

Effect of BaF₂ flux on the photoluminescence properties of Y_{2.94}Al₅O₁₂ : 0.06Ce³⁺ phosphors for white LED applications

H. Kim^a, J. Kim^b, J. S. Han^c and K. Park^{a,*}

^aFaculty of Nanotechnology and Advanced Material Engineering, Sejong University, Seoul 143-747, Korea

^bDepartment of Advanced Materials Engineering, Hoseo University, Asan 336-795, Korea

^cRegional Innovation Center, Hoseo University, Asan 336-795, Korea

We prepared Y_{2.94}Al₅O₁₂ : 0.06Ce³⁺ phosphors by sol-gel method using BaF₂ flux (0–8 wt%). The effect of BaF₂ flux content on the crystal structure, morphology, and photoluminescence properties of the Y_{2.94}Al₅O₁₂ : 0.06Ce³⁺ phosphors was investigated. XRD patterns revealed that all the prepared phosphors had the cubic crystal structure. The emission spectra had a broad emission band covering 460–750 nm, with a maximum emission intensity at 553 nm. The added BaF₂ flux significantly improved the photoluminescence properties. The emission intensity peaking at 553 nm of 6 wt% BaF₂-containing Y_{2.94}Al₅O₁₂ : 0.06Ce³⁺ phosphors was above twice higher than that of BaF₂-free Y_{2.94}Al₅O₁₂ : 0.06Ce³⁺ phosphors. This result indicates that the BaF₂ used as a flux was highly effective for improving the photoluminescence properties.

Key words: Phosphor, BaF₂ flux, LED, Ce³⁺, YAG

Introduction

In recent years, white light-emitting diodes (LEDs) have been used as an illumination light source as well as components of display devices because they have high efficiency to convert electrical energy into light, high energy saving, high reliability, long lifetime, fast response, and non-pollution [1–7]. Most commercially available white LEDs combine InGaN blue LEDs with a Y₃Al₅O₁₂ : Ce³⁺ (YAG : Ce) yellow phosphor. The absorption and emission transitions of the activator Ce³⁺ in YAG : Ce involve the 5d and 4f energy levels. The transitions depended strongly on the crystal field environment and the site symmetry of the host lattice [8].

Generally, YAG : Ce phosphors have been synthesized by the solid-state reaction method. To obtain desired phase purity and optical quality, the solid-state reaction method needs long ball-milling and high-temperature heat treatment of constituent oxides (~1600 °C), which generally introduce additional impurities and defects [9]. Therefore, to synthesize high-quality YAG : Ce phosphors, several liquid-chemical synthesis methods are widely studied, including sol-gel, co-precipitation, spray pyrolysis, solution combustion methods [10]. Among these methods, sol-gel method is attracting significant attention because of its high phase-purity, which is due to the molecular level mixing at relatively low processing temperature, and its low crystallization temperature, which is due to the extended networks of cross-linked metal centers

[3, 11].

The addition of flux to the reactants is an effective way to accelerate the formation of the desired compounds by enhancing diffusivity of the components and to enhance the annealing [12]. To date, H₃BO₃, NH₄Cl, NH₄F, NH₄Br, BaCl₂, BaBr₂, CaF₂, and BaF₂ as fluxes have been used for fabricating phosphors [13]. The flux used during sol-gel process affects the ionic diffusions, crystallization, and emission efficiency. In this work, Y_{2.94}Al₅O₁₂ : 0.06Ce³⁺ phosphors were prepared by sol-gel method with the addition of BaF₂ flux and then the effects of BaF₂ flux on the crystal structure, morphology, and photoluminescence intensity of the phosphors were investigated.

Experimental

Y_{2.94}Al₅O₁₂ : 0.06Ce³⁺ powders were synthesized via the sol-gel method. An appropriate amount of Y(NO₃)₃ and Al(NO₃)₃ · 9H₂O was mixed in a beaker containing ethanol. The mixture was stirred for 30 min at room temperature. Then, Ce(NO₃)₃ · 6H₂O was added into the prepared mixture following by stirring the solution for 1 h. After stirring, acetone was added into the solution. The obtained solution was heated at 60 °C in an electric oven to form a white gel. Subsequently, the gel was heated at 300 °C for 4 h in an electric furnace to form dry powders. BaF₂ (2, 4, 6, and 8 wt%) was added as a flux into the dried powders followed by mixing the powders for 12 hrs. The mixed powders were annealed at 1400 °C for 4 hrs in air.

The crystal structure of the annealed Y_{2.94}Al₅O₁₂ : 0.06Ce³⁺ phosphors was analyzed with an X-ray diffractometer (XRD; Rigaku RINT2000) with Cu-Kα

*Corresponding author:
Tel : +82-2-3408-3777
Fax: +82-2-3408-4342
E-mail: kspark@sejong.ac.kr

($\lambda = 1.5406 \text{ \AA}$) at 40 KV and 100 mA. Morphology and size of the annealed phosphors were investigated with a field-emission scanning electron microscopy (FE-SEM; Hitachi S4700). Emission spectra were obtained with a spectrofluorometer (FS-2 Scinco Co.) equipped with a xenon lamp.

Results and Discussion

Fig. 1 shows the XRD patterns of the annealed $\text{Y}_{2.94}\text{Al}_5\text{O}_{12} : 0.06\text{Ce}^{3+}$ phosphors fabricated by adding different amounts of BaF_2 . All the phosphors had high-purity, single-phase with cubic structure, irrespective of the amount of BaF_2 flux. These XRD patterns are in good agreement with JCPDS Card 33-0040. No peak due to barium and fluorine components present in BaF_2 is detected in the XRD patterns. This means that BaF_2 was mainly eliminated from the phosphor powders by evaporation during the annealing treatment. The crystallite size (D) of the annealed $\text{Y}_{2.94}\text{Al}_5\text{O}_{12} : 0.06\text{Ce}^{3+}$ phosphors is calculated from the Scherrer's formula: $D = (0.9\lambda)/(\beta\cos\theta)$, where λ is the wavelength of radiation, θ is the angle of the diffraction peak, and β is the full width at half maximum of the diffraction peak (in radian) [14]. The calculated crystallite sizes gradually increase with increases in the BaF_2 amount, i.e., 46.9, 59.2, 60.5, 62.3, and 63.8 nm for 0, 2, 4, 6, and 8 wt%, respectively.

FE-SEM images of the $\text{Y}_{2.94}\text{Al}_5\text{O}_{12} : 0.06\text{Ce}^{3+}$ phosphors fabricated by adding different amounts of BaF_2 are shown in Fig. 2. The phosphors consist of spherical-like particles. With increasing amount of BaF_2 , the powder size gradually increases and the morphology of some powders changes from spherical-like shape to multifaceted shape. For example, the mean sizes of the $\text{Y}_{2.94}\text{Al}_5\text{O}_{12} : 0.06\text{Ce}^{3+}$ phosphors fabricated by adding 0, 4, and 8 wt% BaF_2 are 0.7, 1.1, and 1.7 μm , respectively.

Fig. 3 shows the excitation spectra of the $\text{Y}_{2.94}\text{Al}_5\text{O}_{12} : 0.06\text{Ce}^{3+}$ phosphors fabricated by adding different amounts of BaF_2 , monitored at 553 nm. These phosphors show similar excitation characteristics, irrespective of the amounts of BaF_2 , except for the excitation intensity. The excitation intensity increases with increasing BaF_2 amount, reaching a maximum intensity at 6 wt% BaF_2 . The excitation spectra of the $\text{Y}_{2.94}\text{Al}_5\text{O}_{12} : 0.06\text{Ce}^{3+}$ phosphors have two bands: one is a weak band with a maximum intensity at 345 nm, and the other is a strong band with a maximum intensity at 452 nm. These bands are attributed to the allowed electric-dipole inter-configurational 4f-5d transition of Ce^{3+} ions. The ground state is split into the $^2F_{7/2}$ and $^2F_{5/2}$ levels with an energy difference of about 2200 cm^{-1} , and the next higher 5d state is split into several 5d sub-levels by crystal-field of the host matrix [15,16]. The excitation bands peaked at 345 and 452 nm are caused by transitions from the 4f ground state ($^2F_{5/2}$ or $^2F_{7/2}$) to the first excited 5d energy level ($5d^1$) and from the 4f

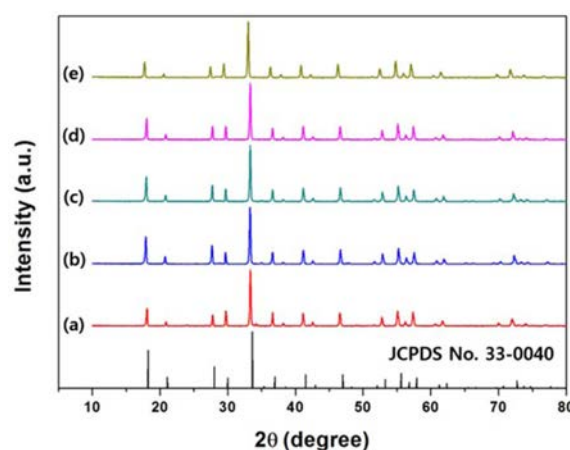


Fig. 1. XRD patterns of the annealed $\text{Y}_{2.94}\text{Al}_5\text{O}_{12} : 0.06\text{Ce}^{3+}$ phosphors fabricated by adding different amounts of BaF_2 : (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 wt% BaF_2 .

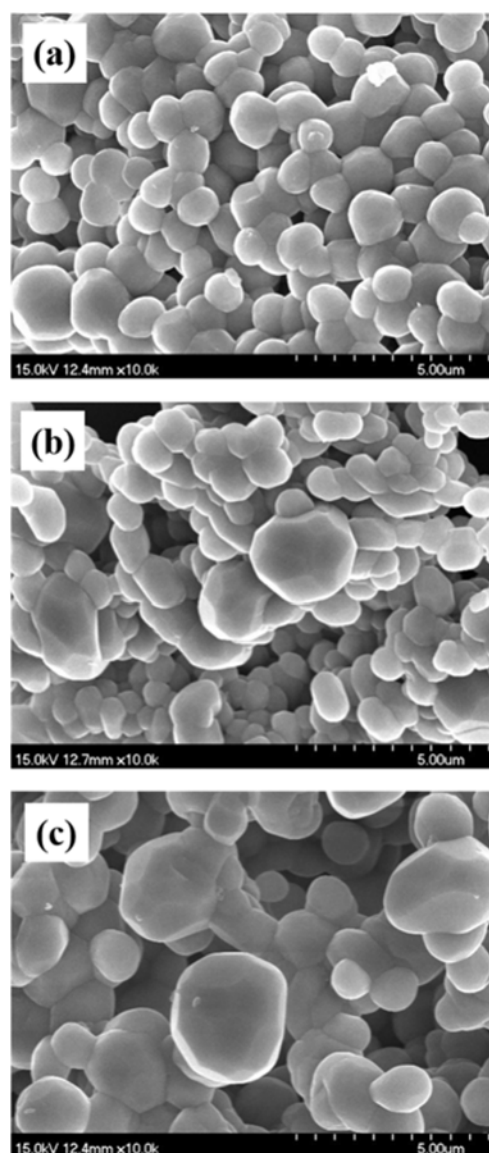


Fig. 2. FE-SEM images of the $\text{Y}_{2.94}\text{Al}_5\text{O}_{12} : 0.06\text{Ce}^{3+}$ phosphors fabricated by adding different amounts of BaF_2 : (a) 0, (b) 4, and (c) 8 wt% BaF_2 .

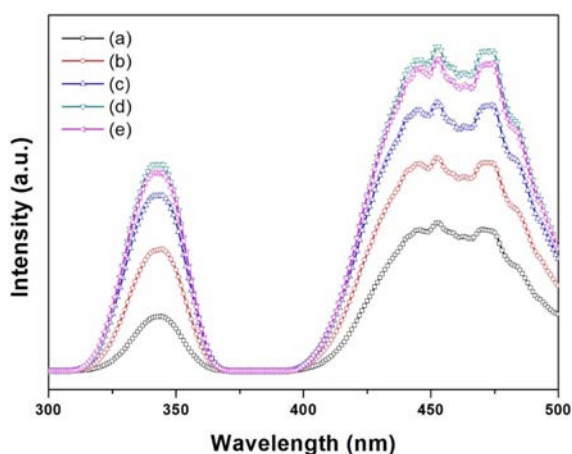


Fig. 3. Excitation spectra of the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors fabricated by adding different amounts of BaF₂: (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 wt% BaF₂.

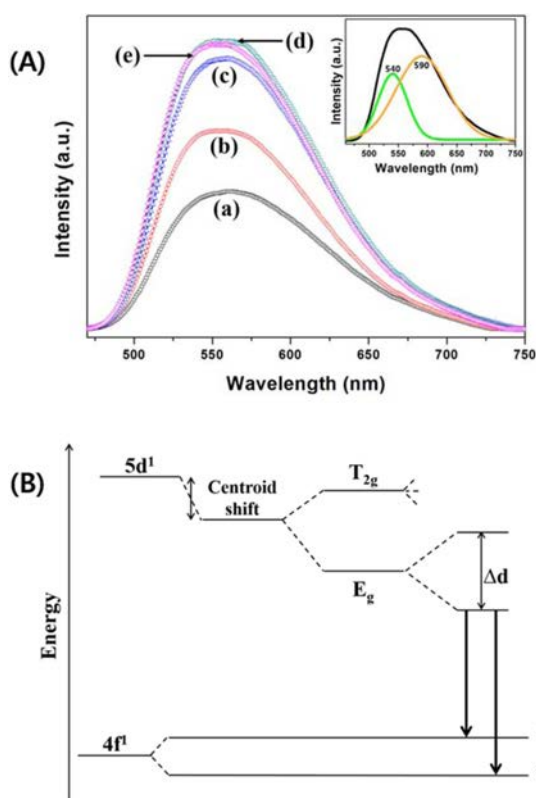


Fig. 4. (A) Emission spectra of the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors fabricated by adding different amounts of BaF₂: (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 wt% BaF₂. (B) A schematic diagram showing the photoluminescence mechanism of Ce³⁺ ions in the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors.

ground state (²F_{5/2} or ²F_{7/2}) to the second excited 5d energy level (5d²), respectively [17, 18]. The intensity of excitation band at 452 nm is stronger than that at 345 nm so that the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors can be efficiently excited by blue LED chips, generating white light. The emission wavelength of commercially available blue LED chips is in the range of 400–500 nm.

The emission spectra of the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺

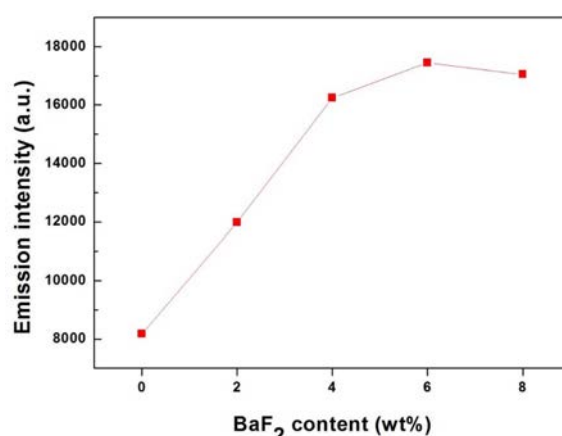


Fig. 5. The emission intensity peaking at 553 nm for the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors as a function of BaF₂ content.

phosphors fabricated by adding different amounts of BaF₂ under 452 nm excitation are shown in Fig. 4(A). This figure shows broad and asymmetric band covering from 460 to 750 nm with a maximum intensity at around 553 nm, which corresponds to greenish yellow emission. It can be seen that the location and shape of the emission spectra are not significantly changed with the variation of BaF₂ amount. This means that the added BaF₂ does not affect the crystal-field strength of the host matrix. The light emitted is attributed to the transition of Ce³⁺ ions from the 5d to the 4f energy state. Because the radial wave function of the excited 5d electron extends spatially well beyond the closed 5s²5p⁶, their states are strongly perturbed by the crystal field [17]. The emission spectra obtained here can be deconvoluted into two Gaussian curves centered at about 540 and 590 nm. For example, the inset shown in Fig. 4(A) represents the two Gaussian curves of the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors fabricated by adding 6 wt% BaF₂. These two Gaussians can be attributed to the allowed electric-dipole interconfigurational transitions from the lowest crystal field component (5d¹) to the two levels of the ground state (²F_{5/2} and ²F_{7/2}), i.e., 5d¹ → ²F_{7/2} and 5d¹ → ²F_{5/2} transitions [18, 19].

The luminescence mechanism of Ce³⁺ ions in the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors can be explained by the energy-level diagram, as shown in Fig. 4(B). When the 453 nm light is applied to the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors, Ce³⁺ ions are excited from the ground state to excited state and then fall down to the lowest excited state (5d¹) through non-radiative relaxation. Subsequently, the Ce³⁺ ions in the excited state fall into the ground states (²F_{5/2} and ²F_{7/2}), 5d¹ → ²F_{7/2} and 5d¹ → ²F_{5/2} transitions. Consequently, greenish yellow light is emitted by the energy difference between the two states of Ce³⁺ ions.

The emission intensity peaking at 553 nm for the Y_{2.94}Al₅O₁₂: 0.06Ce³⁺ phosphors as a function of BaF₂ amount is shown in Fig. 5. The emission intensity increases with increasing BaF₂ amount up to 6 wt% due to the improved crystallinity and reduced defects and then

decreases with more BaF₂ amount due to the partially melted powders. The emission intensity peaking at 553 nm of 6 wt% BaF₂-containing Y_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphors is above twice higher than that of BaF₂-free Y_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphors. This result indicates that the BaF₂ used as a flux is highly effective for enhancing the emission intensity.

Conclusions

The Y_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphors fabricated by adding BaF₂ (0-8 wt%) crystallized in the cubic crystal structure. The powder size and photoluminescence properties of the Y_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphors were strongly affected by the amounts of BaF₂ flux. With increasing amount of BaF₂, the powder sizes increased gradually, and the morphology of some powders changed from spherical-like shape to multifaceted shape. Two broad excitation bands were located at 345 and 452 nm, irrespective of the amount of BaF₂ flux. The phosphors showed a broad emission band covering 460 and 750 nm, with a maximum emission intensity at 553 nm. The added BaF₂ flux significantly improved the photoluminescence properties. The Y_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphor fabricated by adding 6 wt% BaF₂ flux showed the strongest emission intensity. The emission intensity peaking at 553 nm of 6 wt% BaF₂-containing Y_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphors was greater than above twice in comparison with BaF₂-free Y_{2.94}Al₅O₁₂:0.06Ce³⁺ phosphors. We believe indicates that the BaF₂ used as flux is highly effective for improving the photoluminescence properties.

References

1. H.S. Jang, W.B. Im, D.C. Lee, D.Y. Jeon, and S.S. Kim J. Lumin. 126 (2007) 371-377.
2. L. Zhang, Z. Lu, J. Zhu, H. Yang, P. Han, Y. Chen, and Q. Zhang, J. Rare Earths 30 (2012) 289-296.
3. S. Xu, L. Sun, Y. Zhang, H. Ju, S. Zhao, D. Deng, H. Wang, and B. Wang, J. Rare Earths 27 (2009) 327-329.
4. S.J. Yoon, S.J. Dhoble, and K. Park, Ceram. Int. 40 (2014) 4345-4350.
5. A. Hakeem, K.N. Shinde, S.J. Yoon, S.J. Dhoble, and K. Park, J. Nanosci. Nanotechnol. 14 (2014) 5873-5876.
6. S.J. Yoon and K. Park, Inter. J. Hydro. Ener. 40 (2015) 825-832.
7. K.Y. Kim, S.J. Yoon, and K. Park, J. Lumin. 160 (2015) 78-84.
8. J.D. Furman, G. Gundiah, K. Page, N. Pizarro, and A.K. Cheetham, Chem. Phys. Lett. 465 (2008) 67-72.
9. P. Rai, M.K. Song, H.M. Song, J.H. Kim, Y.S. Kim, I.H. Lee, and Y.T. Yu, Ceram. Int. 38 (2012) 235-242.
10. X. Li and W. Wang, Powder Technol. 196 (2009) 26-29.
11. A. Boukerika, L. Guerbous, and N. Brihi, J. Alloys Compd. 614 (2014) 383-388.
12. S.J. Yoon and K. Park, Opt. Mater. 36 (2014) 1305-1310.
13. V. Sivakumar and A. Lakshmanan, J. Lumin. 145 (2014) 420-424.
14. H.J. Lee, K.P. Kim, and G.Y. Hong, and J.S. Yoo, J. Lumin. 130 (2010) 941-946.
15. R. Praveena, L. Shi, K.H. Jang, V. Venkatramu, C.K. Jayasankar, and H.J. Seo, J. Alloys Compd. 509 (2011) 859-863.
16. H.T. Kim, J.H. Kim, J.-K. Lee, and Y.C. Kang, Mater. Res. Bull. 47 (2012) 1428-1431.
17. W.Q. Chen, D.S. Jo, Y.H. Song, T. Masaki, and D.H. Yoon, J. Lumin. 147 (2014) 304-309.
18. A. Boukerika and L. Guerbous, Opt. Mater. 40 (2015) 14-19.
19. S.R. Naik, T. Shripathi, and A.V. Salker, J. Lumin. 161 (2015) 335-342.