The effect of flux addition to Eu$^{2+}$-doped Ca-$\alpha$-SiAlON phosphor

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A yellow-emitting Eu$^{2+}$-doped Ca-$\alpha$-SiAlON phosphor is a promising candidate to make white LEDs by combining with blue LED. In the current research, the effect of flux (NH$_4$Cl or NH$_4$F) addition on the Ca-$\alpha$-SiAlON:Eu$^{2+}$ phosphor was investigated. The formation of both the compound and liquid phase between the flux and raw materials resulted in the decreased photoluminescence (PL) intensity in the early stage. However, the subsequent melting of second phases and retarded crystallization enhanced the PL intensity with increasing the synthesis temperature and time. The increased PL intensity for the luminescence (PL) intensity in the early stage. However, the subsequent melting of second phases and retarded crystallization enhanced the PL intensity with increasing the synthesis temperature and time. The increased PL intensity for the flux-added compositions is attributed to the less surface damages due to grinding of as-synthesized agglomerate-like phosphors. Further, the flux addition enhanced the particle growth by forming agglomerates in the early stage and it also influenced the particle morphology from the typical acicular shape to pseudo-equiaxed shape.©2013 The Ceramic Society of Japan. All rights reserved.

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1. Introduction

In recent times, the (oxy)nitride phosphors have been developed and are now at the early stages of commercialization.12)–14) Because of higher efficiency of absorption, emission in the long wavelength region and excellent thermo-mechanical properties including small thermal quenching (oxy)nitride phosphors are better suited for white LEDs when compared to oxide and sulfide phosphors. In the literature, the various issues of oxynitride SiAlON phosphors related to their wide range of emission covering from green to red have been reported.4–7,11) The SiAlONs are modification of silicon nitride (Si$_3$N$_4$) ceramics, and they are made from powder mixture including the main ingredient of Si$_3$N$_4$ and other additives such as AlN, rare earth oxides, and alkaline earth oxides.12,13) The liquid phase formation due to the eutectic reaction between the additives and Si$_3$N$_4$ works as a vehicle for the material transportation to synthesize SiAlON phosphors. Theoretically, the liquid phase for the synthesis of SiAlONs is transient so that the final product is free from the amorphous phase due to complete crystallization.12,13) However, it is conventional that there is a remnant amorphous phase after cooling. The SiAlON phosphors are softly agglomerated and the residual amorphous phase between particles. Consequently, it is inevitable to employ a high energy milling process to reduce the agglomerated phosphor particles to the appropriate size for the packaging process. During this process, phosphors are prone to the surface defects of particles, which may cause a decrease in the luminescence and efficiency.

In this work, Ca-$\alpha$-SiAlON:Eu$^{2+}$ phosphors with controlled particle morphology were synthesized with the addition of NH$_4$Cl or NH$_4$F as a flux. The addition of these two flux materials were effective for the easier pulverization of the synthesized phosphors in the preliminary works done by the authors. The selection of the current flux materials was also based on the expectation of acting as the nitrogen source of the SiAlON phase in addition to the main role as the flux. The relation between the evolution of particle morphology and PL characteristics was investigated.

2. Experimental

The starting materials used for the synthesis of Ca-$\alpha$-SiAlON: Eu$^{2+}$ phosphor were Si$_3$N$_4$ (SN-E10, Ube industries, Ltd.), AlN (99.99%, H. C. Starck), and CaCO$_3$ (99.9%, Kanto Industries, Ltd.) and Eu$_2$O$_3$ (99.99%, Aldrich). The amount of flux, NH$_4$Cl (99.99%, Aldrich) or NH$_4$F (99.99%, Aldrich), was fixed at 6 wt % (Table 1). The composition employed in this research was (m, n, x, y) = (2, 1, 0.895, 0.07) located on m = 2n line in the so-called SiAlON phase plane, where the nominal composition is expressed as Ca$_{Si_{12-m-n}}$Al$_{m+n}$O$_n$N$_{16-2m}$Eu$_x$. Appropriate amount of starting powders were mixed intimately in dry state using Teflon-coated blade. The dry-mixed powder (approximately 10 g) were loosely packed into BN crucibles and fired at 1600–1800°C for 5 min–16 h under nitrogen pressure of 0.5 MPa. The heating was carried out up to 900°C under vacuum in order to ventilate

| Specimen* | Si$_3$N$_4$ | AlN | CaCO$_3$ | Eu$_2$O$_3$ | NH$_4$Cl | NH$_4$F |
|-----------|-----------|-----|---------|------------|--------|--------|
| B         | 65.22     | 19.08 | 13.81   | 1.90       | —      | —      |
| Cl        | 61.30     | 17.93 | 12.98   | 1.78       | 6.00   | —      |
| F         | 61.30     | 17.93 | 12.98   | 1.78       | —      | 6.00   |

*ff: flux-free, Cl: NH$_4$Cl-added, F: NH$_4$F-added.

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the decomposed CO₂ gas from CaCO₃ raw powder. The nitrogen gas was introduced into the chamber when the temperature reached to 900°C and with further increasing the temperature the gas pressure was built at about 0.5 MPa. The particle morphology was examined by scanning electron microscopy (JSM-6700F, Jeol). The phases of the synthesized phosphors were identified by X-ray diffractometer (D/Max 2200, Rigaku) using Cu Kα radiation operating at 36 kV and 26 mA. The PL spectra were measured using fluorescent spectrophotometers (Darsa Pro-5200, PSI Ltd.) equipped with 200 W Xe-lamp as an excitation source.

3. Results & discussion

Figure 1 illustrates the SEM micrographs of the Ca-α-SiAlON:Eu²⁺ phosphors synthesized at 1800°C for 4 h (T18t4h, ‘T’ for temperature and ‘t’ for time) and reference phosphor for the comparison. The acicular particle morphology observed in Figs. 1(a) and 1(d) is typical for Si₃N₄ and SiAlON ceramics.5,7,15) Owing to ‘solution-reprecipitation’ mechanism for the synthesis of SiAlON ceramics in which liquid phase as a vehicle for the material transportation, generally SiAlON phosphors form agglomerates as can be observed in Figs. 1(a) and 1(b). It is interesting to note that NH₄Cl-added phosphor changed to soft agglomerates and composed of round shape particles [Fig. 1(b)]. On the other hand, typical rod-like shape of separate particles was noticed for NH₄F-added composition, while the aspect ratio of particles was substantially reduced from the conventional shape. Typically, the aspect ratio of SiAlON particles are larger than 5,7,15) so fracture in length direction is indispensable during the post-treatment as shown in Fig. 1(d). Therefore, one of the engineering implications of the current research is in reducing the deterioration of PL intensity caused by fracture defects. The evolution of the particle morphology for NH₄F-added composition was traced at isothermal soaking at 1800°C from 5 min to 8 h (see Fig. 2). It is postulated that agglomerates in the early stage grow into large crystals with prolonged synthesis time. The particle size of flux-added composition is larger than that of flux-free composition as illustrated in Fig. 1, which is known for the original role of the flux for the phosphor synthesis.16)

The phase distribution of the intermediate stage was analyzed by stepwise XRD patterns. Indexed XRD patterns of T18t5m specimen and T18t16h specimen are illustrated in Fig. 3. Si was partially coated onto the surface of the specimen as a standard material for the correction of the peak position.11) Single phase α-SiAlON was detected for ‘T’ and ‘Cl’ specimen after processing at 1800°C for 5 min, while secondary phases of CaF₂ and 33R together with remnant α-Si₃N₄ and α-SiAlON [Fig. 3(a)]. When the synthesis time is further increased to 16 h a complete phase transformation with single phase α-SiAlON is evident [Fig. 3(b)].

The two major peak positions for the (201) plane and (102) plane of the SiAlONs nearest to the (100) plane of the standard Si were employed for the calculation of the lattice parameter according to Bragg’s law. Then, the ‘m’ values of the synthesized phosphors in Fig. 4 were induced by the calculated lattice parameter and the equations suggested by Rutten et al.17)

\[
a(Å) = 7.749 + 0.0673m + 0.0023an \\
c(Å) = 5.632 + 0.0550m - 0.0054n
\]

Flux-free composition exhibited higher ‘m’ values for all the synthesis conditions. Lower ‘m’ value for the flux-added compositions is attributed to the formation of second phases for NH₄F-added and ‘Ca–Cl’ liquid phase for NH₄Cl-added. Further, the highest ‘m’ value was measured for the α-SiAlONs formed at the early stage, '1600°C–5 min' in this research, where starting materials, such as Si₃N₄ and AlN, were still the major phases. As synthesis temperature and time increases, ‘m’ value converges regardless of flux addition. Hence it can be realized that higher ‘m’ value for flux-added compositions was derived by the remelting of solid compound and crystallization.

Normalized PL intensity along with the reference materials excited by 450 nm source is plotted in Fig. 5. Flux-free pho-
Fig. 2. SEM micrographs of F (NH₄F-added) specimen. (a) T18t5m, (b) T18t2h, (c) T18t4h, (d) T18t8h.

Fig. 3. Phase analysis of synthesized phosphors by XRD. (a) T18t5m, (b) T18t16h. (○: α-Si₃N₄, ●: α–SiAlON, ▲: CaF₂, ×: SiAl₁₀O₂N₁₀ (33R), Si: silicon)

Fig. 4. Calculated ‘m’ values of α-SiAlON phosphors.

Fig. 5. Normalized PL intensity (λₑₓ = 450 nm).
phor exhibits higher PL intensity up to synthesis condition of ‘1800°C–2 h’, whereas the PL intensity of flux-added phosphor exceeds that of flux-free for longer synthesis time of ≥4 h. The gain in PL intensity for flux-added phosphors can be attributed to improved crystallinity and less incorporation of surface defects. It is agreed that particle growth itself is one of proofs for the enhanced crystallinity for Si3N4 and SiAlON ceramics. That is, self-purification of particles is induced during the particle growth through ‘solution-reprecipitation’ mechanism.18,19 Further, as presumed by the observation in Fig. 1, higher energy grinding is needed for flux-free composition, which imparts surface damages on the phosphors eventually deteriorating the PL intensity. It was measured that the dominant wavelength of flux-added compositions was controlled by adding NH4Cl or NH4F as a flux for high rendition LED illumination.

4. Conclusions

The particle morphology of Eu2+–doped Ca-α-SiAlON phosphor was controlled by adding NH4Cl or NH4F as a flux. The particle morphology of the NH4Cl-added composition transformed from the typical acicular shape to an equiaxed shape, while the NH4F-added composition retained their acicular shape with reduced aspect ratio. An increase in PL intensity for the flux-added compositions is attributed to; 1) less grinding damage imparted due to both the weakened strength of phosphor agglomerates and controlled morphology with smaller aspect ratio, and 2) improved crystallinity evidenced by particle growth.

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References

1) B. S. B. Karunaratne, R. J. Lumby and M. H. Lewis, J. Mater. Res., 11, 2790–2794 (1996).
2) J. W. H. van Krevel, H. T. Hintzen, R. Metselaar and A. Meijerink, J. Alloys Compd., 268, 272–277 (1998).
3) S. Gutzov, M. Kohls and M. Lerch, J. Phys. Chem. Solids, 61, 1301–1309 (2000).
4) J. W. H. van Krevel, J. W. T. van Rutten, H. Mandal, H. T. Hintzen and R. Metselaar, J. Solid State Chem., 165, 19–24 (2002).
5) R. J. Xie, M. Mitomo, K. Uhed, F. F. Xu and Y. Akimune, J. Am. Ceram. Soc., 85, 1229–1234 (2002).
6) R. J. Xie, N. Hirosaki, S. Sakuma, Y. Yamamoto and M. Mitomo, Appl. Phys. Lett., 84, 5404–5406 (2004).
7) N. Hirosaki, R. J. Xie, K. Kimoto, T. Sekiguchi, Y. Yamamoto, T. Suehiro and M. Mitomo, Appl. Phys. Lett., 86, 211905 (2005).
8) K. Uhed, H. Takizawa, T. Endo, H. Yamane, M. Shimada, C. M. Wang and M. Mitomo, J. Lumin., 87–89, 967–969 (2000).
9) H. A. Hoppe, H. Lutz, P. Morys, W. Schnick and A. Selmieier, J. Phys. Chem. Solids, 61, 2001–2006 (2000).
10) K. Uhed, N. Hirosaki, Y. Yamamoto, A. Naito, T. Nakajima and H. Yamamoto, Electrochem. Solid-State Lett., 9, H22–H25 (2006).
11) Y. J. Park, S. H. Lee, W. K. Jang, C. B. Yoon and C. S. Yoon, J. Korean. Ceram. Soc., 47, 503–508 (2010).
12) S. Hampshire, H. K. Park, D. P. Thompson and K. H. Jack, Nature, 274, 880–882 (1978).
13) G. Petzow and M. Herrmann, Silicon nitride ceramics, Structure and Bonding, vol. 102, Springer-Verlag, Berlin, Heidelberg (2002).
14) C. L. Hewett, Y. B. Cheng, B. C. Muddle and M. B. Trigg, J. Am. Ceram. Soc., 81, 1781–1788 (1998).
15) I. W. Chen and A. Rosen, J. Amer. Chem. Soc., 120, 12027 (2004).
16) H. J. Lee, K. P. Kim, G. Y. Hong and J. S. Yoo, J. Lumin., 130, 941–946 (2010).
17) J. W. T. van Rutten, H. T. Hintzen and R. Metselaar, J. Eur. Ceram. Soc., 16, 995–999 (1996).
18) N. Hirosaki, Y. Okamoto, M. Ando, H. Munakata and Y. Akimune, J. Am. Ceram. Soc., 79, 2878–2882 (1996).
19) X. Zhu, Y. Zhou, K. Hirao and Z. Lenček, J. Am. Ceram. Soc., 89, 3331–3339 (2006).
20) R. J. Xie, N. Hirosaki, M. Mitomo, Y. Yamamoto and T. Suehiro, J. Phys. Chem. B, 108, 12027–12031 (2004).