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The z value dependence of photoluminescence in Eu^{2+}-doped β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$) with $1 \leq z \leq 4$

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ABSTRACT

Eu^{2+}-doped β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$) phosphors with $1 \leq z \leq 4$ were synthesized by gas pressure sintering. The emission spectra exhibit two broad bands with maxima at about 415 nm (violet) and 540 nm (green) under ultraviolet excitation. The green emission is dominant at $z \leq 2$, while the violet emission becomes dominant at $z > 2$. The combination of two emission bands in a compound could lead to a white emission in Eu^{2+}-doped β-SiAlON with $2 < z \leq 3$.

1. Introduction

Si_3N_4-based ceramics are the leading engineering ceramics for high-temperature structural application of excellent thermal and mechanical properties [1]. Si_3N_4 occurs in two major crystalline phases: α and β [2]. Both phases have a hexagonal structure consisting of corner-sharing SiN_4 tetrahedra but different stacking sequences; it is ABCD in α and AB in β. They have their respective solid solutions, known as α- and β-SiAlON, described by the general formulae $M_{m/\nu}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ (ν is the valence of the metal M ion) and $Si_{6-z}Al_zO_zN_{8-z}$ ($0 < z \leq 4.2$) [3]. Both α- and β-SiAlONs have been used as host lattices for rare-earth (RE) ions to generate efficient luminescence [4–8]. For example, Eu^{2+}-doped Ca-α- and β-SiAlONs give yellow and green emissions, respectively. The RE-doped SiAlON phosphors have expected to be used in white light-emitting diodes (LEDs), owing to the high thermal and chemical stabilities [9].

The β-SiAlON has received less attention as a host material for phosphors in comparison with the α-SiAlON. This may be due to the fact that the α-SiAlON has interstitial sites for RE ions, whereas the β-SiAlON has no apparent crystallographic sites for RE ions. Despite this, in the β-SiAlON structure there are continuous channels parallel to the c-axis [10]. In 1985, RE-doped β-SiAlON phosphors were first developed by Popma [7] to be used in luminescent screens excited by ultraviolet (UV), electron and X-ray radiation, with a focus on the case of $z = 3$. They showed various color emissions, depending on the type of RE, e.g., Eu^{2+} for violet-blue emission at 410–440 nm and Sm^{2+} for red emission at 685–740 nm. Recently, Hirosaki et al. [8] reported a green emission at 535 nm under the UV or blue light excitation in β-SiAlON:Eu^{2+} with $z = 0.14$. Xie et al. [11] reported the red shift in emission wavelength from 528 to 550 nm with increasing z value in β-SiAlON:Eu^{2+} phosphors at $z \leq 2$. They also showed that the critical concentration depends on the z value and the β-SiAlON:Eu^{2+} phosphors have a small thermal quenching. Ryu et al. [12] further studied the concentration and thermal quenching of β-SiAlON:Eu^{2+} phosphors with $z = 0.23$. The green emission was also reported in the β-SiAlON:Eu^{2+} with $z \leq 2$ produced by combustion synthesis [13]. These studies indicate that the RE ions like Eu^{2+} can indeed be incorporated into the β-SiAlON structure, being assumed to exist in continuous channels [8,9,14]. Very recently, this assumption has been experimentally demonstrated by direct observation using scanning transmission electron microscopy (STEM) [15].

Previous studies indicate that the β-SiAlON:Eu^{2+} emits the green light for $z \leq 2$ but the violet-blue lights for $z = 3$. The color change appears to be consistent with the decrease in its N/O ratio, because RE-doped oxynitride materials usually show shorter emission wavelengths with decreasing N/O ratio, due to the reduced nephelauxetic effect and crystal-field splitting [4,9]. However, it is unclear whether the β-SiAlON:Eu^{2+} shows a continuous shift in emission band from green to violet lights as well as the mixed emission bands at particular wavelengths with varying z values within the whole range of 0–4.2. Tuning z values in β-SiAlON:Eu^{2+} may have a possibility to lead to the phosphors generating emissions

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ranging from violet to green colors. This is of interest to expand applications of β-SiAlON as luminescent materials. Unfortunately, the study dealing with the effect of *z* value on the photoluminescence of β-SiAlON:Eu^{2+} within the whole *z* range is not found yet. The objective of this paper is to investigate the effect of *z* value on the photoluminescence of β-SiAlON:Eu^{2+} within the range of $1 \le z \le 4$.

2. Experimental

The starting materials used for producing Eu^{2+}-doped β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$) were α-Si_3N_4 (SN-E10, Ube Industries, Ltd., Japan), Al_2O_3 (99.99%, Kojundo Chemical Laboratory, Japan), AlN (Grade H, Tokuyama Corp., Japan) and Eu_2O_3 (99.9%, Wako Pure Chemical Industries Ltd., Japan). The *z* value was varied from 1 to 4 at a fixed Eu concentration of 0.5 mol.% with respect to β-SiAlON. The raw powders were homogeneously mixed with absolute ethanol in a plastic bottle with Si_3N_4 balls by ball milling. After vacuum drying, the powder mixtures were packed into BN crucibles, and then fired in a gas pressure sintering furnace at 1900 °C for 3 h under a nitrogen pressure of 0.5 MPa. After firing, the power was shut off and the samples were cooled down in the furnace. Phase identification of the synthesized powders were conducted by powder X-ray diffraction (XRD) (Ultima IV, Rigaku, Tokyo, Japan) with monochromatized Cu Kα radiation of 40 kV/40 mA at a scanning speed of 2°/min in the 2θ range of 10–120°. Morphologies of the products were observed by a scanning electron microscope (SEM) (JSM-6390LV, JEOL, Tokyo, Japan). Photoluminescence spectra of the synthesized powders were measured at room temperature by a spectrofluorometer (FP-6500, JASCO, Tokyo, Japan) with a 150 W xenon lamp as an excitation source.

3. Results and discussion

Fig. 1(a) shows that at *z* = 1, the sample consists of a β-SiAlON phase; at *z* = 2, the sample consists of a major β-SiAlON phase and a trace amount of impurity phases AlN and 15R AlN-polytypoid ($SiAl_4O_2N_4$); at *z* = 3 and 4, the samples consist of a major β-SiAlON phase and an impurity 15R. The relative amount of the impurity 15R increases with *z* value increasing from 2 to 4. Xie et al. [11] have reported the formation of Eu-doped β-SiAlON with $z \le 2$ by gas pressure sintering. They obtained the pure β-SiAlON phase

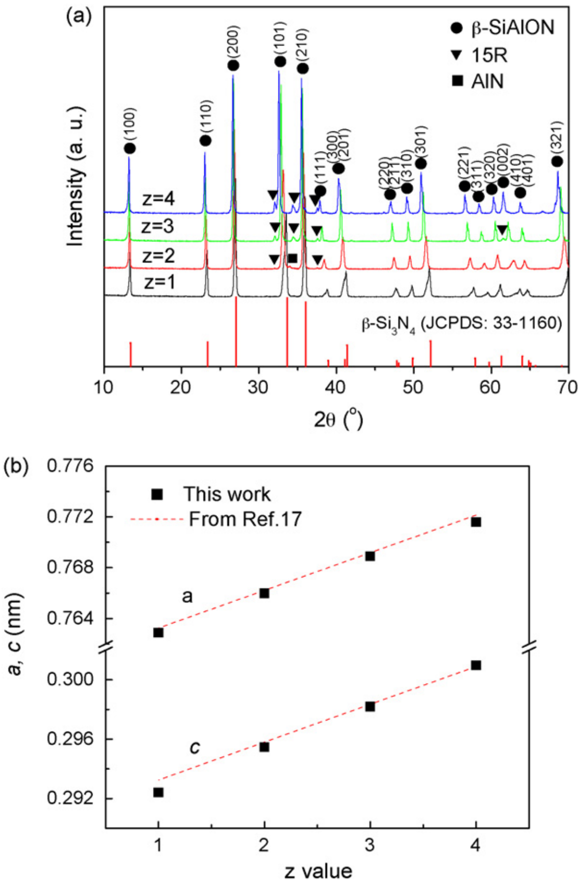

Fig. 1. (a) XRD patterns and (b) lattice parameters of the synthesized Eu^{2+}-doped β-SiAlON powders with various *z* values.

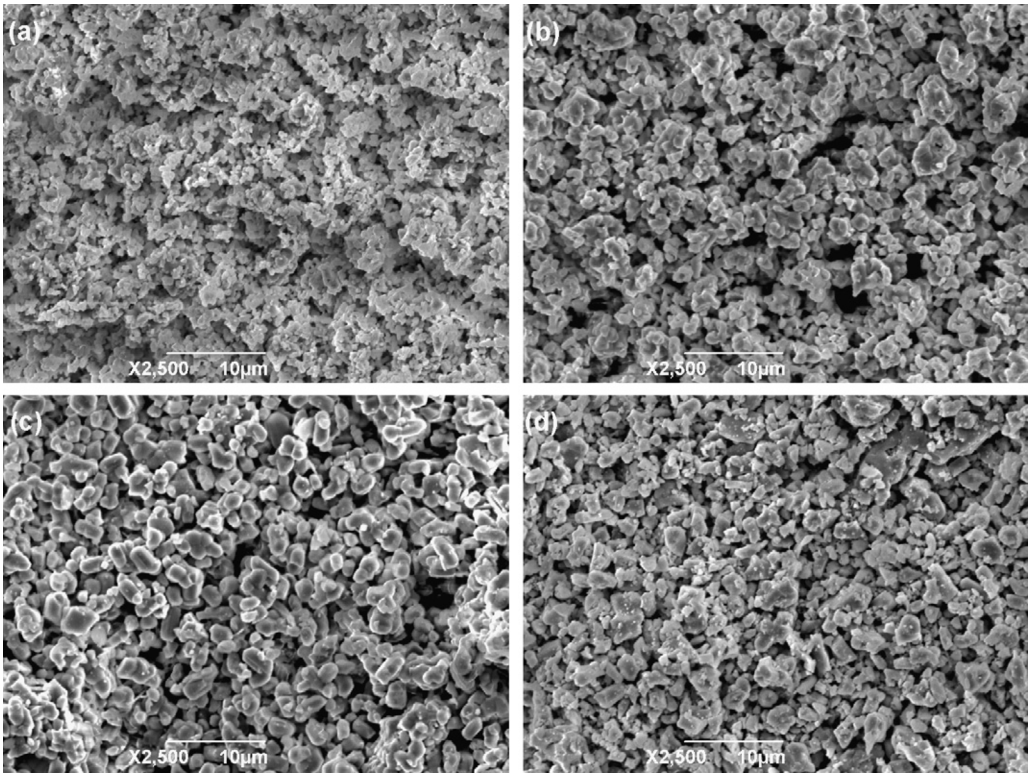

Fig. 2. SEM photographs of the synthesized Eu^{2+}-doped β-SiAlON powders with *z* values of (a) 1, (b) 2, (c) 3 and (d) 4.

only at lower z values of $z < 1$, above which AlN-polytypoid impurities (e.g., 12H, 21R and 27R) were present regardless of the Eu concentration. They assume that this phenomenon is attributed to the decreased solubility of Eu^{2+} in β-SiAlON with increasing z values. In the work of Zhou et al. [13], no secondary AlN-polytypoid phases were observed in the 4 mol.% Eu-doped β-SiAlON with $z \leq 2$ by combustion synthesis method. This implies that the formation of β-SiAlON is not associated with the solubility of Eu^{2+} but its composition, which is affected by the starting powders and processing conditions. According to the phase diagram of the Si_3N_4–SiO_2–Al_2O_3–AlN system, β-SiAlON is compatible with 15R in the region of Si/Al < 3 or $z > 1.5$ [16]. As a result, in case of $z \geq 2$, the formation of the impurity 15R is reasonable when a small change occurs in the composition during firing. Fig. 1(a) also shows that the diffraction peaks of β-SiAlON shift to smaller diffraction angles 2θ with increasing z value. This is due to the substitution of Al–O (0.175 nm) for Si–N (0.174 nm), thereby resulting in the lattice expansion. Fig. 1(b) reveals that the lattice parameters show a linear increase with increasing z value, which is in good agreement with the report of Ekström et al. [17]. This confirms that the resultant β-SiAlON powders have the nominal compostions $Si_{6-z}Al_zO_zN_{8-z}$ as designed.

Fig. 2 shows the SEM photographs of the synthesized Eu^{2+}-doped β-SiAlON powders with various z values. In call cases, the grains show predominantly near-equiaxed shapes, whereas the grain size shows a significant increase with increasing z value from 1 to 4. For example, the grain size is ~0.5 μm for $z = 1$ and ~2 μm for $z = 3$. This result is consistent with previous studies that the Eu^{2+}-doped β-SiAlON grains show a rod-like shape at $z < 1$ but a near-equiaxed shape at $z \geq 1$ [11,13]. The changed shape and size of the β-SiAlON grains with increasing z value are generally thought to be associated with the increased amount of the transient liquid phase that promotes the dissolution-precipitation process for the grain growth.

As shown in Fig. 3(a), the shape of excitation spectrum depends on the emission condition. The excitation spectra under emission at 412 nm have two broad bands centered at about 277 and 321 nm. As reported previously [8,11,13], the excitation spectra under emission at 540 nm have several broad bands centered at about 301, 336, 411 and 450 nm. The broad band excitation is attributed to the $4f^7 \rightarrow 4f^6 5d$ transition of Eu^{2+}. Meanwhile, at $z \leq 2$, the excitation intensity under emission at 412 nm is weaker than that under emission at 540 nm, whereas at $z > 2$, the former becomes substantially stronger than the latter.

The emission spectrum under excitation at 301 nm depends strongly on the z value, as shown in Fig. 3(b). At $z = 1$, 2, and 3, the emission spectra exhibit two broad bands centered at about 415 and 540 nm. These two broad emissions should be attributed to the $4f^6 5d \rightarrow 4f^7$ transition of Eu^{2+}. No line emission peaks of Eu^{3+} (590–615 nm) are observed. This suggests that Eu^{3+} ions in the Eu_2O_3 raw material is reduced to Eu^{2+} ions in the β-SiAlON products in a reducing nitrogen atmosphere, similar to the previous reports [8,11–14]. The reduction may be due to the reaction $6Eu^{3+} + 2N^{3-} \Rightarrow 6Eu^{2+} + N_2$, as proposed by de Graaf [18]. At $z = 4$, the emission spectrum exhibits a single broad band with a maximum at 409 nm. This means that the violet emission intensity increases but the green emsision intensity decreases with increasing z value. The rapid change in the emission occurs between $z = 2$ and 3. In addition, the violet emission at $z = 4$ is signficantly stronger than the green emission at $z = 1$. The violet emission was reported at $z = 3$ by Pompa [7]. The emisson peak at about 420 nm was also observed at $z = 2$ by Zhou et al. [13]. In their work, no AlN-polytypoid phases were present. Although the impuirty phase 15R is present at $z = 2$, 3 and 4 in the present work, the Eu^{2+}-doped 15R has been found to exhibit an emission band with a maximum at about 450 nm, which is less affeced by the synthesizing conditions [19]. The violet emission should result from the Eu^{2+}-doped β-SiAlON, and this emisson becomes dominant over the green one when $z > 2$.

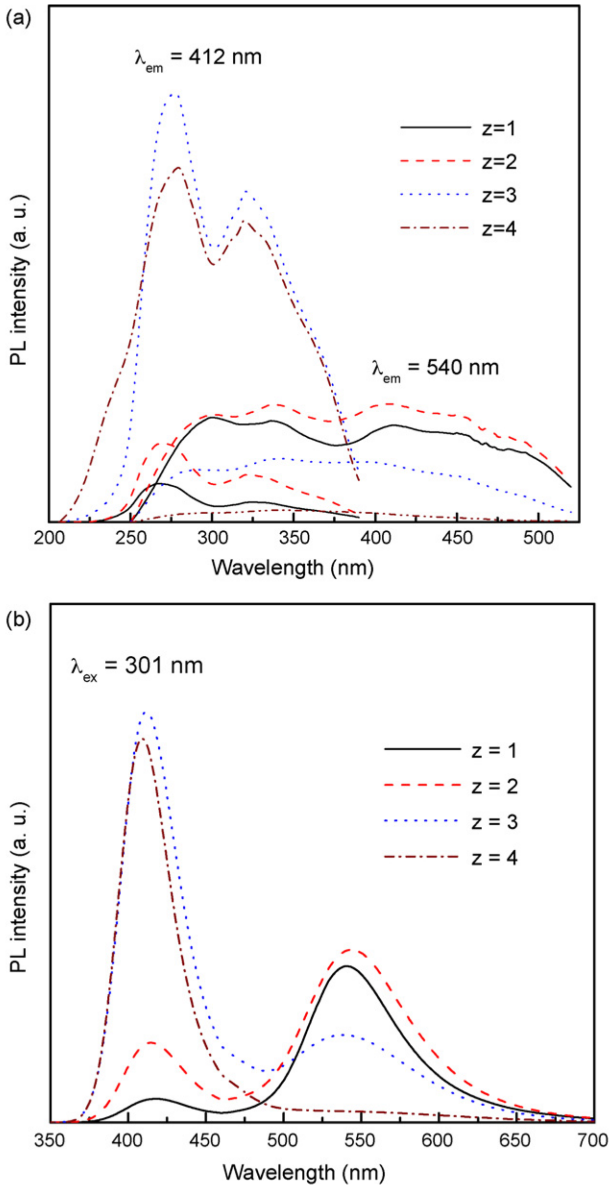

Fig. 3. (a) Excitation and (b) emission spectra of the synthesized Eu^{2+}-doped β-SiAlON powders with various z values.

Morevoer, the two emission peaks obsvered against z value are summarized in Table 1. As reported previously, the green emission wavelength shows a slight increase (i.e., red shift) with increasing z value from 1 to 2. Xie et al. [11] suggested that the red shift of green emission is attributed to the Stokes shift as a result of the decreased rigidity of the β-SiAlON lattice with increasing z value. However, with z value increasing to 3, the green emission shows a slight decrease in wavelength and eventually disappears at $z = 4$. In contast, the violet emission band shifts gradually toward shorter

Table 1
Effect of z value on the emission peaks observed under excitation at 301 nm.

z Value	Violet emission peak (nm)	Green emission peak (nm)
1	418	541
2	415	543
3	412	540
4	409	ND

wavelenths (i.e., blue shift) with increasing *z* value. The blue shift may be related to the expansion of the unit cell and the decreased covalence of the chemical bonds with increasing *z* value.

The emission spectra showing two broad bands in a comound is possible in Eu^{2+}-doped nitride and oxide materials. Höppe et al. [20] observed two emission bands with maxima at 610 and 630 nm in Eu^{2+}-doped $Ba_2Si_5N_8$ under excitation with intense laser light at 1.047 μm. They are attributed to two crystallographic Eu^{2+} sites in the channels along [1 0 0]. Denis et al. [21] reported that the Eu^{2+}-doped $(Ba,Sr)_{13-x}Al_{22-2x}Si_{10+2x}O_{66}$ exhibits two broad emission bands with maxima at 438 and 534 nm, resulting in the white fluorescence and phosphorescence. This luminescence is attributed to the three crystallographic Ba sites labeled Ba1, Ba2 and Ba3 in $Ba_{13-x}Al_{22-2x}Si_{10+2x}O_{66}$. The occupation of Eu^{2+} at the Ba1 and Ba2 sites gives the blue-violet emission (438 nm), while the occupation of Eu^{2+} at the Ba3 site gives the green emission (534 nm). Kikkawa et al. [22] reported three emission bands with maxima at 400, 475 and 520 nm in the Eu^{2+}-doped AlON with an impurity of $EuAl_{12}O_{19}$ under excitation at 254 nm. The authors attributed the possible reason for the three emission bands to the different coordination environments of Eu^{2+} with O^{2-}/N^{3-} in the magnetoplumbite structure.

There is no available crystallographic site for Eu^{2+} ion in β-SiAlON, so it is difficult to correlate the luminescence with the chemical environment of Eu^{2+} in β-SiAlON. It has continuous channels to accommodate for Eu^{2+} ions, as confirmed by STEM without any detailed crystallographic information [15]. By modeling analysis, Li et al. [14] showed that the Eu^{2+}ion occupies the 2b site (0,0,0) in the channels and coordinates to six (N/O) atoms. They also suggested the general formula $Eu_xSi_{6-z}Al_{z-x}O_{z+x}N_{8-z-x}$ for the Eu^{2+}-doped β-SiAlON. Generally, the luminescence of RE-doped (oxy)nitride depends on the coordination of the RE ion with N and O ions. When the activator ion (e.g., Eu^{2+} or Ce^{3+}) coordinates to more N than O ions, the nephelauxetic effect is enhanced and the crystal-field splitting of the 5d band is enlarged, thereby resulting in the longer excitation and longer emission wavelengths. The N/O ratio decreases in Eu^{2+}-doped β-SiAlON with increasing *z* value, so the excitation and emission wavelength are expected to decrease.

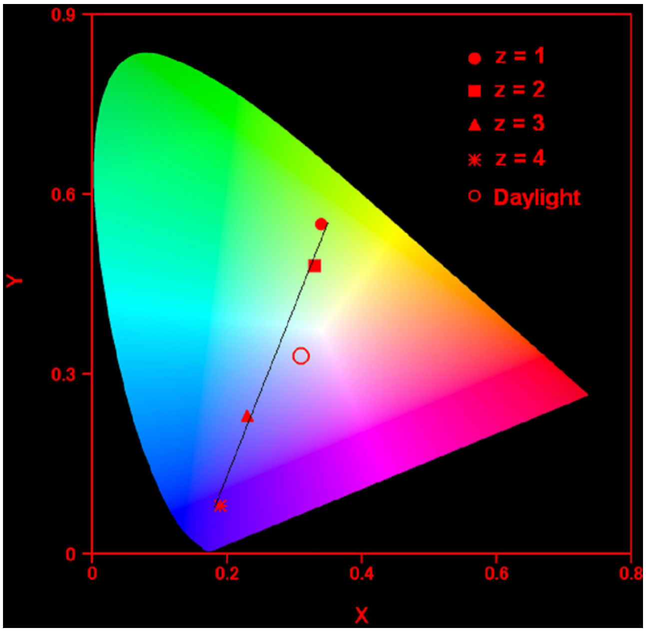

Fig. 4. CIE 1931 chromaticity coordinates of the synthesized Eu^{2+}-doped β-SiAlON powders with various *z* values under excitation at 301 nm. CIE coordinates calculated using the software GoCIE obtained from http://www.geocities.com/krjustin/gocie.html .

This appears to agree with the fact: the green emission at $z < 1$ and the violet emission at $z > 3$. The present results suggest that there are two different kinds of N/O coordinations around Eu^{2+} ions in β-SiAlON; one with oxygen-rich gives the violet emission (∼415 nm), and the other with nitrogen-rich gives the green emission (∼540 nm). The green emission is dominant at lower *z* values, while violet emission is dominant at higher *z* values.

Fig. 4 shows the Commission International del' Eclairage (CIE) 1931 chromaticity coordinates of the synthesized Eu^{2+}-doped β-SiAlON phosphors. The chromaticity index (*x*, *y*) shifts from (0.34, 0.55), (0.33, 0.48), (0.23, 0.23) to (0.19, 0.08) with an increasing *z* value from 1 to 4, corresponding to the colors of green, greenish-yellow, pale violet, and to violet. It is of interest to see that the chromaticity index can be located at near the white color region by changing *z* value between 3 and 4. This means that the Eu^{2+}-doped β-SiAlON alone may give a white emission under UV excitation. Particularly, we have observed a near-white emission from the sample with $z = 3$ in a handy UV lamp under 365 nm excitation. The white emission should be attributed to the coexistence of the violet and green emssions. This suggests the possibility to obtain the white emssion from the single phase of Eu^{2+}-doped β-SiAlON by carefully adjusting its *z* value as well as Eu content. The Eu^{2+}-doped β-SiAlON itself may act as a potential single-phased white-emitting phosphor for UV LEDs.

4. Conclusions

The emission spectra of Eu^{2+}-doped β-SiAlON phosphors with $1 \le z \le 4$ were found to exhibit two broad emission bands with maxima at about 415 nm (violet) and 540 nm (green) under UV excitation, resulting in a white emission. The violet emission becomes dominant with increasing *z* value, while the green emission eventually disappears with *z* value increasing to 4. The results suggest that there are probably two different kinds of N/O coordinations around Eu^{2+} ions in β-SiAlON; one with oxygen-rich and the other with nitrogen-rich. This study implies that the Eu^{2+}-doped β-SiAlON itself may act as a potential single-phased white-emitting phosphor for UV LEDs.

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