 0.02° was used with a scan speed of 2° min\(^{-1}\).

Diffuse reflection spectra were recorded using a UV-vis spectrophotometer with an integrating sphere (JASCO, Ubest V-560). The reflection spectrum of diffuse white standard was used for calibration.

PL spectra of the phosphors were measured at room temperature using a fluorescent spectrophotometer (F-4500, Hitachi Ltd, Tokyo, Japan) with a 150 W Xe lamp as the excitation source. The emission spectra were corrected for the spectral response of the monochromator and a Hamamatsu R928P photomultiplier using a light diffuser and a tungsten lamp (Noma, 10 V, 4 A). The excitation spectra were corrected for the spectral distribution of the Xe lamp intensity by measuring PL from Rhodamine-B.

Quantum efficiency (QE) and temperature-dependent PL measurements (25–250 °C) were conducted using an Otsuka MPCD-7000 multichannel photodetector with a 200 W Xe lamp as the excitation source. QE was measured as follows: the excitation light from the Xe lamp was filtered by the excitation monochromator (300–600 nm range). A white Spectralon standard was illuminated with the resulting monochromatic light. The reflected light was collected by an integrating sphere and sent to an MPCD-7000 multichannel photodetector; this spectrum was used for calibration. Then, the standard was replaced by the tested sample. Excitation \( E(\lambda) \), reflection \( R(\lambda) \) and emission spectra \( P(\lambda) \) were also obtained using the method mentioned above.

Internal \( (\eta_{in}) \) and external \( (\eta_{ex}) \) efficiencies of the sample were calculated with the following equations [27]:

\[
\eta_{ex} = \frac{\int \lambda P(\lambda) d\lambda}{\int \lambda E(\lambda) d\lambda},
\]

\[
\eta_{in} = \frac{\int \lambda P(\lambda) d\lambda}{\int \lambda [E(\lambda) - R(\lambda)] d\lambda},
\]

where \( E(\lambda)/h\nu, R(\lambda)/h\nu, \) and \( P(\lambda)/h\nu \) are the number of photons in the excitation, reflectance and emission spectra of the phosphor, respectively.

3. Results and discussion

3.1. Phase identification

Figure 1 shows the XRD patterns of \( \beta \)-SiAlON : Yb\(^{2+}\) (\( \varepsilon = 0.1 \)) as a function of Yb\(^{2+}\) doping amount. A single hexagonal was revealed for the entire Yb\(^{2+}\) doping range of 0.2–0.7 mol%. It can be concluded that Yb\(^{2+}\) has a relatively large solubility in the \( \beta \)-SiAlON host lattice, comparable to the case of Ce\(^{3+}\) ions in \( \beta \)-SiAlON but a little different from \( \beta \)-SiAlON : Eu\(^{2+}\) [20]. This solubility may be ascribed to the location of rare-earth ions in the continuous channel parallel to the c-axis of \( \beta \)-SiAlON. In this case, small Yb\(^{2+}\) (6 CN, 1.02 Å) and Ce\(^{3+}\) (6 CN, 1.01 Å) ions, which are smaller than Eu\(^{3+}\) (6 CN, 1.17 Å), should be easily introduced into the crystal structure of \( \beta \)-SiAlON.

Figure 2 shows the XRD patterns of \( \beta \)-SiAlON : Yb\(^{2+}\) (Yb\(^{2+}\) = 0.4 mol%) with various \( \varepsilon \) values (\( \varepsilon = 0.1, 0.5, 1.0, 1.5 \) and 2.3). No impurity phases could be detected for any \( \varepsilon \) value. A slight variation in the peak position (inset in figure 2) was observed and assigned to the progressive replacement of shorter Si–N bonds (1.74 Å) by longer Al–O bonds (1.75 Å).
Figure 1. XRD patterns of β-SiAlON doped with Yb$^{2+}$ at various concentrations ($z = 0.1$).

Figure 2. XRD patterns of β-SiAlON : Yb$^{2+}$ ($Yb = 0.4$ mol%) for various $z$ values.

Figure 3. Photoluminescence spectra of β-SiAlON : Yb$^{2+}$ for $z = 0.5$ and Yb $= 0.4$ mol% (ex. = excitation and em. = emission).

Figure 4. Photoluminescence intensity of β-SiAlON as a function of Yb$^{2+}$ concentration at $z = 0.5$.

for larger $z$ values, which caused the expansion of the crystal lattice and the shift of the diffraction peaks toward the lower angles. This high purity of β-SiAlON for various $z$ values implies that the luminescent properties of β-SiAlON : Yb$^{2+}$ can be adjusted to some extent by tailoring the composition, just like for rare-earth-doped α-SiAlON phosphors.

3.2. Photoluminescence properties

Figure 3 shows PL spectra of β-SiAlON : Yb$^{2+}$ ($z = 0.5$, Yb $= 0.4$ mol%). Excitation spectrum, monitored at 540 nm, contains broad bands centered at 260, 305, 355 and 480 nm, which correspond to the crystal field components of 5d level in the excited 4f$^{13}$5d configuration of Yb$^{2+}$. The crystal-field splitting of the 5d level of Yb$^{2+}$ can be estimated as 17 630 cm$^{-1}$ from the figure, which is larger than that of Yb$^{2+}$ in α-SiAlON (12 864 – 13 089 cm$^{-1}$) [17]. This indicates the higher local symmetry around Yb$^{2+}$ in β-SiAlON than in α-SiAlON. Under 480 nm excitation, the emission spectrum shows a typical broad band centered at 540 nm, resulting from the 5d–4f transition in Yb$^{2+}$, and the full width at half maximum (FWHM) of the emission band is about 66 nm. This broad emission band indirectly indicates that Yb ions in the β-SiAlON host lattice assumed the divalent state, owing to the reductive atmosphere of CO produced from the graphite heater in the sintering furnace. This assignment is consistent with the viewpoint that some rare-earth ions, like Eu and Yb, are divalent rather than trivalent in α-SiAlON [10, 11, 17]. The emission spectra of the divalent rare-earth ions, usually arising from the 4f–5d electronic transitions, differ markedly from those of the trivalent ions arising from the 4f–4f transitions [28–30]. They are characterized by broad bands, as shown in figure 3 for Yb in the +2 state in the β-SiAlON host lattice, whereas those of the trivalent ions generally consist of several narrow lines. The Stokes shift can be estimated as 2300 cm$^{-1}$, assuming that the excitation band is the mirror image of the emission band. This relatively small value may be caused by the stiff crystal structure consisting of Si–N or Al–N tetrahedra; it is consistent with the narrow emission band (FWHM = 66 nm) and a good thermal stability described in the following section.

Figure 4 shows the peak PL intensity as a function of Yb$^{2+}$ concentration. The PL intensity reaches the
maximum when the Yb$^{3+}$ concentration is increased to 0.4 mol% and decreases at higher Yb$^{3+}$ doping levels. This critical concentration of Yb$^{3+}=0.4$ mol% was taken as the percolation threshold. The concentration quenching, which is mainly caused by the non-radiative energy transfer between Yb$^{3+}$ ions, may have two causes. Firstly, because the 4f–5d transition of Yb$^{3+}$ is allowed, energy transfer will only occur as a result of an electric multipolar interaction. With increasing Yb$^{3+}$ concentration, the distance among the Yb$^{3+}$ ions shortens, favoring the non-radiative pathway via the energy transfer between the Yb$^{3+}$ ions. Secondly, the overlapping of the excitation and emission spectra at about 470–530 nm, as shown in figure 3, may also contribute to the concentration quenching. The red shift of the emission band as the Yb$^{3+}$ doping amount increases, which is usually observed in rare-earth doped phosphors [11, 31, 32], has not been detected in this study, possibly owing to the pronounced concentration quenching effect of β-SiAlON : Yb$^{3+}$ at Yb$^{3+}=0.4$ mol%.

Figure 5 shows the emission intensity and peak wavelength of the emission and excitation bands as a function of z in β-SiAlON : Yb$^{3+}$ (Yb$^{3+}=0.4$ mol%). The compositional dependence of PL is mainly attributed to the phase purity, crystallinity, and particle morphology [20]. In this experiment, for mixtures with low z value did not crystallize well, so that the defects in each particle trapped or scattered the emitting light, thereby reducing the luminescence intensity. Meanwhile, at higher z values, crystal grains agglomerated easily, decreasing the packing density of the powders and causing strong light scattering. Another phenomenon related to the z value is the red shift of the emission band. This red shift can be considered as follows. The host lattice of β-SiAlON softens when longer bonds of Al–O (1.75 Å) and Al–N (1.87 Å) replace shorter Si–N (1.74 Å) bonds as the z value was increased, resulting in a large Stokes shift and the redshift of the peak emission wavelength. The absence of such redshift in excitation bands further proves that the redshift of emission band is due to the softening of host lattice but not crystal field splitting, as demonstrated in figure 5. The radiation reabsorption due to the overlap between the excitation and emission bands may also reduce the emission in the blue wavelength range.

3.3. Quantum efficiency

Figure 6 shows the spectra of optical absorption and PL quantum efficiency as a function of excitation wavelength for β-SiAlON : Yb$^{3+}$ at z = 0.3 and Yb$^{3+}=0.4$ mol%. The values of $\eta_{in}$ and $\eta_{ex}$ at 480 nm are 28% and 9%, respectively. Generally, the quantum efficiency is markedly affected by the probability of non-radiative processes. The non-radiative recombination is reduced when the phosphor particles are well crystallized and are free of surface defects. Therefore, the quantum efficiency can be improved by controlling the particle size, size distribution, morphology and crystalline defects through optimization of the processing conditions.

3.4. Temperature-dependent luminescence

In general, phosphors should retain the emission intensity at 150 °C, a usual working temperature for LEDs, over a long
and its intensity depends on the Yb$^{2+}$ concentration and the chemical composition of the host lattice. The $\beta$-SiAlON : Yb$^{2+}$ phosphor has a high thermal stability in the temperature range of 25–250 °C. At 150 °C, the relative emission intensity is as high as 82% of that measured at room temperature, which is attributed to the rigid host lattice based on a (Si, Al)(O, N)$_4$ tetrahedral network. Although the quantum efficiency is low in this work, it can be improved by optimizing processing conditions. Our results demonstrate that the $\beta$-SiAlON : Yb$^{2+}$ is a good green-emitting phosphor for white LEDs.

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4. Conclusions

Yb$^{2+}$-doped $\beta$-SiAlON phosphors (0.05 ≤ z ≤ 2.3, 0.03 mol% ≤ Yb$^{2+}$ ≤ 0.7 mol%) have been synthesized by solid-state reaction at 1900 °C under a nitrogen gas pressure of 1.0 MPa. They were characterized by x-ray powder diffraction, excitation and emission spectroscopy, temperature-dependent luminescence and quantum efficiency measurements. A pure $\beta$-SiAlON phase was obtained for the phosphors with various z and x values. $\beta$-SiAlON : Yb$^{2+}$ exhibits green emission at 540 nm under 480 nm excitation.

![Figure 8. Temperature dependence of emission spectra for $\beta$-SiAlON : Yb$^{2+}$ at z = 0.3 and Yb$^{2+}$ = 0.4 mol%.](image-url)
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