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Short communication

Effect of composition variation on phases and photoluminescence properties of β-SiAlON:Ce^{3+} phosphor

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Abstract

Ce^{3+}-doped β-SiAlON blue phosphors with composition of $Ce_xSi_{6-z}Al_zO_zN_{8-z}$ ($0.2 \leq z \leq 4$) at a fixed $x=0.01$ were synthesized by the gas pressure sintering method. The phases and photoluminescence properties were found to be directly correlated to the z value. Higher z value would result in the formation of AlN polytypoid impurity phases. The optimal z value resides in the range $0.3 \leq z \leq 0.5$, by which high purity of β-SiAlON phase, good crystallinity and fine grain size were obtained, leading to the best luminescence properties. These phosphors could be a good candidate for application in white light-emitting diodes using InGaN-based near–ultraviolet chips.

Keywords: C. Optical properties; D. SiAlON; Composition

1. Introduction

In recent years, rare earth (RE)-doped nitride/oxynitride phosphors have attracted increasing interest due to their promising luminescence properties and excellent thermal and chemical stabilities which make them good candidates for the application in white light-emitting diodes (LEDs) [1]. Si_3N_4 is a parent body of nitride/oxynitride based luminescence materials, which has two major crystalline phases: α and β. Both phases have a hexagonal structure consisting of corner-shared SiN_4 tetrahedra with different staking sequences of ABCD for α and ABAB for β. α- and β-SiAlONs are solid solutions isostructural with α- and β-Si_3N_4 respectively. α-SiAlON is well established with the general formula $M_xSi_{12-m-n}Al_{m+n}O_nN_{16-n}$ ($x=m/v$, v is the valence of metal M, m and n are the numbers of Si–N bonds replaced by Al–N and Al–O bonds respectively) [2]. The general formula of β-SiAlON can be written as $Si_{6-z}Al_zO_zN_{8-z}$ ($0<z\leq 4.2$, z is the number of Si–N bonds replaced by Al–O bonds) [3]. A series of intense research has been reported with respect to the luminescence properties of α-SiAlONs doped by various RE ions (RE$=Eu^{2+}$, Ce^{3+}, Sm^{3+}, Dy^{3+}, Tb^{3+}, Pr^{3+} and Yb^{2+}) [4–10]. On the contrary, the study on RE-doped β-SiAlON is much less. A significant reason is probably due to the fact that α-SiAlON has large interstitial sites in the crystal structure to accommodate RE ions for charge compensation, while β-SiAlON has no apparent crystallographic sites for RE ions [11]. Despite of this, Eu^{2+}, Ce^{3+} and Pr^{3+}-doped β-SiAlONs have been reported as high performance phosphors [12–14]. Meanwhile, Kimoto et al. [15] directly observed Eu^{2+} ions in the continuous channels parallel to the c-axis in the β-SiAlON lattice by scanning transmission electron microscopy (STEM).

The optical properties of RE-doped β-SiAlON can be tailored by z-value and doping concentration. Liu et al. reported blue-emitting β-SiAlON:Ce^{3+} phosphors with z

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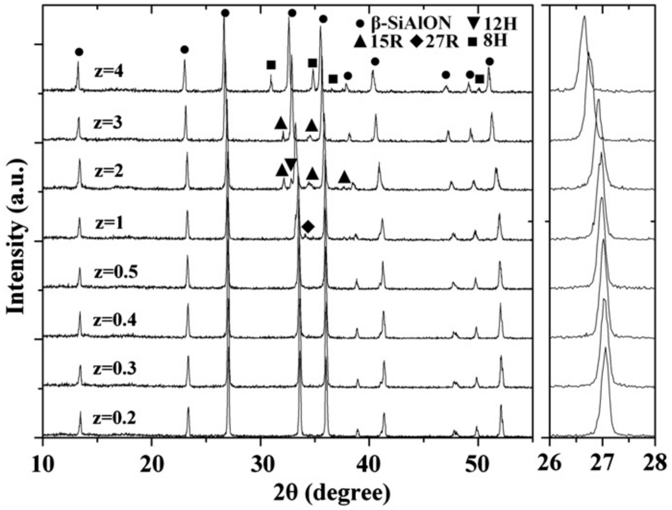

Fig. 1. XRD patterns of the synthesized Ce^{3+}-doped β-SiAlON phosphors with various z values.

values from 0.3 to 2.5 [13]. Ryu et al. studied the influence of Ce^{3+} doping concentration on luminescence properties of β-SiAlON with $z=0.25$ [16]. It has shown that the z value can vary in a large range ($0<z\leq 4.2$) so that β-SiAlON can be changed from a nitrogen-rich host to an oxygen-rich host for RE dopants. The 5d–4f transition luminescence properties of Ce^{3+} and Eu^{2+} depend very strongly on the host structure and the composition. The emission wavelength decreases with increase of O/N ratio due to the reduced nephelauxetic effect and crystal–field splitting, and the increased lattice parameter. For instance, Zhu et al. reported the two bands emission (415 nm violet and 540 nm green) of β-SiAlON:Eu^{2+} phosphors with $1\leq z\leq 4$ [11]. The violet emission became dominant with the increase in z value, whereas the green emission gradually reduced and finally disappeared when z value increased to 4. They attributed this phenomenon to the two different coordination environments for Eu^{2+} in β-SiAlON matrix, i.e. nitrogen-rich or oxygen-rich. It is then interesting to evaluate the effect of z value in the extreme range of 0–4.2 on the luminescence of RE-doped β-SiAlON, aiming to seek the possibility to tune the optical properties simply by adjusting the composition.

The phosphors applied for white LEDs must have high phase purity, uniform particle size distribution and high luminescence efficiency. Therefore in this work, Ce^{3+}-doped β-SiAlON phosphors with composition of $Ce_xSi_{6-z}Al_zO_zN_{8-z}$ ($0.2\leq z\leq 4$) at a fixed $x=0.01$ were synthesized by the gas pressure sintering (GPS) method. The influence of z value on phases and luminescence properties was investigated in detail.

2. Experimental procedures

β-SiAlON:Ce^{3+} phosphors with nominal compositions of $Ce_xSi_{6-z}Al_zO_zN_{8-z}$ ($0.2\leq z\leq 4$, $x=0.01$) were synthesized from α-Si_3N_4 (SN-E10, Ube Industries, Japan), AlN (Type F, Tokuyama Corp., Japan), Al_2O_3 (99.99%, Shanghai Yuelong, China) and CeO_2 (99.99%, Aladdin, China) powders. Eight samples with $z=0.2$, 0.3, 0.4, 0.5, 1, 2, 3 and 4 correspondingly were prepared with a fixed $x=0.01$. The raw material powders were mixed homogeneously in an agate mortar and then granulated using a test sieve. Subsequently, the powder mixture was loaded into boron nitride crucibles and heated in GPS furnace at 1900 °C for 5 h under a N_2 gas pressure of 0.6 MPa. After firing, power was shut off and the samples were cooled down naturally to the room temperature in the furnace. The fired samples were ground in the agate mortar for further characterizations.

Phase identification of the synthesized powders was performed by X-ray diffraction (XRD, AXS D8 Focus, Bruker, Germany) analysis using Cu Kα radiation ($\lambda=1.5406$ Å) at 40 kV and 40 mA with a graphite monochromator. The step size of 0.02° was used with a scan speed of 6°/min. Morphologies of the phosphor particles were observed by a scanning electron microscopy (SEM, JEM-6390, JEOL, Japan). Photoluminescence spectra were measured by a fluorescence spectrophotometer (FluoroMax-4, Horiba, Japan) at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the synthesized samples with various z values at a fixed $x=0.01$ in their nominal compositions. It can be seen that the samples with $z\leq 0.5$ consist of single β-SiAlON phase, while AlN polytypoid impurity phases are identified in the samples with $z\geq 1$. Small amount of polytypoid phases of 27R, 15R+12H and 15R appear in the samples with $z=1$, 2 and 3 respectively. However, the $z=4$ sample contains comparatively high amount of 8H AlN polytypoid phase. Upon increasing the z value, the diffraction peaks of β-SiAlON (see inset in Fig. 1) gradually shift to lower diffraction angles, implying a continuous expansion of the crystal lattice caused by the partial replacement of the shorter Si–N (1.74 Å) bonds by longer Al–O (1.75 Å) bonds. There should be small discrepancy between the nominal and the actual composition of β-SiAlON phase owing to possible presence of oxide impurities on the surfaces of raw materials and/or formation of small amount of amorphous phases on the surfaces of the as-sintered crystallites. Anyway, it is widely believed that the nominal composition determines the actual composition of β-SiAlON phase to a large extent.

Secondary AlN polytypoid phases have been detected previously in GPS synthesized Eu^{2+}-doped β-SiAlON with $z\geq 1$ regardless of the Eu^{2+} doping concentration [17,18]. However, Zhou et al. [3] have reported the synthesis of Eu^{2+}-doped β-SiAlON free of AlN polytypoid phases with $z\leq 2$ by the combustion synthesis method. Further, Zhu et al. [11] suggested that the formation of β-SiAlON was not associated with the solubility of RE ions but the compositions, which was affected by the starting powders

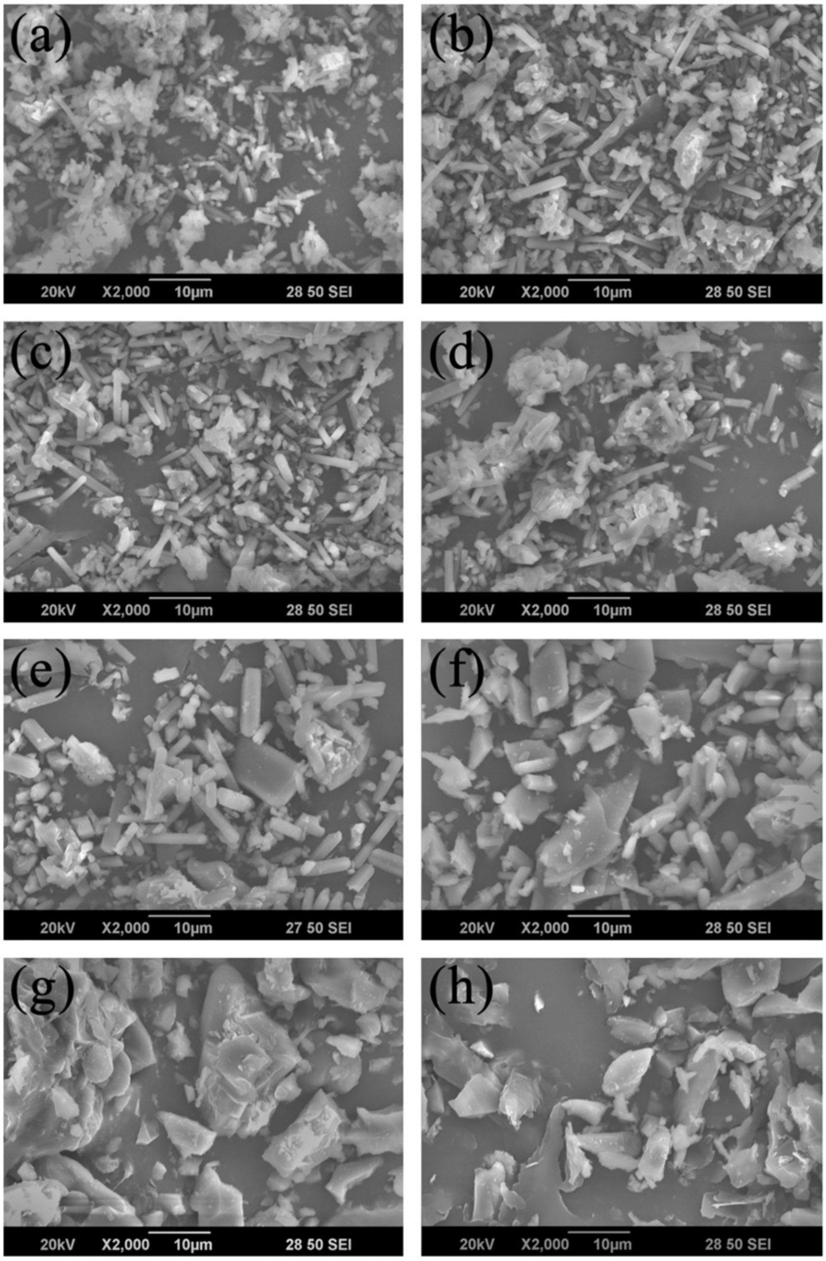

Fig. 2. SEM images of the synthesized Ce^{3+}-doped β-SiAlON phosphor powders with z values of (a) 0.2, (b) 0.3, (c) 0.4, (d) 0.5, (e) 1, (f) 2, (g) 3 and (h) 4.

and processing conditions. It is generally believed that both α- and β-SiAlONs form by a solution-reprecipitation mechanism from an oxynitride melt, which is a transient reaction product among the starting oxide and nitride powders [19]. Thus, the transient liquid phase plays an important role in nucleation and growth of β-SiAlON. According to Hwang and Chen [20], the β-SiAlON crystallites are nucleated from various seed crystals including α-Si_3N_4, β-Si_3N_4 and β-SiAlON. The β-SiAlON seeds and the subsequent initial precipitates have a higher content of Al and O, indicating that a large transient supersaturation of Al and O in the liquid is instrumental for β-SiAlON formation. The supersaturation is transient in nature, resulting from preferential dissolution of AlN in the Si–Al–RE oxide melt formed by RE oxide, and oxide impurities on Si_3N_4 and AlN starting powders. For the samples with $z \geq 1$ in the present study, a relatively higher content of AlN in the starting powder and the preferential dissolution of AlN led to a high content of Al in the transient liquid phase. Therefore, small amount of Al-rich AlN polytypoid nuclei were formed during the initial stage of the reaction before enough amount of Si_3N_4 dissolved in the transient liquid phase for the subsequent formation of β-SiAlON phase. These nuclei would coarsen and eventually form AlN polytypoid impurity phases in the fired samples with $z \geq 1$.

Fig. 2(a–h) are the SEM images of the synthesized Ce^{3+}-doped β-SiAlON phosphor powders, which exhibit changes in grain size and morphology with varying z values from 0.2 to 4. At $z = 0.2$, the β-SiAlON grains show the typical rod-like shape. The rod-like morphology remains whereas the

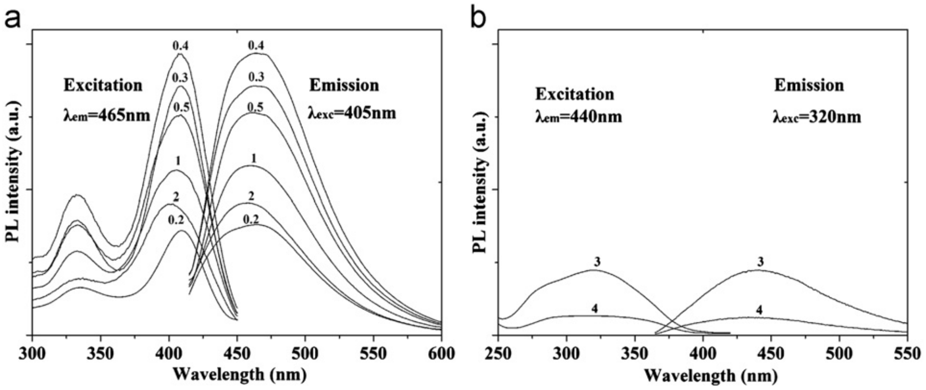

Fig. 3. Excitation and emission spectra of the synthesized Ce^{3+}-doped β-SiAlON phosphor powders with various z values: (a) $z=0.2$–2 and (b) $z=3$ and 4.

gain size and the aspect ratio gradually increase with z rising to 0.3, 0.4 and 0.5. In the sample with $z=1$, plate-like AlN polytypoid appears besides large rod-like β-SiAlON grains. With z value further increasing to 2, a number of large particles with irregular shapes are observed, whereas only irregular shaped agglomerates are formed in the samples with $z=3$ and 4. These changes in grain size and morphology of β-SiAlON with increased z values could be attributed to the increased transient liquid phase that accelerates the dissolution, diffusion and precipitation processes during grain growth. From the viewpoint of practical application for white LEDs, the β-SiAlON:Ce^{3+} phosphors with low z values ($z \leq 0.5$) are more promising than those with high z values ($z \geq 1$) because of their high phase purity, fine particle size and lack of large agglomerates.

Fig. 3 illustrates the excitation and emission spectra of the samples with varying z values at room temperature. In the excitation spectra (Fig. 3(a)) under emission at 465 nm, two excitation bands centered at about 405 nm and 330 nm are observed for the samples with z value from 0.2 to 2. Their emission spectra exhibit a single emission band peaked near 460 nm under excitation at 405 nm. Such emission should be attributed to the $4f^0 5d^1 \rightarrow 4f^1$ transition of Ce^{3+} ions. However, the powders with $z=3$ and 4 show no emission under excitation at 405 nm (see Fig. 3(b)). The excitation spectra for $z=3$ and 4 monitored at 440 nm consist of only one broad band centered near 320 nm and show no intensity above 400 nm. Their emission spectra have a broad band peaked near 440 nm with much lower intensity than that of the samples with $z \leq 2$. The change of the excitation band indicates a large variation in coordination of Ce^{3+} ions when z value increases from 2 to 3.

Fig. 4 shows the variation of emission peak location and photoluminescence emission intensity as a function of the z value. The emission peak presents continuous shift toward short wave side with increasing of the z value. This blue shift can be ascribed to the increase of O/N ratio, which reduces the covalence of β-SiAlON hence a reduced nephelauxetic effect. It seems that possible red shift arose from the lattice expansion (see XRD in Fig. 1) which leads to less rigidity of β-SiAlON structure and a larger stocks shift does not show considerable effects. The photoluminescence intensity enhances with the z value increasing up to 0.4 above which it falls. At $z \leq 0.5$, the samples are phase pure β-SiAlON. Thus the variation in emission intensity is mainly resulted from the crystallinity. As observed by SEM, the sample with $z=0.2$ has the smallest grain size, indicating poor crystallinity due to a smaller amount of transient liquid phase. Therefore, defects in grains could trap or scatter the emitting light and eventually reduce the emission intensity [6]. For the samples with $z=1$ and 2, deterioration of the luminescence can be attributed to the formation of impurity phases and large agglomerates of the β-SiAlON grains, which leads to a relatively low packing density in the measurement and hence a strong light scattering. The luminescence intensity of the samples with further increase of the z value to 3 and 4 are evidently much lower than that of the other samples. Impurity phases and particle morphology may take some effects but the main reason probably is due to the chemical change of the β-SiAlON host with the increase of O/N ratio. As clarified by excitation spectra for $z=3$ and 4, the shape of excitation spectra are completely different from that of samples with lower z values, implying the difference in the coordination of Ce^{3+} ions with N and O.

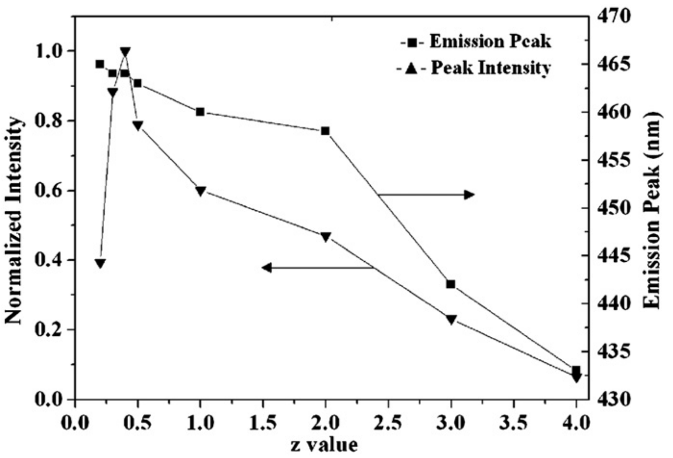

Fig. 4. Emission peak location and normalized emission intensity of the synthesized Ce^{3+}-doped β-SiAlON phosphor powders with various z values.

Unfortunately, there is no critical data available with respect to the accurate coordination of RE ions in β-SiAlON host although direct observation, modeling and calculation on RE-doped β-SiAlON have been reported [15,21,22]. The detail of the change in coordination around Ce^{3+} ions with varying z values is still unclear. However, the variation of photoluminescence spectra suggests that there are probably two different kinds of N and O coordinations around Ce^{3+} ions in β-SiAlON, a nitrogen-rich coordination for $z \leq 2$, whereas, an oxygen-rich one for $z \geq 3$.

4. Conclusions

Blue-emitting Ce^{3+}-doped β-SiAlON phosphors with varying z values in a large range ($0.2 \leq z \leq 4$) were synthesized by solid-state reaction at 1900 °C. At $z \leq 0.5$, phase pure β-SiAlON phosphors were obtained, while AlN polytypoid impurity phases were always detected for $z \geq 1$. The sample with $z=0.4$ has the best luminescence properties owing to high phase purity, good crystallinity and fine grain size. A continuous blue shift was observed for the emission spectra with increasing of the z value due to the reduced nephelauxetic effect. The difference between photoluminescence spectra of the samples with $z \leq 2$ and $z \geq 3$ suggests the change in coordination around Ce^{3+} ions from nitrogen-rich to oxygen-rich. The experimental data clearly indicates that β-SiAlON:Ce^{3+} powder with $0.3 \leq z \leq 0.5$ has great potentials as a down-conversion blue phosphor for white LEDs utilizing InGaN-based near–ultraviolet chips as the primary light source.

Acknowledgments

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References

[1] R.-J. Xie, N. Hirosaki, M. Mitomo, Oxynitride/nitride phosphors for white light-emitting diodes (LEDs), Journal of Electroceramics 21 (2008) 370–373.

[2] F.-F. Xu, E. Sourty, W. Shi, X.-L. Mou, L.-L. Zhang, Direct observation of rare-earth ions in α-SiAlON:Ce phosphors, Inorganic Chemistry 50 (2011) 2905–2910.

[3] Y. Zhou, Y.-I. Yoshizawa, K. Hirao, Z. Lenčéš, P. Šajgalík, Preparation of Eu-doped β-SiAlON phosphors by combustion synthesis, Journal of the American Ceramic Society 91 (2008) 3082–3085.

[4] R.-J. Xie, N. Hirosaki, K. Sakuma, Y. Yamamoto, M. Mitomo, Eu^{2+}-doped Ca-α-SiAlON: a yellow phosphor for white light-emitting diodes, Applied Physics Letters 84 (2004) 5404–5406.

[5] R.-J. Xie, N. Hirosaki, M. Mitomo, Y. Yamamoto, T. Suehiro, N. Ohashi, Photoluminescence of cerium-doped α-SiAlON materials, Journal of the American Ceramic Society 87 (2004) 1368–1370.

[6] R.-J. Xie, N. Hirosaki, M. Mitomo, T. Suehiro, X. Xu, H. Tanaka, Photoluminescence of rare-earth-doped Ca–α-SiAlON phosphors: composition and concentration dependence, Journal of the American Ceramic Society 88 (2005) 2883–2888.

[7] J.W.H. van Krevel, J.W.T. van Rutten, H. Mandal, H.T. Hintzen, R. Metselaar, Luminescence properties of terbium-, cerium-, or europium-doped α-SiAlON materials, Journal of Solid State Chemistry 165 (2002) 19–24.

[8] R.-J. Xie, M. Mitomo, K. Uheda, F.-F. Xu, Y. Akimune, Preparation and luminescence spectra of calcium- and rare-earth (R=Eu, Tb, and Pr)-codoped α-SiAlON ceramics, Journal of the American Ceramic Society 85 (2002) 1229–1234.

[9] Y.-Q. Li, N. Hirosaki, R.-J. Xie, J. Li, T. Takeda, Y. Yamamoto, M. Mitomo, Structural and photoluminescence properties of Ce^{3+}- and Tb^{3+}-activated Lu–α-SiAlON, Journal of the American Ceramic Society 92 (2009) 2738–2744.

[10] B. Dierre, X.-L. Yuan, N. Hirosaki, T. Kimura, R.-J. Xie, T. Sekiguchi, Luminescence distribution of Yb-doped Ca–α-SiAlON phosphors, Journal of Materials Research 23 (2008) 1701–1705.

[11] X.-W. Zhu, Y. Masubuchi, T. Motohashi, S. Kikkawa, The z value dependence of photoluminescence in Eu^{2+}-doped β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$) with $1 \leq z \leq 4$, Journal of Alloys and Compounds 489 (2010) 157–161.

[12] N. Hirosaki, R.-J. Xie, K. Kimoto, T. Sekiguchi, Y. Yamamoto, T. Suehiro, M. Mitomo, Characterization and properties of green-emitting β-SiAlON:Eu^{2+} powder phosphors for white light-emitting diodes, Applied Physics Letters 86 (2005) 211905.

[13] L.-H. Liu, R.-J. Xie, N. Hirosaki, T. Takeda, C.-N. Zhang, J.-G. Li, X.-D. Sun, Optical properties of blue-emitting $Ce_xSi_{6-z}Al_{z-x}O_{z+1.5x}N_{8-z-x}$ for white light-emitting diodes, Journal of the Electrochemical Society 157 (2010) H50–H54.

[14] T.-C. Liu, B.-M. Cheng, S.-F. Hu, R.-S. Liu, Highly stable red oxynitride β-SiAlON:Pr^{3+} phosphor for light-emitting diodes, Chemistry of Materials 23 (2011) 3698–3705.

[15] K. Kimoto, R.-J. Xie, Y. Matsui, K. Ishizuka, N. Hirosaki, Direct observation of single dopant atom in light-emitting phosphor of β-SiAlON:Eu^{2+}, Applied Physics Letters 94 (2009) 041908.

[16] J.H. Ryu, H.S. Won, Y.G. Park, S.H. Kim, W.Y. Song, H. Suzuki, C.B. Yoon, D.H. Kim, W.J. Park, C. Yoon, Photoluminescence of Ce^{3+}-activated β-SiAlON blue phosphor for UV-LED, Electrochemical and Solid State Letters 13 (2010) H30–H32.

[17] R.-J. Xie, N. Hirosaki, H.-L. Li, Y.-Q. Li, M. Mitomo, Synthesis and photoluminescence properties of β-SiAlON:Eu^{2+} ($Si_{6-z}Al_zO_zN_{8-z}$: Eu^{2+}), Journal of the Electrochemical Society 154 (2007) J314–J319.

[18] J.H. Ryu, Y.G. Park, H.S. Won, S.H. Kim, H. Suzuki, C. Yoon, Luminescence properties of Eu^{2+}-doped β-$Si_{6-z}Al_zO_zN_{8-z}$ microcrystals fabricated by gas pressured reaction, Journal of Crystal Growth 311 (2009) 878–882.

[19] S.-L. Hwang, I.-W. Chen, Nucleation and growth of α′-SiAlON on α-Si_3N_4, Journal of the American Ceramic Society 77 (1994) 1711–1718.

[20] S.-L. Hwang, I.-W. Chen, Nucleation and growth of β′-SiAlON, Journal of the American Ceramic Society 77 (1994) 1719–1728.

[21] Y.-Q. Li, N. Hirosaki, R.-J. Xie, T. Takeda, M. Mitomo, Crystal and electronic structures, luminescence properties of Eu^{2+}-doped $Si_{6-z}Al_zO_zN_{8-z}$ and $M_ySi_{6-z}Al_{z-y}O_{z+y}N_{8-z-y}$ (M=2Li, Mg, Ca, Sr, Ba), Journal of Solid State Chemistry 181 (2008) 3200–3210.

[22] D.S. Yoo, J.H. Ryu, S.-H. Lee, H. Cho, Y.-C. Chung, Accurate electronic structures of Eu-doped SiAlON green phosphor with a semilocal exchange-correlation potential, Japanese Journal of Applied Physics 50 (2011) 06GH10.