Effect of boron concentration in $Y_2O_3$:(Eu,B) phosphor on luminescence property

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Abstract

$Y_2O_3$:(Eu,B) red phosphor was obtained by a thermal decomposition technique of a mixture of yttrium–ethylenediaminetetraacetic acid (Y–EDTA), Eu–EDTA and boric acid. The doping ratio of boron, $[B]/([Y]+[Eu])$, in the starting material was varied from 0 to 1. The properties of morphology, crystallization behavior, metal composition and photoluminescence of resulting $Y_2O_3$:(Eu,B) powder were examined. The $Y_2O_3$:(Eu,B) powder had spherical shape with a diameter of 1–5 μm with some hollows on the surface. No secondary cohesive particles were seen. X-ray diffractometry revealed that although the crystallinity of powder was improved with addition of small amounts of boron, it decreased with excess amounts of boron. Several peaks indexed as the impurity phases of $Y_3BO_6$ and $YBO_3$ were observed on the samples obtained under condition of excess amounts of boron. The photoluminescence intensity observed at 611 nm was dependent upon crystallinity of the sample.

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1. Introduction

Europium-doped yttria, $Y_2O_3$:Eu, is a well-known red phosphor excited by ultraviolet (UV) and electron irradiation. It is typically used for the electronic display devices such as cathode ray tube (CRT), field emission display (FED) and plasma display panel (PDP). These applications need well-organized particles with a large surface area and well-fluidity to achieve formation of closed packing of the phosphor particle layer.

In our previous study, pressing products of a mixture of powders of strontium–ethylenediaminetetraacetic acid (Sr–EDTA), Ba–EDTA and Ti–EDTA complexes formed by a spray-dry technique were used as a target on the laser deposition method for the synthesis of (Sr,Ba)TiO$_3$ thin films [1]. The metal–EDTA complex target mixed homogeneously achieved surface morphological control, well designated metallic composition and decline of the deposition temperature of the films. The EDTA molecule forms stable and water-soluble metal chelate with the metal ion having two or more valences. The spray drier solidifies solution of the mixture of metal–EDTA’s momentarily. In our previous study, $Y_2O_3$:Eu red phosphor having spherical shape with a diameter of 1–30 μm was obtained [2]. The photoluminescence intensity of the $Y_2O_3$:Eu powder increased with increasing the crystallite size. This suggests that the crystallite size is the most important parameter to vary the photoluminescence intensity.

To assist the sintering reaction, addition of the flux is a popular method to accelerate the sintering and/or crystal growth reaction. Boron compounds are widely used as the flux for the conventional solid-state reaction because of its low melting point. Boron oxide (B$_2$O$_3$) having the melting point of 460 °C is the most available boron compounds for the flux. A phosphor oxide, YBO$_3$:Eu, is one of the good examples. Various synthesis techniques have been developed to prepare YBO$_3$:Eu phosphor, such as solid-state reaction [3], coprecipitation [4], spray pyrolysis [5].
and sol–gel [6] methods. However, it is easy to deviate the boron composition due to the evaporation of boron during the firing, as a result, impurity phase of Y$_3$BO$_6$ is produced [7,8].

In this study, Y$_2$O$_3$:(Eu,B) phosphor powder was obtained by the thermal decomposition of the mixture of Y–EDTA, Eu–EDTA and boric acid, formed by a spray-dryer with solution of metal–EDTA and boric acid. The properties of morphology, crystallization behavior, metal composition and photoluminescence of resulting Y$_2$O$_3$:(Eu,B) powder were described and discussed.

2. Experimental

The following materials were used: EDTA·2NH$_4$(99.9%) was from Chubu Chelest; Y$_2$(CO$_3$)$_3$·3H$_2$O(99.99%), Eu$_2$O$_3$(99.95%) and boric acid(99.9%) were supplied by Kanto Chemical. First, EDTA·2NH$_4$ was solved into deionized water followed by gentle stirring for 0.5 h at a temperature of 60 °C. Then, Y$_2$(CO$_3$)$_3$·3H$_2$O and Eu$_2$O$_3$ weighted accurately were added into EDTA·2NH$_4$ solution with the mole ratio of EDTA/([Y] + [Eu]) of 1 so as to be [Y]/[Eu] composition of $x$ = 0.10 of Y$_2$:Eu$_x$. The mixture was stirred for 2 h at a temperature of 100 °C, then cooled at ambient temperature. Boric acid was added and dissolved at the [B]/([Y] + [Eu]) composition ratios of 0–1. EDTA becomes good inhibitor for deposition of metal borates in boric acid solution. Finally, mixed solution of Y–EDTA, Eu–EDTA and boric acid was obtained by further addition of deionized water till the concentration of the solution becomes 15 wt%.

The mist of solution was instantly dried using a spray-dryer, SD-1000, Tokyo Rikakikai Co. A twin-fluid nozzle was attached to the spray and employed in this experiment. The twin-fluid nozzle consists of an air cap and a liquid cap. We selected appropriate nozzles, 64-SS with an internal diameter of 1.27 mm and 1050-SS with an internal diameter of 0.25 mm as air cap and liquid cap, respectively. The following conditions were used during spray-drying: inlet temperature of 160 °C; outlet temperature of 95 °C; feeding rate of solution of 300 ml/h and dry air flow of 0.6 m$^3$/min. The powder form of the mixture of Y–EDTA, Eu–EDTA and boric acid was fired to decompose EDTA using an air-opened electric muffle furnace at a temperature of 1000 °C for 0.5 h.

Scanning electron microscopy (SEM: T-300, JEOL) was conducted to determine the particle size and observe morphology of the unfired chelate and fired metal oxide powder. The average particle diameter was estimated from measurement of approximately 200 particles each micro-image. X-ray diffractometry (XRD: M03XHF22, MAC Science Co., Ltd) with Cu K$\alpha$ radiation was employed to determine the crystal structure. The luminescence spectra, excited by UV at 254 nm, were examined using a photoluminescence spectrometer (FP-6500D, JASCO Co.). The metal composition of Y$_2$O$_3$:(Eu,B) phosphor was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES: Optima3300DV, PerkinElmer, Inc.).

3. Results and discussion

Fig. 1 shows the SEM images of resultant Y$_2$O$_3$:(Eu,B) powder obtained with metal–EDTA complexes mixed at

Fig. 1. SEM images of morphology of Y$_2$O$_3$:(Eu,B) powders fired at 1000 °C for 0.5 h. The [B]/([Y] + [Eu]) ratio was varied from 0 to 1.
the \([B]/([Y]+[Eu])\) composition ratios of 0–1. The particles had spherical shape with a diameter of 1–5 \(\mu\)m with some hollows on the surface. This result had a good agreement with the result that \(Y_2O_3:Eu\) was obtained through thermal decomposition of \((Y,Eu)\)--EDTA complexes formed by the spray-dryer [2]. There is no relationship between the particle size and the doping amount of boric acid. The number of hollows existing on the surface of the \(Y_2O_3:(Eu,B)\) particle increased with increasing the doping amount of boron.

Fig. 2 shows the average particle diameter of \(Y_2O_3:(Eu,B)\) powder obtained at the \([B]/([Y]+[Eu])\) composition ratios of 0.0001–1. The logarithm of \([B]/([Y]+[Eu])\) and average particle diameter, respectively. The average particle diameter was approximately 2\(\mu\)m, suggesting that no relationship between average particle diameter and doping boron content in \(Y_2O_3:(Eu,B)\) powder. The \(Y_2O_3:(Eu,B)\) formation reaction proceeds through following two steps. First, the metal–EDTA complex is decomposed in the temperature range of 300–400 \(^\circ\)C [9]. For example, \(Y\)--EDTA complex and \(Eu\)--EDTA complex are decomposed at the temperature range of 350–400 and 340–390 \(^\circ\)C, respectively. Second, crystallization of the \(Y_2O_3\) occurs by additional heating. The single phase of \(Y_2O_3:Eu\) has been obtained by thermal decomposition of \((Y,Eu)\)--EDTA powder at the reaction temperature of 600 \(^\circ\)C [2].

Fig. 3 demonstrates X-ray diffraction pattern of \(Y_2O_3:(Eu,B)\) powder obtained with the \([B]/([Y]+[Eu])\) composition ratios of 0–1. The sample with the compositions under 0.1 indicated (222), (400), (440) and (622) peaks of \(Y_2O_3\) phase. Especially, the diffraction intensity of \(Y_2O_3:(Eu,B)\) with the \([B]/([Y]+[Eu])\) composition ratios of 0.0001 and 0.0005 is stronger than that of non-doped \(Y_2O_3:Eu\), implying the improvement of the crystallinity by addition of boron. In contrast, the diffraction intensity suddenly decreased with increasing the boron composition over 0.001. This suggests that overdoping of boron inhibits crystal growth of \(Y_2O_3:(Eu,B)\) particle. Further boron doping may produce the impurity phase. For example, the \(Y_3BO_6\) phase was observed from the sample with the \([B]/([Y]+[Eu])\) composition ratios of 0.2 and 0.5. Other diffraction peaks observed from the sample with the \([B]/([Y]+[Eu])\) composition ratio of 1 are attributable to diffraction lines of (102), (002), (100) and (101) of \(YBO_3\) crystalline phase.

Fig. 4 shows the crystallite size of \(Y_2O_3:(Eu,B)\) powder obtained with the \([B]/([Y]+[Eu])\) composition ratios of 0.0001–1. The crystallite size \(t\) was calculated from the half-width of the peak at 29.0\(^\circ\) on the X-ray diffraction pattern using Scherrer’s equation,

\[
T = \frac{0.9\lambda}{B \cos \theta_B},
\]

where \(\lambda\), \(B\) and \(\theta_B\) are wavelength of X-ray (\(\lambda = 1.5405 \times 10^{-1}\) nm), half-width of the diffraction peak and the diffraction angle, respectively. The average crystallite
sizes of Y$_2$O$_3$:Eu,B powder obtained with the [B]/([Y]+[Eu]) composition ratios of 0.0001 and 0.0005 were determined to be 70 and 66 nm, respectively. These values slightly larger than 64 nm that is average crystallite size of non-doped Y$_2$O$_3$:Eu, implying that very small effect was observed. This result suggests that although boron doping works as the flux at the firing process, the crystallite size decreased with increasing the boron composition over 0.001.

Boric acid becomes boron oxide at 800 °C by dehydration via metaboric acid,

$$2\text{H}_3\text{BO}_3 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}.$$  

As the vapor pressure of boron oxide at 800 °C is relatively high, $1.16 \times 10^{-9}$ Pa, boron oxide is known as high volatile material. Therefore, lack of boron may occur by evaporation of boron during the firing process. To prevent this phenomenon, excess amounts of boron is generally added to the sample during the preparation. For example, Cohen-Adad et al. synthesized $(1-x)\text{Ln}_2\text{O}_3 - x\text{B}_2\text{O}_3$ ($\text{Ln} = \text{Gd,Y,Yb}$) using the solid-state reaction method with Ln$_2$O$_3$ and 5–10 mol% boric acid [10]. Sohn et al. also synthesized $(\text{Y,Gd})\text{BO}_3$;Eu using the spray pyrolysis technique from solution that contains 30 mol% excess boron based on stoichiometric composition [8]. Table 1 shows the composition of Y, Eu and B obtained with the [B]/([Y]+[Eu]) composition ratios of 0.0001–1. Note that $x$ represents the fraction in Y$_{2-x}$O$_3$:Eu$^+$. The doping fraction of Eu in the fired sample, $x$, was kept constant at 0.1 for each [B]/([Y]+[Eu]) composition ratio, suggesting that no deviation of europium composition was occurred. In addition, the [B]/([Y]+[Eu]) ratio was unvaried before and after firing. This result implies that evaporation of boron was completely prevented during the firing process.

The reaction process without vaporization of boron from the sample is explained using homogeneous dispersion phenomenon in the EDTA mixture. During the reaction, Y$_2$O$_3$ and Eu$_2$O$_3$ are formed at the temperature of 350–400 °C by thermal decomposition of Y–EDTA and Eu–EDTA, respectively. As the (Y,Eu)–EDTA powder formed by the spray-dryer may be mixed homogeneously in molecular scale, solid solution with homogeneous dispersion of Eu in Y$_2$O$_3$ would be achieved momentarily by thermal decomposition of the (Y,Eu)–EDTA powder. Boron is also thought to exist homogeneously in each (Y,Eu)–EDTA particle through the solidified process from solution. Fig. 5 demonstrates the photoluminescence spectra of Y$_2$O$_3$:Eu,B powders as a function of the [B]/([Y]+[Eu]) ratio. The emission spectrum comprised of lines in the red spectral area corresponded to transition from the excited $5D_0$ level to $7F_J$ ($J=0,1,2,3,4$) level of $^4F_6$ configuration of Eu$^{3+}$ ion was observed at the [B]/([Y]+[Eu]) composition and after firing.

| Before firing | After firing |
|---------------|-------------|
| [B]/([Y]+[Eu]) | x (as Y$_{2-x}$O$_3$:Eu$^+$) | [B]/([Y]+[Eu]) | x (as Y$_{2-x}$O$_3$:Eu$^+$) |
| 0.0001        | 0.10        | 0.00011       | 0.093          |
| 0.0005        | 0.10        | 0.00050       | 0.096          |
| 0.001         | 0.10        | 0.0011        | 0.096          |
| 0.005         | 0.10        | 0.0049        | 0.096          |
| 0.01          | 0.10        | 0.0103        | 0.102          |
| 0.05          | 0.10        | 0.0499        | 0.103          |
| 0.1           | 0.10        | 0.128         | 0.096          |
| 0.2           | 0.10        | 0.247         | 0.101          |
| 0.5           | 0.10        | 0.535         | 0.098          |
| 1.0           | 0.10        | 1.097         | 0.097          |

Fig. 4. Crystallite size of Y$_2$O$_3$:Eu,B powders as a function of the [B]/([Y]+[Eu]) ratio.

Fig. 5. Photoluminescence spectra of Y$_2$O$_3$:Eu,B powders as a function of the [B]/([Y]+[Eu]) ratio.
ratios under 0.2 [11]. The most intense peak at 611 nm is assigned to the $^5D_0$/$^7F_2$ transition. On the other hand, a weak emission peak was observed at 611 nm from the sample formed at the \([\text{B}]/(\text{Y} + \text{Eu})\) composition ratio of 0.5. Two weak emission peaks at 590 and 611 nm can be assigned to the $^5D_0$/$^7F_1$ transition and $^5D_0$/$^7F_2$ transition of YBO$_3$, respectively, were observed at the \([\text{B}]/(\text{Y} + \text{Eu})\) composition ratio of 1.

Fig. 6 shows relative photoluminescence intensity obtained from Y$_2$O$_3$:Eu:B powder as a function of the \([\text{B}]/(\text{Y} + \text{Eu})\) ratio. Note that relative photoluminescence intensity of Y$_2$O$_3$:Eu powder, at the \([\text{B}]/(\text{Y} + \text{Eu})\) ratio of 0, was 0.71. It decreased to 0.67 at the \([\text{B}]/(\text{Y} + \text{Eu})\) composition ratio of 0.0001. Furthermore it kept constant under the range of the \([\text{B}]/(\text{Y} + \text{Eu})\) composition ratio of 0.0001–0.1. The drastic decrease of the relative photoluminescence intensity may be induced by formation of the impurity phase, Y$_3$BO$_6$, observed in the sample synthesized with the metal complex having the \([\text{B}]/(\text{Y} + \text{Eu})\) composition ratio of more than 0.2.

4. Conclusion

Y$_2$O$_3$:Eu:B phosphor powder was obtained by the thermal decomposition method of the mixture of Y–EDTA, Eu–EDTA and boric acid at firing conditions of the temperature of 1000 °C and duration of 0.5 h. Improvement of crystallinity of Y$_2$O$_3$:Eu:B was observed at the \([\text{B}]/(\text{Y} + \text{Eu})\) composition ratio of 0.0001 and 0.0005. In contrast, crystallite size of Y$_2$O$_3$:Eu:B decreased with further increasing the \([\text{B}]/(\text{Y} + \text{Eu})\) ratio. The impurity phase, Y$_3$BO$_6$, was observed at the \([\text{B}]/(\text{Y} + \text{Eu})\) composition ratio of 0.2 and 0.5. In addition, YBO$_3$ was obtained at the further \([\text{B}]/(\text{Y} + \text{Eu})\) composition ratio. The relative photoluminescence intensity of Y$_2$O$_3$:Eu powder decreased from 0.71 to 0.67 by addition of boron. Excess amounts of boron doping decrease relative photoluminescence intensity drastically. The formation of Y$_3$BO$_6$ phase is one of the possible reasons for the depression of the luminescence.

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References

[1] A. Nakamura, R. Sato, S. Ohshio, N. Nambu, H. Saitoh, Laser deposition of (Sr,Ba)TiO$_3$ films with metal–ethylenediaminetetraacetic acid complexes, Jpn J. Appl. Phys. 41 (2002) 3033–3038.

[2] A. Nakamura, N. Nambu, K. Kawahara, S. Ohshio, H. Saitoh, Y$_2$O$_3$:Eu red phosphor powder synthesized with EDTA complexes, J. Ceram. Soc. Jpn 111 (2003) 142–146.

[3] M. Ren, J.H. Lin, Y. Dong, L.Q. Yang, M.Z. Su, L.P. You, Structure and phase transition of GdBO$_3$, Chem. Mater. 11 (1999) 1576–1580.

[4] K.N. Kim, H.K. Jung, H.D. Park, D. Kim, Synthesis and characterization of red phosphor (Y,Gd)BO$_3$:Eu by the coprecipitation method, J. Mater. Res. 17 (2002) 907–910.

[5] D.S. Kim, R.Y. Lee, Synthesis and photoluminescence properties of (Y,Gd)BO$_3$:Eu phosphor prepared by ultrasonic spray, J. Mater. Sci. 35 (2000) 4777–4782.

[6] D. Boyer, G. Bertrand-Chadeyron, R. Mahiou, C. Caperaa, J.C. Cousseins, Synthesis dependent luminescence efficiency in Eu$^{3+}$ doped polycrystalline YBO$_3$, J. Mater. Chem. 9 (1999) 211–214.

[7] Y.C. Kang, S.B. Park, Morphology of (Y,Gd$_{1-x}$)$_3$BO$_6$:Eu phosphor particles prepared by spray pyrolysis from aqueous and colloidal solutions, Jpn J. Appl. Phys. 38 (1999) L1541–L1543.

[8] J.R. Sohn, Y.C. Kang, H.D. Park, S.G. Yoon, (YGd)BO$_3$:Eu Phosphor particles prepared from the solution of polymeric precursors by spray pyrolysis, Jpn J. Appl. Phys. 41 (2002) 6007–6010.

[9] A. Mercandante, M. Ionashiro, L.C.S. De Oliveira, C.A. Ribeiro, L. Monscardi d’Assunção, Preparation and thermal decomposition of solid state lanthanide(III) and yttrium(III) chelates of ethylenediaminetetraacetic acid, Thermochim. Acta 216 (1993) 267–277.

[10] M.Th Cohen-Adad, O. Alioui-Lebbou, C. Goutaudier, G. Panczer, C. Dujardin, C. Pedrini, P. Florian, D. Massiot, F. Gerard, Ch. Kappenstein, Gadolinium and yttrium borates: thermal behavior and structural considerations, J. Solid State Chem. 154 (2000) 204–213.

[11] G. Blasse, B.C. Geiabmaier, Luminescence Materials, Springer, Berlin, 1994, p. 117.