Hydrothermal synthesis and photoluminescence properties of nano-crystalline GdBO$_3$:Eu^{3+} phosphor

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Abstract

Nanocrystalline GdBO$_3$:Eu^{3+} was prepared by a hydrothermal method. The as-synthesized powders were spherical shaped agglomerates of nano particles. The luminescent properties were compared with samples synthesized by conventional solid-state reaction method. Both the photoluminescence intensity and chromaticity were improved and a red-shift in the CT band was observed for the hydrothermally synthesized samples.

1.   Introduction

Eu doped borate phosphors, $(Y_y Gd_{1-y})_{1-x} BO_3$:Eu$^{3+}_x$ with a vaterite structure are used in plasma display panels (PDP) because of the high vacuum ultraviolet (VUV) transparency and exceptionally high optical damage threshold of this material.[1-5] However, its main emission spectra is centered at a wavelength of 593nm corresponding to the $^5D_o \rightarrow {}^7F_1$ transition of Eu^{3+}, which results in an orange-red light instead of red. This characteristic color is the property of the host lattice, since it is determined by the symmetry of Eu^{3+} in the host lattice. When the Eu^{3+} occupies a site with inversion symmetry, the $^5D_o \rightarrow {}^7F_1$ transition is prominent. However, the $^5D_o \rightarrow {}^7F_2$ transition, corresponding to a red emission, becomes dominant if no inversion symmetry exists. [6] This optical change has recently been utilized as a method to improve the chromaticity of (Y,Gd)BO$_3$:Eu^{3+} phosphors by making nano-sized particles. As the particle size decreases, the number of Eu^{3+} ions located in the surface area with deviation from inversion symmetry increases. This leads to an enhanced emission from $^5D_o \rightarrow {}^7F_2$ transition. It has been reported that nano-sized YBO$_3$:Eu^{3+} phosphors synthesized by hydrothermal [7] and thermal decomposition [8] methods showed an improved luminescent intensity and color purity. In this study, a GdBO$_3$:Eu^{3+} phosphor was synthesized by the hydrothermal method in order to investigate the effect of nano particles on the luminescent properties of the product.

2.   Experimental

For the hydrothermal synthesis, stoichiometric amounts of Gd$_2$O$_3$ and Eu$_2$O$_3$ were dissolved in 100ml of distilled water acidified by the addition of nitric acid. After the complete dissolution of these oxides, NH$_4$OH solution was added drop-wisely until the pH of the solution reached 9. White precipitates were instantaneously formed and so-obtained precipitates were washed several times with distilled water by centrifugation. The washed precipitates were mixed with 50ml solution of H$_3$BO$_3$ and distilled water. The amount of H$_3$BO$_3$ in the solution was adjusted so as to have an appropriate mole ratio with respect to Gd and Eu to give GdBO$_3$:Eu^{3+}. NH$_4$OH was used to adjust pH of the precursor solution to 7~10. After vigorous stirring, the precursor solution was placed in a Teflon-lined stainless steel autoclave with a volume of 100ml. The solution was heated at 200 , 240 for 3~10h and cooled to room temperature. The resulting powders were filtered and washed several times with distilled water by centrifugation, and finally suspended in ethanol then dried at 60 for 5h.

For comparison, the bulk GdBO$_3$:Eu^{3+} samples are prepared by a solid-state(SS) reaction at 500 and 1100 each for 2h respectively, from the mixture of Gd$_2$O$_3$, Eu$_2$O$_3$, and H$_3$BO$_3$ (20wt% excess). XRD analysis was done by a diffractometer (MAC Science Co. M18XHF) using CuK$_\alpha$ radiation. The size of the crystallites was then estimated by means of the Scherrer equation. In addition, the size of the particles was measured directly by transmission electron microscopy (JEOL JEM-3000F). Excitation and emission spectra were measured by a spectrofluorometer (JASCO FP-5600). All spectra were recorded at room temperature.

3.   Results and discussion
3.1   XRD analysis

Fig. 1a shows that the crystallinity of the precipitates was found to be quite low based on the peak intensity

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and width. Therefore, it is hard to identify the phase by this XRD result, but the observed peak was assumed to be the main peak of Gd_2O_3. Fig. 1b~1e show XRD patterns of powders hydrothermally treated for 4h~10h at 200   . The amorphous phase changed to a gadolinium borate phase as with increasing reaction time. However, the main peak for gadolinium oxide still remained after a 10h hydrothermal treatment. The peak intensity of the gadolinium borate phase is quite weak, indicating poor crystallinity.
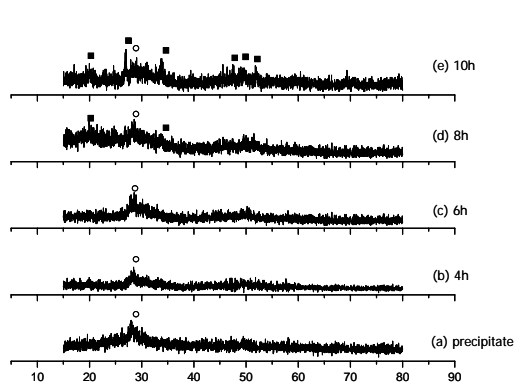

Fig. 1 XRD patterns of $Gd_{0.9}BO_3:Eu^{3+}_{0.1}$ powders of (a) precipitate and (b)-(e)hydrothermally treated at 200   for 4-10h with pH 8

Fig. 2 shows a similar pattern for powders produced at pH9. The formation of the borate phase, however, is different from the case of pH8, since it began to form after 4hr of treatment. The relative intensity among the peaks is also different from the pH8 case. The (002) peak appeared first (Fig. 2b) and its intensity is higher than the (100) main peak. This indicates that the synthesized particles are in a preferred orientation. Based on SEM observation, these particles are found to have plate morphology, consistent with previously reported result. [9] These results show that phase formation takes places early in a preferred orientation under conditions of high pH. This tendency was reconfirmed when high pH values (pH10 ~ 12) were used.
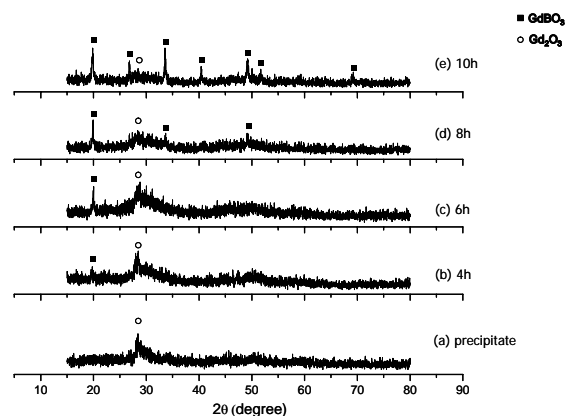

Fig. 2 XRD patterns of $Gd_{0.9}BO_3:Eu^{3+}_{0.1}$ powders of (a) precipitate and (b)-(e)hydrothermally treated at 200   4-10h with pH 9

Fig. 3a~c show XRD patterns for the samples, with different amounts of H_3BO_3, hydrothermally treated at 200   for 10h. Otherwise, the same conditions were used as in Fig. 1e. With a 50wt% excess of H_3BO_3, $GdBO_3$ with a vaterite structure was obtained and the relative intensity was about the same as that in the JCPDS(16277) data. A gadolinium oxide main peak is not observed and the intensity of all peaks is enhanced. This indicates that a pure $GdBO_3$ phase was synthesized and that the product had a good crystallinity. Further, the addition of H_3BO_3, however, resulted in the different peak intensity in the patterns. That is, the (002) peak of the $GdBO_3$ phase in Fig. 3c shows the highest intensity, which is similar to the result of high pH results shown in Fig. 2. This result shows that the presence of excess H_3BO_3 accelerates phase formation and also enhances crystallinity. Thus, it appears that a high pH and excess H_3BO_3 promote the growth of $GdBO_3$ in a preferred orientation i.e., (200).

For comparison, XRD patterns of samples synthesized by the solid-state reaction are shown in Fig 3d. These data show that a pure $GdBO_3$ phase was obtained without Gd_2O_3. The peak intensities are high compared to those of the hydrothermally synthesized powders.
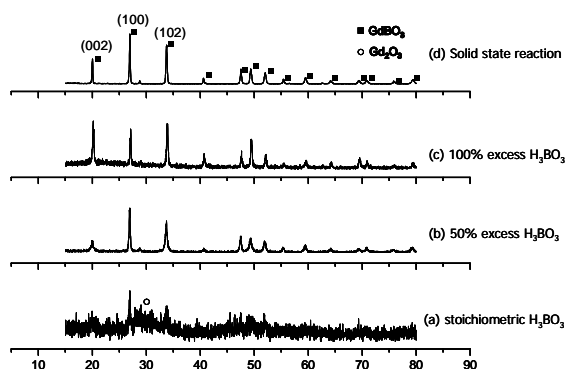
Fig. 3 XRD patterns of Gd$_{0.9}$BO$_3$:Eu$^{3+}_{0.1}$ powders synthesized with (a) stoichiometric, (b)-(c) excess amount of H$_3$BO$_3$ by hydrothermal method (at 200 , 10h, pH8) and (d) by solid state reaction

3.2   Powder morphology

The crystallite size was qualitatively compared for the differently processed powders. The powders produced by the hydrothermal process (Fig. 3b) exhibit broader peaks, especially for the (002) direction, than those by a solid-state reaction. The crystallite size is estimated to be in the 20-50nm by the Scherrer method. It can be seen from the TEM images that the crystallite size is about 50~100nm in length and 20~50nm in width. This is in agreement with values calculated using the Scherrer's equation.

However, the SEM images in Fig. 4 are much different from those of crystallites. Spherical agglomerates, with a diameter of 5~10   , consisting of nano-sized needle or plate appear to be produced. It seems that homocentric growth occurred, which was recently proposed for the synthesis of YBO$_3$.[10,11] That is, nano particles are aggregated in an orderly manner, to form particular shaped agglomerates in the middle of the hydrothermal synthesis.
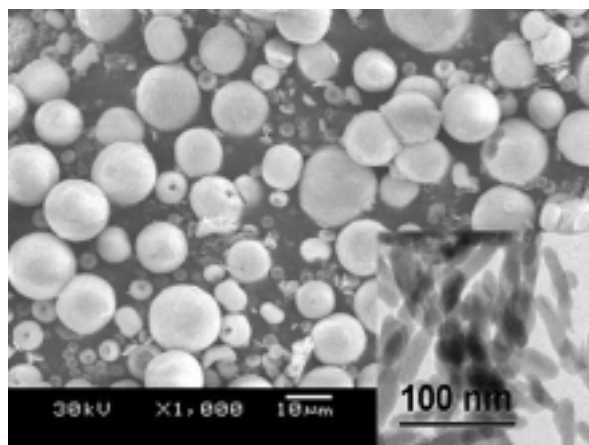

Fig. 4 **TEM and SEM images of Gd$_{0.9}$BO$_3$:Eu$^{3+}_{0.1}$ synthesized by hydrothermal method**

3.3   Luminescent properties

Fig. 5 shows the emission and excitation spectra of Gd$_{0.9}$BO$_3$:Eu$^{3+}_{0.1}$ synthesized by hydrothermal and solid state reactions. The three main emission peaks, which are associated with the transition from the excited ^{5}D$_0$ level to ^{7}F$_J$ (J=1~3) levels of Eu^{3+}, can be seen in both cases. However the hydrothermal (HT) samples have a higher luminescent intensity than the solid-state (SS) samples. The relative intensity ratios among the peaks are also different. That is, the emission peak for the 613nm wavelength is stronger in the HT samples than in the SS samples, as shown in Fig. 5a. This peak corresponds to red light relative to an orange light of 593nm. This change is known as the nano-effect, which occurs when the inversion symmetry of Eu^{3+} ions is destroyed for Eu^{3+} located near the surface of nano particles. [8,12,13]

The excitation spectra are also changed in the hydrothermal case, as can be seen in Fig. 5b. In addition to the relative increase in intensity, the CT band in the 220~270nm range is shifted in the long wavelength direction with peak broadening. As a result, HT sample can absorb 240~270nm excitation light more effectively than the SS sample. This is a possible reason for why the emission intensity increased when 254nm was used for excitation. Considering that the CT band is related to the covalency between O^{2-} and Eu^{3+}[6,12], it can be interpreted by the nano effect.

The environment of Eu^{3+} ions located near the surface area is different from that in the matrix site. Therefore, this result suggests that Eu^{3+} occupies the

position where the Eu^{3+} - O^{2-} covalency is higher than the original one. Further experiments and characterizations are underway to confirm this interpretation. These observations of emission and excitation spectra of nano crystallites may be distinct from other reported results since both luminescent and chromaticity improvements are obtained by reducing crystallite size. It is likely that the size effect of the nano crystallites contributes to the improvements in luminescent intensity in hydrothermal synthesis.
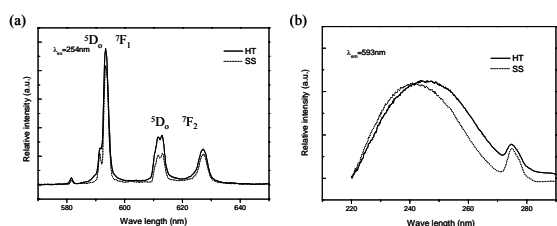

Fig. 5 (a) Emission and (b) excitation spectra of $Gd_{0.9}BO_3$:$Eu_{0.1}$ synthesize by hydrothermal and solid state method

Fig. 6 shows the effect of Eu^{3+} concentration on the chromaticity. It can be seen the portion of 615nm red light increases with Eu^{3+} concentration in the case of HT samples. This suggests that the portion of Eu^{3+} located near the surface area increases with Eu^{3+} concentration in the hydrothermally synthesized samples, resulting in a high red emission.
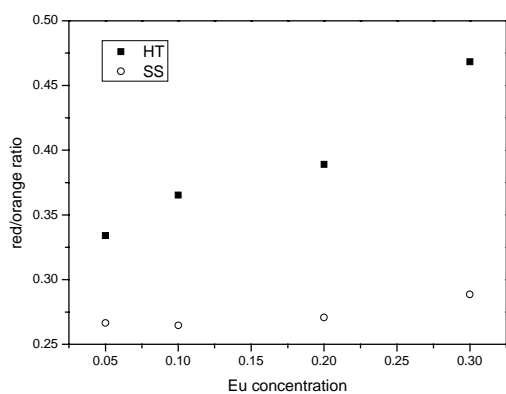

Fig. 6 Effect of Eu^{3+} concentration on r/o ratio

4.   Conclusions

Nano-crystalline $Gd_{1-x}BO_3$:Eu^{3+}_x red phosphors were synthesized by a hydrothermal route using a solution of precipitated amorphous oxide mixture as the precursor

Both the luminescent intensity and the chromaticity of the hydrothermal samples increased compared to samples prepared by conventional solid-state reactions. These changes can be attributed to the red shift in the CT band and to the surface effect of nano crystalline particles, i.e., a loss of inversion symmetry.

7.   References

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