

## Effect of pH on the Luminescence of (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup> Phosphor Prepared by the Coprecipitation Method

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### Abstract

The (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup> phosphor was made by coprecipitation method. The precipitated powders were amorphous. The value of pH in the process of coprecipitation was critical for the luminescence of phosphors. The particle size and morphology were influenced by pH value. The lower calcination temperature and hydrothermal synthesis leads to the distortion of lattices. The distorted lattices changed the symmetry of Eu<sup>3+</sup> site. The broken inversion symmetry in the distorted lattice caused the increased emission of <sup>5</sup>D<sub>0</sub>? <sup>7</sup>D<sub>2</sub> transition.

### 1. Introduction

Rare earth borates are important plasma phosphor materials because of its excellent VUV absorption property.[1] (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup> has been used as the red phosphors for PDP. In PDP, the host lattice of (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup> absorbs the VUV wavelength, followed by transfer of absorbed energy to activator (Eu<sup>3+</sup>) or sensitizer (Gd<sup>3+</sup>). The sensitizer, Gd<sup>3+</sup>, plays an important role to improve the efficiency of the energy transfer to activator, reducing the non-radiative emission. The (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup> phosphor shows the emission of orange-red light. When the surrounding of Eu<sup>3+</sup> site has an inversion symmetry, <sup>5</sup>D<sub>0</sub> <sup>7</sup>F<sub>1</sub> transition is dominant. On the other hand, when there is no inversion symmetry in the surrounding of Eu<sup>3+</sup> site, the <sup>5</sup>D<sub>0</sub> <sup>7</sup>F<sub>2</sub> transition dominates.[2] Therefore, as a solution to improve the chromaticity, the production of phosphor nanoparticles has been proposed.[3,4,5]

The coprecipitation method was applied in this study to obtain the uniform nanometer-sized (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup> phosphor. The prepared powders were retreated by calcination or hydrothermal synthesis. In this study, the effect of pH on the luminescence and morphology of (Y,Gd)BO<sub>3</sub>:Eu<sup>3+</sup> phosphor was investigated.

### 2. Experimental

As precursor materials, Y<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub> (Aldrich, 99.99%) were dissolved in a mixed solution of distilled water (180ml) and nitric acid (20ml). After complete dissolution, NH<sub>4</sub>OH solution (25%) was added drop by drop. As soon as NH<sub>4</sub>OH solution was added, the precipitates were formed. The final pH values of the solution containing the precipitates were varied from 7 to 11. The powders obtained by the coprecipitation method were separated from the solution by centrifuging (2500rpm, 5min) and dried in an oven of 80°C for a day. The as-made powders were calcined at various temperatures for 2h.

As another heat treatment, hydrothermal synthesis was used. The solution containing the precipitates was put into the steel autoclave with a Teflon liner (digestion bomb 4748, Parr instrument, USA) without any purification. The autoclave was kept in an oven of 200°C for 10h. After cooling, the powders were separated from the solution by centrifuging and dried in an oven of 80°C for a day.

### 3. Results and Discussion

#### 3.1 Characteristics of the powders prepared by the coprecipitation method

The powders prepared by the coprecipitation method were analyzed by TEM and XRD. The precipitates were the amorphous particles smaller than 20nm. The FT-IR spectra of fig. 1 show that the precipitates have the various ligand bonds. The ligand bonds are attributed to the ions in the solution containing NH<sub>4</sub>OH, HNO<sub>3</sub>, and water. Because the precipitates were amorphous, the excitation by charge transfer in Eu-O, which occurs by absorbing the UV light of 246nm, was not found. On the other hand, the excitation by activators, Eu<sup>3+</sup> ions, was observed so that the precipitates emitted the red light by the transition within 4f<sup>n</sup> of Eu<sup>3+</sup>. In the emission spectra, two broad peaks occurred at 593 and 617nm, which are associated with <sup>5</sup>D<sub>0</sub> <sup>7</sup>F<sub>1</sub> and <sup>5</sup>D<sub>0</sub> <sup>7</sup>F<sub>2</sub> transitions,

respectively. The stronger intensity at 617nm than that at 593nm is due to the nonexistence of inversion symmetry. It could be concluded that the  $\text{Eu}^{3+}$  ions doped in the amorphous precipitates have a weak crystal field and no inversion symmetry due to the disordered structure of amorphous matrix.

### 3.2 Effect of pH on the luminescence and morphology of the calcined powder

The results of ICP-AES showed that the amounts of elements remaining in the solution of each step were dependent on the pH values. The pH value higher than 9 must be applied for full coprecipitation. In addition, it was confirmed that the difference in solubility among Y, Gd, and Eu ions is small enough for the coprecipitation, while the boron ions were not fully precipitated. After the powders precipitated at different pH values were calcined at 1100°C for 2h, the excitation and emission spectra were measured as shown in fig. 2. Figure 2(a) shows the excitation spectra monitored by 594nm. The broad peak at 246nm and the narrow peaks at 360~420nm are attributed to the excitations of charge transfer and activator, respectively. Figure 2(b) and (c) show the emission spectra of the powders excited by 246nm and 395nm, respectively. For comparison, the starting powders were mixed using ballmilling and fired under the same condition with the precipitated powders. The emission of powders produced from the precipitates was stronger than that from the ballmilled powders. The changes of emission intensities with respect to pH values were plotted in fig. 3(a) and (b). The trends in changes of emission intensities were different in two cases of 246nm- and 395nm-excitation. The emission intensities were almost same for 246nm-excitation regardless of pH values, while powders prepared at pH=9 showed the strongest emission intensity for 395nm-excitation. Furthermore, the emission at 594nm was influenced more strongly by the pH value than the others. The strong emission of  $^5\text{D}_0$ ?  $^7\text{F}_1$  transition means that the more  $\text{Eu}^{3+}$  sites has inversion symmetry.

XRD results showed that the powders produced by calcination of precipitates had the same crystalline structure regardless of pH values. However, SEM micrographs showed that the morphology and the size of particles were dependant on the pH values. The particle size was smallest (submicron, <500nm) with a uniform size distribution for pH=9. All the particles

had the smooth surface and necking shape. On the other hand, the powder produced by firing the ballmilled mixture had the irregular shape and large size (micron, >1 $\mu\text{m}$ ). Difference in the particle size according to the pH value is attributed to the ligand bonds on the surface of precipitates. These results lead us to the conclusion that the pH value in the process of coprecipitation affects the luminescence and the morphology of the produced powders.

The strongest emission intensity of phosphor prepared at pH=9 (excited by 395nm) is thought to be caused by larger amount of  $\text{Eu}^{3+}$  ions on the surface of particles. The smaller is the particle size, the more  $\text{Eu}^{3+}$  ions on the surface can absorb the energy by the direct excitation of themselves. If the phosphor is excited by 246nm, the emission intensity would not differ with respect to the particle size due to the indirect excitation through the charge transfer. Therefore, the emission is proportional to the number of  $\text{Eu}^{3+}$  ions on the unit surface area to be illuminated. Moreover, it has been known that, if the ionic radius of an activator is larger than that of a cation in a host lattice, the activator ions segregate on the surface to relax the strain.[2] When the  $\text{Eu}^{3+}$  ions are directly excited by 395nm, therefore, the emission can be enhanced by the segregation of  $\text{Eu}^{3+}$  ions on the surface.

### 3.3 Effect of the hydrothermal synthesis

The powders prepared by the coprecipitation method were hydrothermally treated at 200°C for 10h. The overall emission intensities of powders produced by the hydrothermal synthesis were lower than those produced by the calcination. However, the enhancement of emission intensity corresponding to the  $^5\text{D}_0$ ?  $^7\text{F}_2$  transition (613nm) was observed in the powders produced by the hydrothermal synthesis. When excited by 246nm, the powder prepared at pH=8 showed the strongest emission intensity while, when excited by 395nm, that prepared at pH=9 was most efficient as shown in fig. 4(a) and (b).

The particles in the powder produced by the hydrothermal synthesis have a plate shape as shown in fig. 5(a). In the TEM micrograph of fig. 5(b), the thickness of plate-like particles was so thin. The electron diffraction in the inset of fig. 5(b) shows that a particle is a single crystal with a (001) plane.

To compare the relative emission intensities in the powders produced through different processes and

calcined at various temperatures, the emission spectra of the powders excited by 246nm were plotted in fig. 6. The emission intensities in Y-axis were normalized. Figure 6 shows the enhancement of the emission intensity corresponding to  $^5D_0 \rightarrow ^7F_2$  transition in the powders produced by the hydrothermal synthesis or calcined at lower temperature. As mentioned before, the inversion symmetry at the site of the  $\text{Eu}^{3+}$  ion influences the relative emission of  $^5D_0 \rightarrow ^7F_1$  and  $^5D_0 \rightarrow ^7F_2$  transitions. Therefore, the enhancement of the emission intensity corresponding to  $^5D_0 \rightarrow ^7F_2$  transition means that the smaller particles have less inversion symmetry than bigger ones. To certify the distortion of lattices, lattice constants were calculated from XRD results. Table 1 shows the relative emission intensities of  $^5D_0 \rightarrow ^7F_2$  transition to  $^5D_0 \rightarrow ^7F_1$  transition ( $I_{613\text{nm}}/I_{594\text{nm}}$ ) and the lattice constants. It turned out that the distortion of lattices became larger as the relative emission intensity increased. Especially, the powders produced by the hydrothermal synthesis, which has a plate shape with the (001) plane, shows the large expansion along the  $\langle 001 \rangle$  direction, c-axis. Therefore, it seems reasonable to conclude that the size-dependent chromaticity results from the distortion of the lattices, which is related to the destruction of inversion symmetry at the site of the  $\text{Eu}^{3+}$  ion.

#### 4. Conclusions

The study in the effect of pH value on the luminescence has been focused because solution techniques like coprecipitation method applied to produce nanocrystalline or uniform-sized particles are affected strongly by pH value. The fact that pH value influences the size and morphology of phosphor particles would be helpful in the application of the solution techniques. The improved color chromaticity of phosphors due to the distortion of lattices provides a motive to understand the importance of symmetry in phosphor and provides chances to get better color chromaticity in the well-known phosphors.

#### 5. References

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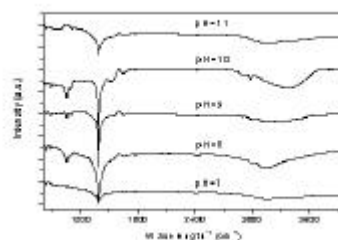


Figure 1. FT-IR results of  $(\text{Y}_{0.65}\text{Gd}_{0.35})_{0.75}\text{BO}_3:\text{Eu}^{3+}_{0.25}$  powders prepared by coprecipitation method.

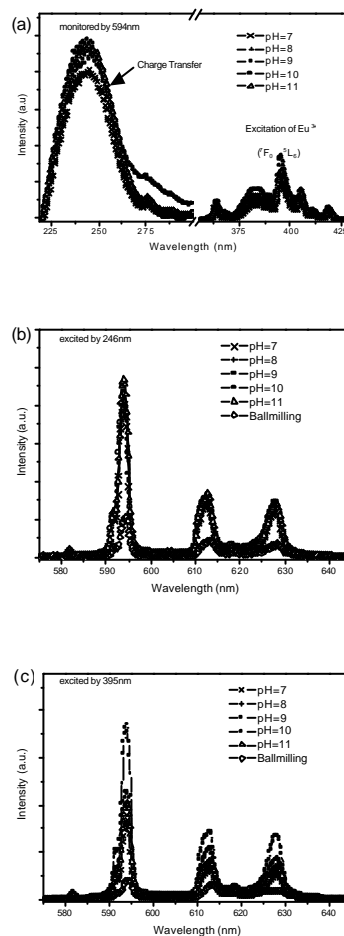


Figure 2. (a) the excitation and the emission spectra of  $(Y_{0.65}Gd_{0.35})_{0.75}BO_3:Eu^{3+}$  powders precipitated at different pH and heated at  $1100^{\circ}C$  for 2h.

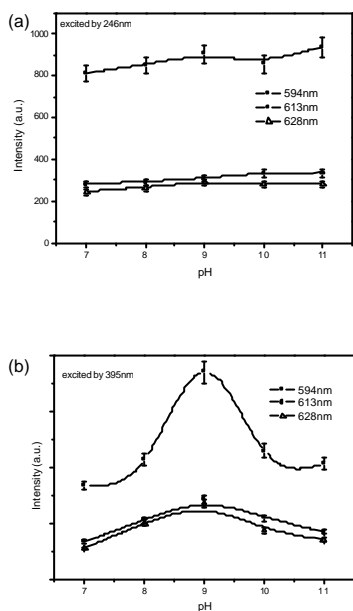


Figure 3. Intensities of three main peaks in the  $(Y_{0.65}Gd_{0.35})_{0.75}BO_3:Eu^{3+}$  powders precipitated at different pH and heated at  $1100^{\circ}C$  for 2h.

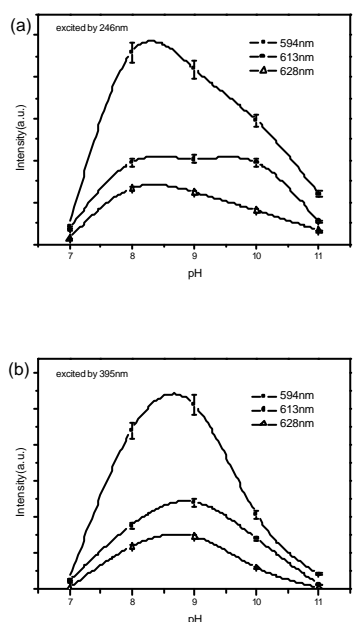


Figure 4. Intensities of three main peaks in the  $(Y_{0.65}Gd_{0.35})_{0.75}BO_3:Eu^{3+}$  powders precipitated at

different pH and hydrothermally heated at  $200^{\circ}C$  for 10h.

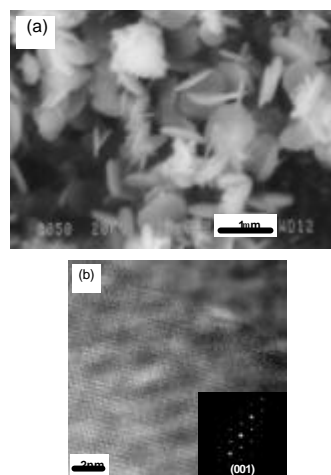


Figure 5. (a) SEM and (b) TEM micrograph of  $(Y_{0.65}Gd_{0.35})_{0.75}BO_3:Eu^{3+}$  powders precipitated at pH=9 and hydrothermally-treated at  $200^{\circ}C$  for 10h.

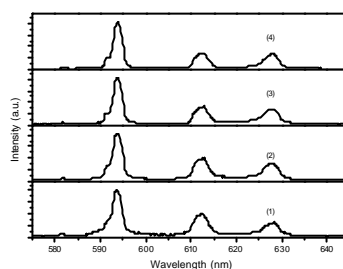


Figure 6. emission spectra of  $(Y_{0.65}Gd_{0.35})_{0.75}BO_3:Eu^{3+}$  powders precipitated at pH=9 and followed by (1) hydrothermal synthesis ( $200^{\circ}C$ , 10h) and calcination at (2)  $700^{\circ}C$ , (3)  $1000^{\circ}C$ , and (4)  $1100^{\circ}C$  for 2h.

Heating Process	$I_{613nm}/I_{594nm}$	a (Å)	c (Å)	Cell Volume (Å <sup>3</sup> )
(a) Hydrothermal Synthesis ( $200^{\circ}C$ , 10h)	0.4837	$3.8072 \pm 0.0038$	$8.8722 \pm 0.0089$	$111.37 \pm 0.11$
(b) Calcination ( $700^{\circ}C$ )	0.4766	$3.8050 \pm 0.0038$	$8.8405 \pm 0.0088$	$110.85 \pm 0.11$
(c) Calcination ( $1000^{\circ}C$ )	0.4018	$3.8004 \pm 0.0038$	$8.8431 \pm 0.0088$	$110.73 \pm 0.11$
(d) Calcination ( $1100^{\circ}C$ )	0.3393	$3.8025 \pm 0.0038$	$8.8429 \pm 0.0088$	$110.73 \pm 0.11$

Table 1. The relative emission intensities of the  ${}^5D_0 \rightarrow {}^7F_2$  transition to the  ${}^5D_0 \rightarrow {}^7F_1$  transition ( $I_{613nm}/I_{594nm}$ ) and the lattice constants calculated from XRD results.