JOURNAL OF MATERIALS SCIENCE **35** (2000) 4777–4782

Synthesis and photoluminescence properties of $(Y,Gd)BO_3:Eu$ phosphor prepared by ultrasonic spray

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The mixed solution of acetate of Y, Gd, Eu and boric acid diluted in water was used as the precursor for the ultrasonic spray for the synthesis of $(Y,Gd)BO_3:Eu$ phosphor. It was found that $(Y,Gd)BO_3:Eu$ phosphor made by ultrasonic spray pyrolysis had a spherical shape and a narrow size distribution having a mean size of 1.3 μm, while it had irregular, coarse and non-uniform size distribution for the phosphor formed by solid-state reaction. The as-sprayed particles was amorphous but they converted into the same polycrystalline phase of solid state reaction after post heat treatment at 1100 °C for 2 hr. The emitting intensity under 147 nm VUV excitations for the spray-formed $(Y,Gd)BO_3:Eu$ phosphor, however, was inferior to the later one. It was found that the optimum concentrations of Gd and Eu were 30% and 5%, respectively in $(Y_{1-x}Gd_x)_{1-y}BO_3:Eu_y$ phosphors prepared both by spray and solid state reaction. *© 2000 Kluwer Academic Publishers*

1. Introduction

$(Y,GD)BO_3:Eu$ has been widely used for the red phosphor in plasma display panel (PDP) due to the high quantum efficiency and good color coordinates under 147 nm VUV (vacuum ultraviolet) irradiation [1]. For the application of high resolution display, the mean particle size of phosphor particle is very important [2]. Furthermore, the phosphor particles must have narrow size distribution, non-agglomeration and spherical shape for good luminescent characteristics. It has been known that the optimum phosphor characteristics can be obtained with particle sizes on the order of 1 μm having a spherical shape [3]. Commercially available phosphor particles are in the size range of 3–10 μm without regular shape. They are mainly prepared by solid-state reaction, resulting in large particles and agglomerates which was presumably inadequate for the application in high resolution display.

The spray pyrolysis is an aerosol process commonly used to form or process a wide variety of materials in powder form. This process involved the atomization of a precursor solution into mist of droplets which were then directed into a reaction furnace. It offered several advantages over conventional solid-states reactions. For the spray method the liquid precursor solutions were used, while the solid particles were used for the formation of phosphors. Therefore, the final chemical composition and distribution of activator atoms in phosphor should be uniform by this spray method compared to the phosphors made by solid-state technique. The main advantage of spray method was the high purity of product of powders with fine particle size and spherical morphology. In solid-state reaction process, milling was usually required to obtain a fine powder. But the formation of nonradiative defects and introduction of nonradiative impurities during the mechanical grinding/milling significantly reduced luminescence efficiency of phosphor. In addition, grinding methods used for particle size reduction resulted in little or no control over particle morphology. Recently, the spray pyrolysis was applied to the preparation of phosphor materials such as $Y_2O_3:Eu$ and $YAG:Tb$ [4, 5]. The prepared particles by this spray pyrolysis had sub-micron size and spherical morphology. At present, $(Y,Gd)BO_3:Eu$ red PDP phosphors were usually made by solid-state reaction technique. In this study, we reported the synthesis of $(Y,Gd)BO_3:Eu$ phosphor by ultrasonic spray pyrolysis, and then the photoluminescence properties of this phosphors under 147 nm VUV and 254 nm UV irradiations were investigated and then compared to those phosphor produced by solid state reaction.

2. Experimental procedure

The experimental work of ultrasonic spray was carried out by a homemade ultrasonic atomizer having a frequency of 1.7 MHz. In this method, a mist of a spraying solution generated by ultrasonic generator was driven, using air as a carrier gas at atmospheric pressure, into the quartz tube furnace where a drying and pyrolytic reaction took place. The spray-formed particles were collected from the ceramic filter installed at the exiting site of tube furnace. The staring materials were acetates of Y, Gd, Eu and boric acid. Stoichiometric amounts of each salt were dissolved in de-ionized water or methanol. The solution concentration was varied from 0.05–0.2 M. For the formation of phosphors by usual solid-state reaction, the starting high purity raw materials of Y_2O_3, Gd_2O_3, H_3BO_3, and Eu_2O_3 were thoroughly mixed and then reacted at 1100 °C for 2 hr in air. In here 10% excess amount of H_3BO_3 was used as a flux to accelerate the reaction. After reaction, the product was washed with de-ionized water to eliminate the possible residue of flux. For the finding best luminescence under 147 nm VUV excitation, the concentration of Gd substitution and Eu activator were varied in the range of 15–45 and 2–12 mol % for both $(Y_{1-x}Gd_x)_{1-y}BO_3 : Eu_y$ phosphors made by spray and solid state reaction, respectively. The crystal structure for the spray-formed particles was analyzed by X-ray diffraction (XRD). Scanning electron microscopy (SEM) and particle size analyzer was used for the observation of particle morphology and size determination, respectively. Infrared (IR) absorption spectrum and wavelength dispersive spectrometer (WDX) for the samples were used to study the chemical state of samples. For the characterizing optical properties such as emission spectrum and color chromaticity under 147 nm excitation, VUV spectrometer equipped with deuterium lamp was employed. The optical property under 254 nm UV excitation was also studied using UV spectrometer.

3. Result and discussion

Fig. 1 shows the XRD spectra for $(Y_{0.65}, Gd_{0.35})BO_3 : Eu$ phosphor particles formed at different process. The primitive particles of as-sprayed at 900 °C was amorphous as shown in Fig. 1a. This amorphous phase was still observed for the sample sprayed at a high temperature of 1100 °C. In the spray process, the liquid aerosol droplet was carried into the flow reactor where the solvent evaporated and subsequently the precursor underwent chemical reaction to form the product particles. It was estimated that the residual time of liquid droplets in the reaction furnace for this experiment was around 5–6 seconds. This indicated that the liquid precursor droplet formed by ultrasonic spray had not enough time of resident in the reactor tube for thermal reactions. Thus, the particles prepared at 900 °C by spray were post heat treated at temperatures between 600 °C to 1200 °C for 2 hr for crystallization. The amorphous structure still remained at a low calcination temperature of 600 °C. But the sharp peak of single polycrystalline phase of $(Y,Gd)BO_3$ was appeared at 800 °C. At this temperature no other phases were observed, suggesting that the formation of $(Y,Gd)BO_3$ was completed at this low reaction temperature by spray method due to the micro-scale reaction within the droplet of micron size. And also it was found that the broadening of diffraction line measured at half maximum intensity decreased with temperature indicating that crystallinity was improved with increasing calcination temperature. Fig. 1b is the XRD pattern for the sample calcinated at 1100 °C for 2 hr.

The X-ray diffraction pattern for $(Y,Gd)BO_3 : Eu$ phosphor formed by solid-state reaction at 1100 °C for 2 hr is also represented in Fig. 1c for comparison. It showed that the same $(Y,Gd)BO_3$ crystalline phase as the solid-state reaction was formed by spray pyrolysis after calcination at 1100 °C.

Fig. 2 is IR spectra for $(Y_{0.65},Gd_{0.35})BO_3 : Eu$ phosphors. IR spectrum for the as-sprayed sample (Fig. 2 (a)) showed the absorption band at 716 and 1320 cm^{-1} due to the stretching and bending vibration of C-H associated with the acetate precursor solution used. The small peaks of C-O and O-H stretching due to the air contamination and moisture absorption during IR measurement were also appeared at 2360 and 3420 cm^{-1}, respectively. The observation of C-H peak for the as-sprayed sample indicated that the liquid droplets sprayed into the reaction furnace had not enough time of thermal pyrolysis reaction during the pass along the tube furnace. But these C-H peaks arising from the precursor solution completely disappeared after calcination at 1100 °C for 2 hr (Fig. 2 (b)), which clearly showed the pyrolysis reaction had occurred with post heat treatment. After caclnation it had a relatively

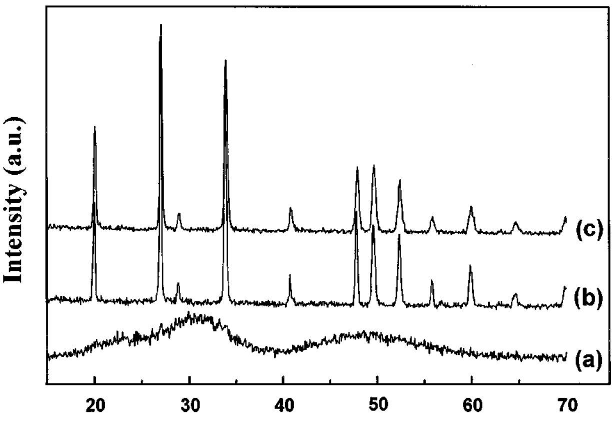


Figure 1 XRD patterns for $(Y_{0.65},Gd_{0.35})BO_3 : Eu$ phosphors. As-sprayed at 900 °C (a), post-heated at 1100 °C (b), and solid-state reacted at 1100 °C (c).

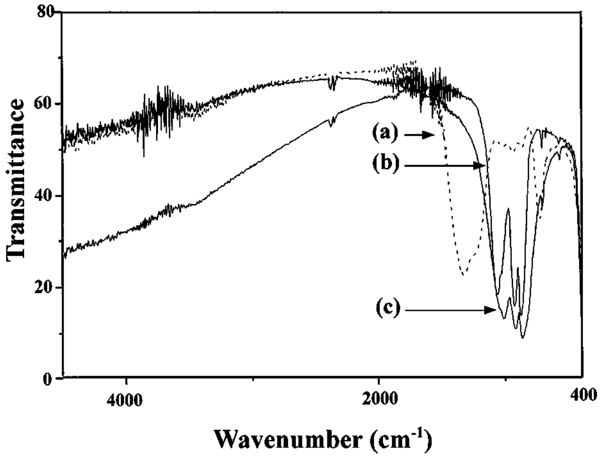


Figure 2 IR spectra for $(Y_{0.65},Gd_{0.35})BO_3 : Eu$ phosphors. As-sprayed at 900 °C (a), post heated at 1100 °C (b), and solid-state reacted at 1100 °C (c).

broad absorption band in the range of 700–1000 cm^{-1} corresponding to B-O vibrations [6]. It had the same absorption band which was the characteristic of solid state reaction shown in Fig. 2 (C).

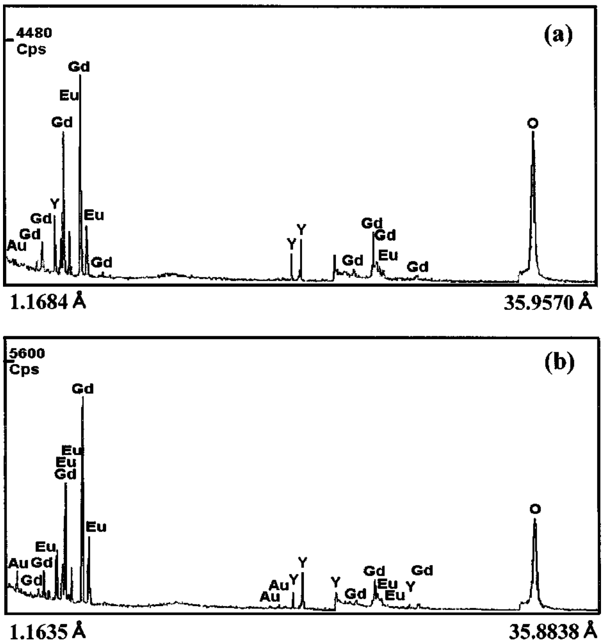
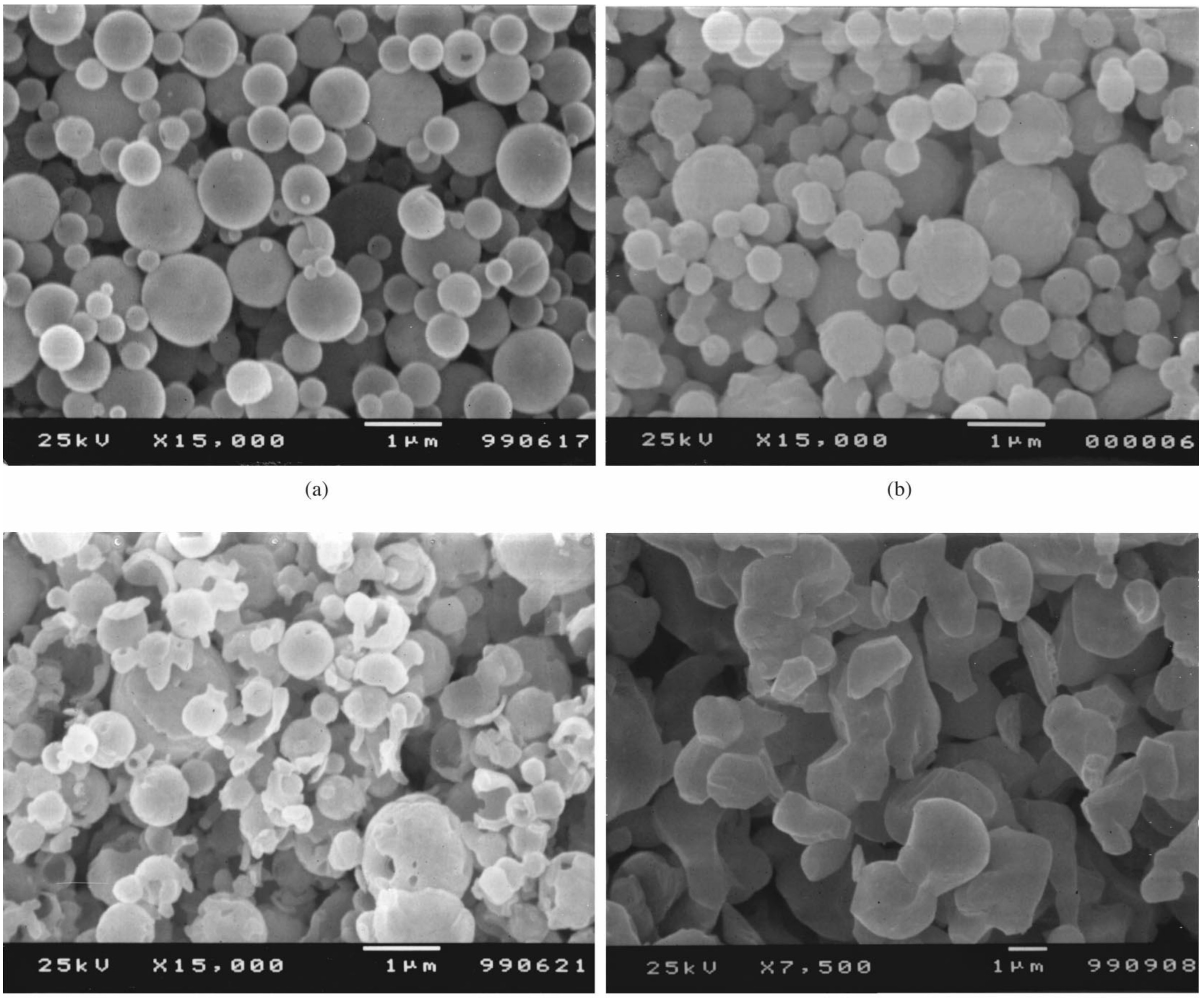


Figure 3 WDX spectra for $(Y_{0.65},Gd_{0.35})BO_3:Eu$ phosphors prepared by spray (a), and solid-state reaction (b).

The chemical analysis on the phosphors was also conducted by WDX. Fig. 3a is the WDX spectrum for $(Y_{0.65},GD_{0.35})BO_3:Eu(10\%)$ phosphors prepared by spray pyrolysis after calcination at 1100 °C for 2 hr. All the chemical constituents of phosphor such as Y, Gd, Eu and O were appeared. But the boron element of phosphor was missed in here due to the sensitivity of WDX. The presence of small Au peak was arised from Au coating on the phosphor. This WDX spectrum was the same with Fig. 3b, which was obtained for $(Y_{0.65},Gd_{0.35})BO_3:Eu(10\%)$ phosphors made by solid-state reaction.

Fig. 4 is SEM photographs for $(Y,Gd)BO_3:Eu$ phosphors synthesized by the spray method using the solution of 0.1 M acetate precursor concentration in water solvent. The phosphor particles of as-sprayed at 900 °C (Fig. 4a) was highly spheroidal and smooth. These primitive particles were non-agglomerated. Since these particles were formed from each individually suspended aerosol droplet, agglomeration could be effectively minimized. The powder particles, however, began to agglomerate with calcination at 1100 °C for 2 hr as shown in Fig. 4b. But it still showed spherical-like shape and fine size, while the phosphor synthesized by solid state reaction at the same temperature was irregular shape and coarse particle size (Fig. 4d). The phosphor particles formed by spray using acetate solution



(a) (b)

(c) (d)

Figure 4 SEM photos of $(Y_{0.65},Gd_{0.35})BO_3:Eu$ phosphors for as-sprayed at 900 °C (a), post-heated at 1100 °C (b, c), and solid-state reacted at 1100 °C (d).

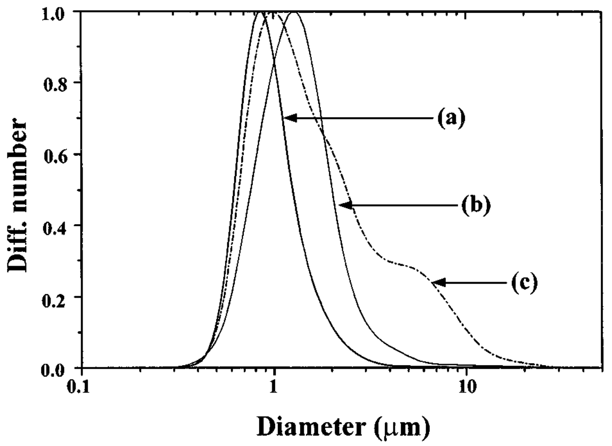


Figure 5 Paticle size analysis of $(Y_{0.65},Gd_{0.35})BO_3:Eu$ phosphors for as-sprayed (a), calcinated at 1100 °C (b), and solid state reacted at 1100 °C (c).

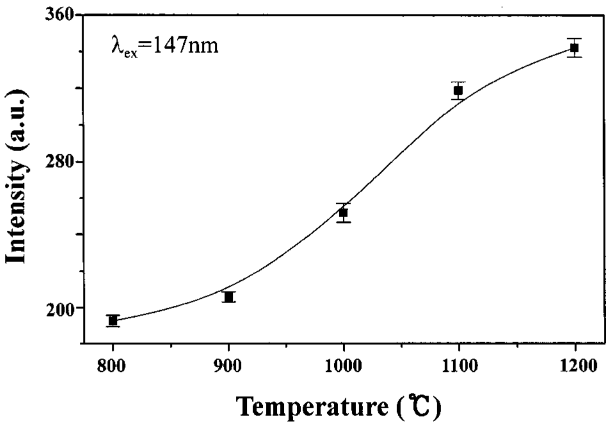


Figure 6 The change of emitting intensity with calcination temperature under 147 nm excitation.

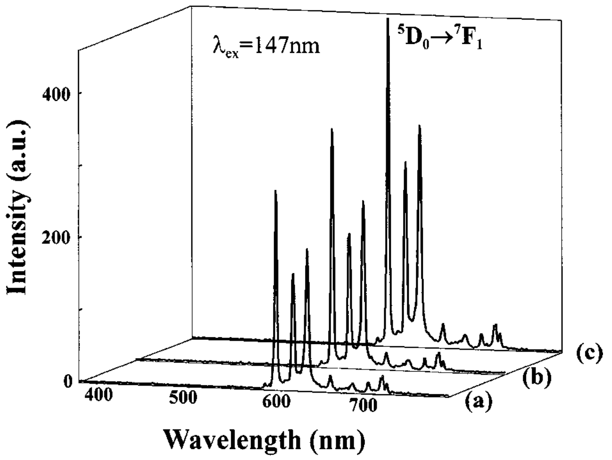


Figure 7 Emission spectra of $(Y_{0.65},Gd_{0.35})BO_3:Eu$ phosphors prepared by spray using 0.05 M (a) and 0.1 M acetate (b), and solid-state reaction (c).

were sometimes found to be hollow or fragmented particles rather than solid particles shown in Fig. 4c. The formation of hollow particles is undesirable in phosphors. But the formations of hollow or shell-like particles were frequently reported in the literatures of spray pyrolysis, which was one of the disadvantages of spray process. Therefore, much investigation had been devoted to obtain solid particle using a proper choice of precursor solutions and control of other process variables [7]. It was found that the chance of hollow particle was decreased by using solvent of water rather than methanol for the formation of $(Y,Gd)BO_3:Eu$ phosphor. Thus the phosphors were made using water solvent in this experiments.

Fig. 5 is the particle size analysis for the phosphors made by spray pyrolysis and solid state reaction. It showed the as-sprayed (Fig. 5 (a)) powder was very fine having a mean size of 1 μm. After calcination at 1100 °C for 2 hr, the phosphor powder (Fig. 5 (b)) was grown a little bit, but it still showed fine size having a mean size of 1.3 μm. This phosphor particle had uniform size with narrow and uni-modal distribution. However, the phosphor particle made by solid state reaction at the same temperature had a coarse particle size (mean size of 2.7 μm) and non-uniform with a wide bi-modal distribution. It was found that more than 40% of powder was coarse greater than 3 μm. A fine particles could be made by grinding or milling after solid state reaction, but the defects generated during this process decreased the brightness of phosphor. Thus it was thought that the spray-formed phosphors was suitable for the application in a high resolution display due to the formation of fine particle size without milling process and spherical shape.

The $(Y,Gd)BO_3:Eu$ particles of as-sprayed did not show any photoluminance (PL) under UV and VUV irradiation because they were amorphous phase associated with an incomplete thermal reaction. They began to emit red light after calcination at over 800 °C where $(Y,Gd)BO_3$ crystalline phase started to form. Fig. 6 is the change of emitting intensity with calcination temperature for 2 hr. This showed that the PL intensity of $(Y,Gd)BO_3:Eu$ sample under 147 nm VUV excitation was increased with calcination temperature due to the enhanced crystallization and activation of phosphor particles. For the sample calcinated at 1200 °C it had a higher emitting intensity than the calcinated at 1100 °C, but a great number of spheres had been sintered thus resulted in the irregular particle shape. Therefore the calcination temperature was hereafter fixed at 1100 °C to maintain the spherical-like shape.

Fig. 7 is the emission spectra for $(Y_{0.65},Gd_{0.35})BO_3:Eu(10\%)$ phosphors under 147 nm VUV irradiation. The PL spectra of these phosphors synthesized by ultrasonic spray followed by calcination at 1100 °C for 2 hr (Fig. 7 (a) and (b)) and solid-state reaction (Fig. 7 (c)) showed the same spectral distribution. It was well known that the observed red emission lines in $(Y,Gd)BO_3:Eu$ phosphors were associated with $^5D_0 \rightarrow {}^7F_j$ transitions of Eu^{3+} activator [8]. The $^5D_0 \rightarrow {}^7F_1$ emission was by far the most intense. But, it showed that the emitting intensity of $(Y,Gd)BO_3:Eu$ phosphors prepared by spray pyrolysis and solid state reaction was slightly different although the same crystalline phase was formed for both process. And also its emitting intensity of spray-formed phosphors was found to depended upon the precursor concentration. The PL intensity for $(Y,Gd)BO_3:Eu$ phosphor formed by 0.1 M acetate concentration (Fig. 7 (b)) was higher than that of 0.05 M concentration (Fig. 7 (a)).

The diameter (D_p) of particles formed from aerosol droplets has been expressed by the following equation [9].

$$D_p = D\left(\frac{C_s M_1}{\rho M_2}\right)^{1/3}$$

where D is size of liquid droplet, C_s is the concentration of precursor solution, M_1 and M_2 are molar masses of produced phosphor and the liquid solution, respectively, and ρ is the phosphor density. From this equation one can expect that the size of phosphor particle will be increased with the acetate concentration. Actually it was observed that the phosphor particle size formed by high concentration of 0.1 M acetate concentration was relatively greater than that of 0.5 M concentration. For the fine particles, it was expected that the dead surface layer acting as non-luminescent or the light scattering area should be increased. Thus the higher PL intensity for (Y,Gd)BO_3 : Eu phosphor formed by higher acetate concentration was thought to be associated with the increased particle size of phosphor. As shown in Fig. 7, the emitting intensity for (Y,Gd)BO_3 : Eu phosphor made by the spray method was smaller than that of solid state reaction. As stated previously, the phosphor particle size prepared by spray pyrolysis was finer than those of solid state reaction, which resulted in the decreased emitting intensity as shown in Fig. 7. The formation of hollow particle by spray pyrolysis (refer to Fig. 4c) could also decrease the emitting intensity because the excitation volume of phosphor under irradiation should be decreased for the hollow particle compared to the rigid solid particle. However, it was found that the color chromaticity of (Y,Gd)BO_3 : Eu phosphors made by spray pyrolysis ($x = 0.649$, $y = 0.351$) and solid state reaction ($x = 0.648$, $y = 0.351$) had the same value each other.

The excitation spectrum of the $^5D_0 \rightarrow {}^7F_1$ emission (i.e., $\lambda = 593$ nm) under 147 nm VUV irradiation for (Y,Gd)BO_3 : Eu is given in Fig. 8. This spectrum showed the host excitation band appeared at about 160–170 nm, and the charge transfer band lied between 200 and 250 nm [1]. For the comparison, the excitation spectra for YBO_3 : Eu and $GdBO_3$: Eu phosphors synthesized both by the spray method and the solid state reaction were represented in Fig. 8. It showed that the excitation intensities in VUV range for (Y,Gd)BO_3 : Eu and $GdBO_3$: Eu phosphors prepared by the spray method were smaller than those of solid-state reaction, while the excitation intensity of YBO_3 : Eu was almost equivalent for both methods. This figure showed that the excitation intensity in VUV range was decreased in the order of YBO_3 : Eu, $(Y_{0.65},Gd_{0.35})BO_3$: Eu and $GdBO_3$: Eu phosphors, which were different from the reported one in the literature [1].

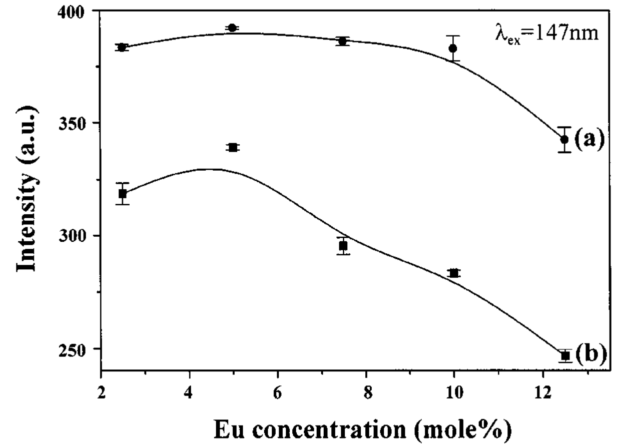


Figure 9 The change of emitting intensity with Eu concentration in $(Y_{0.85}Gd_{0.15})_{1-x}BO_3$: Eu_x phosphors prepared by solid state reaction (a) and spray (b).

Fig. 9 is the change of emitting intensity under 147 nm excitation with activator Eu concentration in $(Y_{0.85}Gd_{0.15})_{1-x}BO_3$: Eu_x phosphor. The optimum Eu concentration was found to be 5% for both phosphors made by spray pyrolysis and solid state reaction, although the emitting intensity of spray-formed phosphors had always smaller emitting intensity compared to those phosphors made by solid state reaction as mentioned before. At the higher concentration of more than 5% the emitting intensity decreased due to the concentration quenching. Fig. 10 is the change in emission intensity with Gd substitution in $(Y_{1-x}Gd_x)_{0.95}BO_3$: Eu(5%) phosphor under 147 nm VUV excitation. The

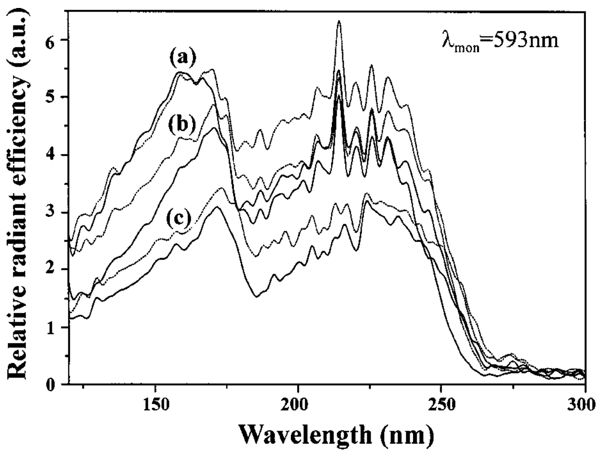


Figure 8 Excitation spectra for various phosphors prepared by spray pyrolysis (solid line) and solid state reaction (dotted line). (a) YBO_3 : Eu, (b) $(Y_{0.65},Gd_{0.35})BO_3$: Eu, (c) $GdBO_3$: Eu.

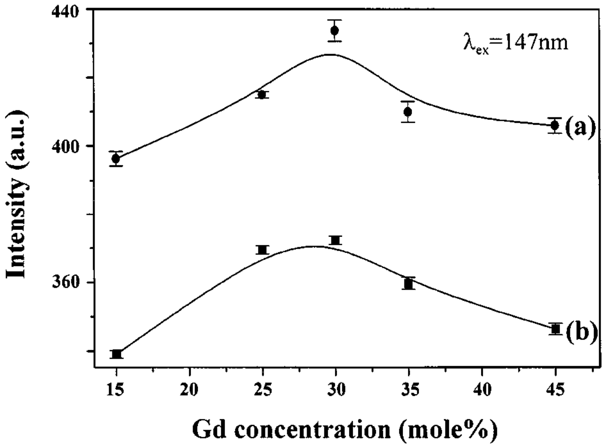


Figure 10 The change of emitting intensity with Gd substitution for $(Y_{1-x}Gd_x)_{0.95}BO_3$: Eu(5%) phosphors prepared solid state reaction (a) and spray (b).

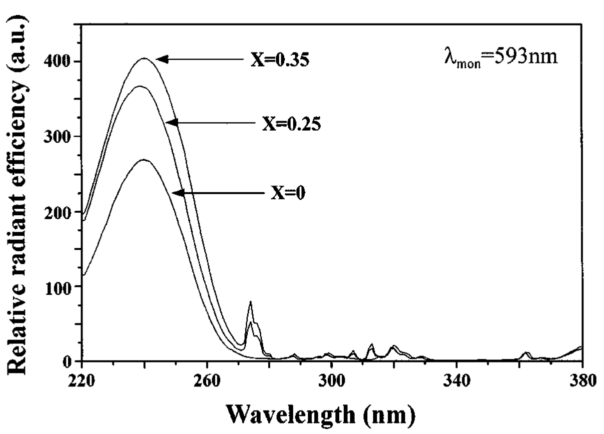


Figure 11 Excitation spectra in UV range with Gd substitution for $(Y_{1-x}Gd_x)_{0.95}BO_3 : Eu(5\%)$ phosphors prepared by spray pyrolysis.

emitting intensity increased with Gd substitution up to 30% and then decreased for more concentration of Gd for the both phosphors made by spray and solid state reaction. The increased emission intensity with Gb substitution was known to be associated with the energy transfer from Gd to the Eu activator.

With VUV spectrometer, the excitation spectrum around ultraviolet range was not satisfactory because the deuterium lamp source employed in VUV spectrometer had a very weak UV wavelength component. Therefore, UV spectrometer equipped with mercury lamp was used here to investigate the optical property of $(Y_{1-x}Gd_x)_{0.95}BO_3 : Eu(5\%)$ phosphor under 254 nm UV irradiation. Fig. 11 is the excitation spectra of $^5D_0 \rightarrow {}^7F_1$ emission of Eu^{+3} for the various phosphors made by spray. The intense broad band at 245 nm corresponded to the charge transfer band of Eu. And also the peaks at 274, 307 and 313 nm were appeared due to the energy transfer from Gd^{3+} to Eu^{3+} activator and their intensities were increased with Gd substitution in $(Y_{1-x}Gd_x)_{0.95}BO_3 : Eu(5\%)$ phosphors. This energy transfer resulted in a higher emitting intensity with Gd substitution in $(Y_{1-x}Gd_x)_{0.95}BO_3 : Eu$ (5%) as shown in Fig. 10.

4. Conclusions

The ultrasonic spray method was used to make $(Y,Gd)BO_3 : Eu$ phosphors and their photoluminance property under 147 nm VUV and 254 nm UV excitations were studied and then compared with those phosphors prepared by conventional solid state reaction technique. The primitive particles of sprayed at 900 °C were amorphous phase and they were very fine having spherical shape. This amorphous phase converted into the polycrystalline structure of $(Y,Gd)BO_3$ with post-heat treatment at temperature greater than 800 °C. The spray formed particles began to agglomerate after calcination at 1100 °C for 2 hr, but they were still spherical-like shape, fine size having mean size of 1.3 μm, and uniform size distribution. On the other hand, the phosphor particles made by solid state reaction were irregular shape and coarse with non-uniform size distribution. The crystal structure and chemical state for spray-formed phosphor with calcination at 1100 °C were found to be identical to those of solid state reaction product except that some phosphor particles made by spray method were hollow rather than rigid solid particle. The emission intensity was increased using by a higher precursor concentration. It was found that a color chromaticity of $(Y,Gd)BO_3 : Eu$ phosphors made by spray and solid state reaction had same value each other. However, the emitting intensity under 147 nm VUV excitation for spray formed phosphors were lower than those phosphors made by solid state reaction. The best luminescence was obtained at the composition of $(Y_{0.65}Gd_{0.35})_{0.95}BO_3 : Eu_{0.05}$ under 147 nm VUV excitation.

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Received 10 November 1999
and accepted 2 March 2000