

# Influences of the Eu Concentration and the Milling Time on Photoluminescence Properties of $Y_2O_3-H_3BO_3:Eu^{3+}$ Powders Prepared by Mechanical Alloying

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**Abstract**  $Y_2O_3-H_3BO_3:Eu^{3+}$  powders are synthesized using a mechanical alloying method, and their photoluminescence (PL) properties are investigated through luminescence spectrophotometry. For samples milled for 300 min, some  $Y_2O_3$  peaks ([222], [440], and [622]) and amorphous formations are observed. The 300-min-milled mixture annealed at 800°C for 1 h with Eu = 8 mol% has the strongest PL intensity at every temperature increase of 100°C (increasing from 700 to 1200°C in 100°C increments). PL peaks of the powder mixture, as excited by a xenon discharge lamp (20 kW) at 240 nm, are detected at approximately 592 nm (orange light,  $^5D_0 \rightarrow ^7F_1$ ), 613 nm, 628 nm (red light,  $^5D_0 \rightarrow ^7F_2$ ), and 650 nm. The PL intensity of powder mixtures milled for 120 min is generally lower than that of powder mixtures milled for 300 min under the same conditions. PL peaks due to  $YBO_3$  and  $Y_2O_3$  are observed for 300-min-milled  $Y_2O_3-H_3BO_3$  with Eu = 8 mol% after annealing at 800°C for 1 h.

**Keywords:** Photoluminescence, Eu-doped  $Y_2O_3-H_3BO_3$  powders, Mechanochemical method

## 1. Introduction

A luminescent material absorbs various types of energy and emits thermal and electromagnetic radiation in the ultraviolet (UV), infrared, and visible ranges with the last being most common. In particular, inorganic luminescent materials have been studied for more than 100 years and are now used everyday in display technologies, such as fluorescent lamps, cathode ray tubes (CRTs), X-ray plates, advertisement signboards, plasma display panels (PDP), and light emitting diodes (LEDs), as well as in applications in fields such as advanced medicine and security, all of which are areas where people require information.

Nanocrystalline and amorphous alloys of a desired composition can be synthesized from pure crystalline powder using a mechanical alloying (MA) method [1-4]. Koch [5] applied MA to  $Ni_{60}Nb_{40}$  production, and Schwarz *et al.* [6] have used it to examine the thermodynamics of amorphous materials.

Although there have been advancements in luminescent materials since the commercialization of GaN blue LEDs in 1966, such as the development of the white

LED, their still requires improvement. Red luminescent materials are not efficient because the difference between their excitation and emission energies is greater than those in the case any other luminescent material. Therefore, highly efficient red luminescent materials, rather than green or blue luminescent materials, for blue LEDs and near-UV LEDs are needed.

Chong *et al.* [7] examined the photoluminescent (PL) properties of  $Y_2O_3:Eu^{3+}$  phosphor films fabricated with a sol-gel process. Dhoble *et al.* [8] prepared the same by using combustion synthesis and precipitation techniques. PL characteristics and X-ray excitation of films fabricated by using the two different methods were compared. Wang *et al.* [9] synthesized  $Y_{0.95-x}M_xBO_3:0.05Eu^{3+}$  ( $M:Bi^{3+}, La^{3+}, Sc^{3+}, 0 \leq x \leq 0.1$ ) for a PDP by using a solid-state reaction and examined it under ultraviolet light. Chen *et al.* [10] reported the preparation and PL properties of  $YBO_3:Eu^{3+}$  powders synthesized by using a solvothermal process with isopropanol used as a solvent.

This study examined the PL properties of  $Eu^{3+}$ -doped  $Y_2O_3-H_3BO_3$  powders synthesized by using MA. X-ray diffractometry (XRD) and luminescence spectrophotome-

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try were used to measure the concentrations of  $Eu^{3+}$  as a function of the annealing time, annealing temperatures, and milling time ( $t_m$ ).

## 2. Experimental

$Y_2O_3-H_3BO_3:Eu^{3+}$  mixtures were prepared by mixing yttrium oxide ( $Y_2O_3$ ) and boric acid ( $H_3BO_3$ ) at a molar ratio of 1:1, followed by the addition of 1, 2, 4, 6, 8, and 10 mol% europium(III) nitrate hexahydrate ( $Eu(NO_3)_3 \cdot 6H_2O$ ) (FW 446.07). The mixtures were then milled using a planetary ball mill at room temperature under the following conditions: 2.68 g powder and 13 zirconia balls, 15 mm in diameter at sample-to-balls weight ratio of 50:1. These were rotated in an 80 mL zirconia jar at 500 rpm. For accurate analysis, a same amount of the mixture was milled under similar conditions, for  $t_m$  of 0, 15, 30, 60, 120, and 300 min. The grinding operation was stopped for 30 min, which was followed by grinding for 15 min to avoid an excessive increase in temperature inside the mill pot. The as-milled powders were annealed at 700, 800, 900, 1000, 1100, and 1200°C for 1, 2, and 3 h, respectively.

XRD (PANalytical, X'pert PRO MPD) was performed at room temperature with Cu K $\alpha$  ( $\lambda = 1.54060 \text{ \AA}$ ) radiation. The acceleration voltage and current were 40 kV and 30 mA, respectively. The irradiation rate was 1 sec/0.03 step over the  $2\theta$  measurement range of 10-100°. The PL of the Eu doped  $Y_2O_3-H_3BO_3$  mixtures was measured between 520 nm and 700 nm as a function of the annealing temperature, annealing time, and  $t_m$ . A xenon discharge lamp (20 kW) was used under the following conditions: excitation at 240 nm, excitation slit at 10.0 nm, emission slit at 8.0 nm excitation, and scan speeds of 300 nm/min.

## 3. Results and Discussion

Fig. 1 shows the XRD patterns of the  $Y_2O_3-H_3BO_3:Eu^{3+}$  mixtures synthesized by MA as a function of  $t_m$ . The  $H_3BO_3$  peak at approximately  $2\theta = 28.0^\circ$  disappeared in the case of 15 min milling, indicating the formation of a solid solution of  $H_3BO_3$  in the  $Y_2O_3$ . After milling for 120 min, the XRD intensity began to decrease, and all elemental lines broadened slightly [11]. This peak broad-

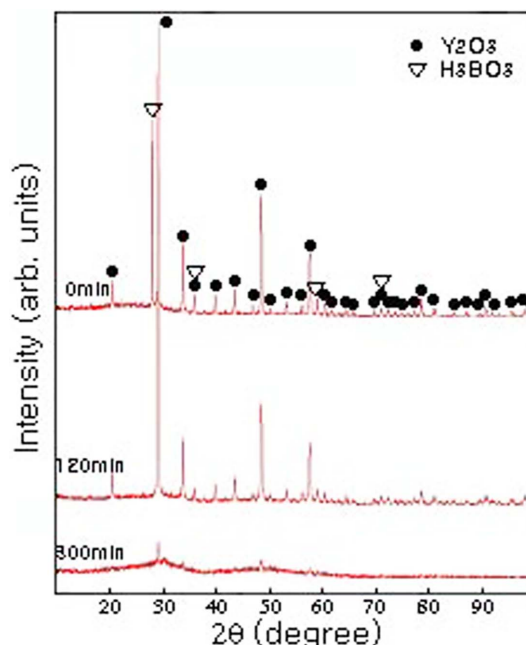


Fig. 1. X-ray diffraction patterns of  $Y_2O_3-H_3BO_3:Eu^{3+}$  powders fabricated by planetary ball milling as a function of different  $t_m$ .

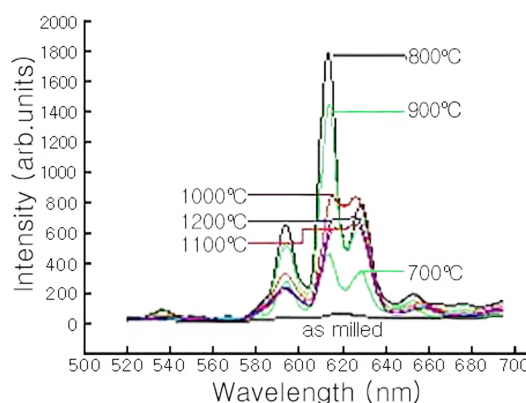


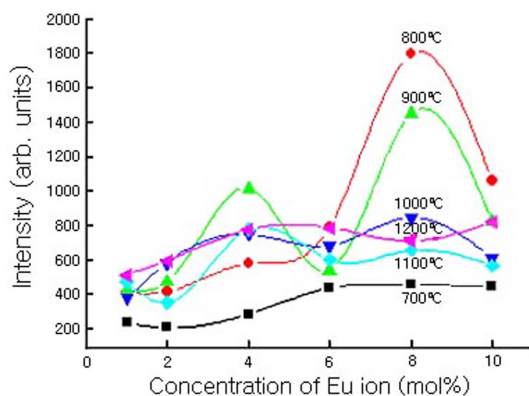
Fig. 2. PL emission spectra for  $Y_2O_3-H_3BO_3:Eu^{3+}$  (Eu: 8 mol%) mixtures milled for 300 min annealed at the indicated temperatures.

ening reflects not only a decrease in crystallite size, but also strain induced by the ball-milling. After milling for 300 min, some  $Y_2O_3$  peaks and amorphous formations were observed[12].

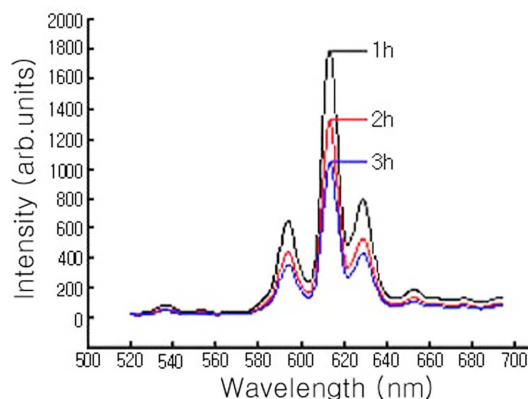
Fig. 2 shows the PL intensity of a 300-min-milled  $Y_2O_3-H_3BO_3:Eu^{3+}$  (Eu = 8 mol%) powder mixture, milled for 300 min, that had been annealed for 1 h at every temperature increase of 100°C from 700°C to 1200°C, and subjected to 240 nm excitation. The intensity was highest when the mixture was annealed at 800°C, and decreased for annealing temperatures above 800°C. The samples showed a more broad emission, and a shift of

the peaks with increasing annealing temperature above 800°C has been recorded. This phenomena of the peaks can be attributed to the changes in the crystal structure [13]. Further investigation on the mechanism of above phenomena and more detailed measurement of  $Y_2O_3-H_3BO_3:Eu^{3+}$  system are need. The PL intensity at 613 nm for the mixture of 800°C was highest for the mixture annealed at 800°C, and whereas the intensity at 628 nm was similar regardless of annealing temperature. The overall shape of the luminescence PL intensity differed a little with from that of a Eu = 4 mol% doped mixture [12]. When the mixtures were subjected to 240 nm excitation, the PL intensities were observed at approximately 592 nm, 613 nm, 628 nm, and 650 nm. This might be due to the transition of free  $Eu^{3+}$  ions from the  $^5D_0$  level to the  $^7F_j$  ( $j = 1-3$ ) level. The orange luminescence peak at approximately 592 nm might be due to the  $^5D_0 \rightarrow ^7F_1$  magnetic dipole transition of the  $Eu^{3+}$  ions. The red luminescence peaks at approximately 613 nm and 628 nm were assigned to the  $^5D_0 \rightarrow ^7F_2$  forced electric-dipole transition [14,15]. The luminescence peak at approximately 650 nm was attributed to a  $^5D_0 \rightarrow ^7F_3$  transition [16]. We compared the PL emission spectra of  $Y_2O_3-H_3BO_3:Eu^{3+}$  mixture by MA with that of  $YBO_3:Eu^{3+}$  samples by electrodeposition and ionic liquid-assisted hydrothermal process [17,18]. While the intensities and the shapes of the PL spectra differed slightly, the peak locations are very similar.

Fig. 3 shows the variations in PL intensity for  $Y_2O_3-H_3BO_3:Eu^{3+}$  powder mixtures due to differing concentrations of Eu and differing annealing temperatures (1 h



**Fig. 3.** The variations in the PL emission spectra for  $Y_2O_3-H_3BO_3:Eu^{3+}$  mixtures ( $t_m = 300$  min) as a function of different temperatures and  $Eu^{3+}$  concentrations.

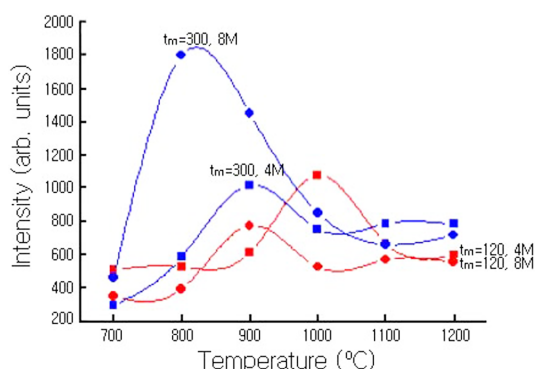


**Fig. 4.** PL emission spectra for  $Y_2O_3-H_3BO_3:Eu^{3+}$  (Eu:8 mol%) mixtures milled for 300 min and annealed 800°C for the indicated time.

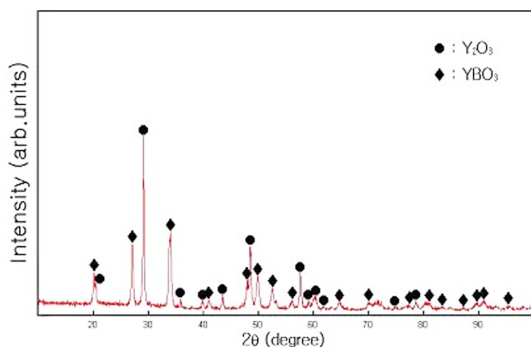
annealing time). The PL intensity of the powder mixture was highest after annealing at 800°C with the addition of Eu = 8.0 mol% for  $Y_2O_3-H_3BO_3$  powder mixture. The PL intensity gradually decreased with increasing annealing temperatures. This phenomenon was different from a Eu = 4.0 mol% doped  $Y_2O_3-H_3BO_3$  mixture, with the highest intensity occurring after annealing at 900°C [12].

Fig. 4 shows the PL intensity of  $Y_2O_3-H_3BO_3:Eu^{3+}$  (Eu: 8 mol%) powder mixture milled for 300 min and annealed for 1, 2, and 3 h at 800°C. Based on the PL intensity dependence annealing time, the highest luminescence intensity was obtained at wavelengths of 613 nm for the 1 h annealed mixture, as it was the case for the mixtures milled for 120 min, regardless of Eu mol%, but the luminescence intensity decreased with increasing annealing time.

Fig. 5 compares the variation in PL intensities of  $Y_2O_3-H_3BO_3:Eu^{3+}$  (Eu:4 mol%, Eu:8 mol%) powder mixtures



**Fig. 5.** The variations in the PL emission spectra for  $Y_2O_3-H_3BO_3:Eu^{3+}$  (Eu:4 mol% and 8 mol%) for milling time of 120 min and 300 min.



**Fig. 6.** X-ray diffraction patterns for  $Y_2O_3$ - $H_3BO_3$ : $Eu^{3+}$  (Eu: 8 mol%) mixtures annealed at  $800^\circ C$  for 1 h.

milled for 120 min and 300 min and then annealed for 1 h at every  $100^\circ C$  from  $700^\circ C$  to  $1200^\circ C$ . The luminescence intensities for powder mixtures milled for 120 min were low, but in general, more than those for powder mixtures milled for 300 min. For the  $Y_2O_3$ - $H_3BO_3$ : $Eu^{3+}$  powder mixtures milled for 120 min, the highest PL intensity was observed for annealing temperatures of  $1000^\circ C$  at Eu = 4.0 mol%. The other luminescence intensities of the powder mixture were similar.

Fig. 6 shows the XRD pattern of the  $Y_2O_3$ - $H_3BO_3$ : $Eu^{3+}$  mixture milled for 300 min and annealed at  $800^\circ C$  for 1 h with Eu = 8 mol%. Peaks corresponding to  $YBO_3$  with  $Y_2O_3$  are observed.

#### 4. Conclusions

$Y_2O_3$ - $H_3BO_3$ : $Eu^{3+}$  powders were synthesized at room temperature using a MA method. In the case of milling for 300 min, some PL peaks due to  $Y_2O_3$  ([222], [440], [622]) and amorphous formations were observed. The 300-min-milled mixture that was annealed at  $800^\circ C$  for 1 h with Eu = 8 mol% had the strongest PL intensity for each annealing temperature investigated (increasing from  $700^\circ C$  to  $1200^\circ C$  at increments of  $100^\circ C$ ). The PL of the powder mixture, excited by a xenon discharge lamp (20 kW) at 240 nm, was detected at approximately 592 nm (orange color,  $^5D_0 \rightarrow ^7F_1$ ), 613 nm, 628 nm (red color,  $^5D_0 \rightarrow ^7F_2$ ), and 650 nm. The highest luminescence intensity was obtained for mixtures annealed for 1 h, but the luminescence intensity decreased with increasing annealing

time. The luminescence intensities of powder mixtures milled for 120 min were low in general, but more than those of powder mixtures milled for 300 min, other conditions being equal, therefore we could know that  $Y_2O_3$ - $H_3BO_3$ : $Eu^{3+}$  powders must be milled for more than 120 min. The PL peaks due to the presence of  $YBO_3$  and  $Y_2O_3$  were observed after annealing at  $800^\circ C$  for 1 h for a 300-min-milled  $Y_2O_3$ - $H_3BO_3$  with Eu = 8 mol%.

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