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Photoluminescence properties of Y_2O_3 co-doped with Eu and Bi compounds as red-emitting phosphor for white LED

W. J. Park · S. G. Yoon · D. H. Yoon

Abstract Bismuth doped Y_2O_3: Eu was used as a red phosphor with a very high efficiency and an appropriate emission wavelength of around 310–400 nm. This red phosphor was synthesized by the solid state reaction which is normally used in the field of white LEDs. In this study, we synthesized Y_2O_3: Eu, Bi phosphors using a solid state reaction. We investigated the effect of the Eu^{3+} and Bi^{3+} concentrations and additive fluxes on the emission characteristics. The fabricated phosphors were investigated by analyzing their particle size and crystal structure with scanning electron microscopy and X-ray diffraction (XRD). Their photoluminescence (PL) spectra were also measured at room temperature.

Keywords Red-emitting phosphor · White light emitting diode · Y_2O_3co-doped Eu and Bi · Photoluminescence properties

1 Introduction

A three-band white-light-emitting diode (LED) consists of an LED device that emits either soft ultraviolet (UV) or blue light, and red-green-blue (RGB) phosphors [1–3]. For the development of the three-band white LEDs, InGaN and GaN chips have been both considered as excitation sources for the RGB phosphors. In this case, either organic dyes or inorganic phosphors can be used as the RGB components for the three band white LEDs [1–4]. However, the inorganic phosphors have some environmental problems during their preparation and use, because they include toxic elements, such as sulfur, chlorine, and cadmium [2–4]. To solve these problems, in the present study, we attempted to develop new oxide for RGB phosphors, bismuth doped Y_2O_3: Eu, which was used as the red phosphor with a very high efficiency and an appropriate emission wavelength of around 340–400 nm. This red phosphor was synthesized by the solid state reaction with flux, which is normally used for the fabrication of white LEDs.

In this study, we investigated the effect of the Eu^{3+} and Bi^{3+} concentrations and additive fluxes on the emission characteristics of the fabricated phosphors, and the particle size and crystal structure were also investigated.

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2 Experimental procedure

Bi doped Y_2O_3: Eu compounds were prepared by the conventional solid-state reaction. Eu and Bi ions were added in the form of Eu_2O_3 and Bi_2O_3, respectively. Commercially available high purity reagents (99.99%) of Y_2O_3, Eu_2O_3, Bi_2O_3, H_3BO_3 and $BaCl_2{\cdot}2H_2O$ were used for the production of the samples. In each case, the total weight of the powders was 10 g, and the powders were mixed together using an alumina mortar and pestle. The mixed batches were fired in an alumina crucible at 1100°C for 3 h in air. The fired specimens were ground using an alumina mortar and pestle, followed by washing and drying procedure. The dried powders were sieved to classify the powder size for the photoluminescence system measurements.

The emission and excitation spectra were measured at room temperature using a fluorescence spectrophotometer in the ranges of 550–700 nm and 250–550 nm, respectively. The crystalline phases of the synthesized samples were characterized by an X-ray diffractometer (CuK_α, 30 KV, 100 mA, Rigaku) and the surface morphologies were observed using a scanning electron microscope (ESEM, XL-30, Philips).

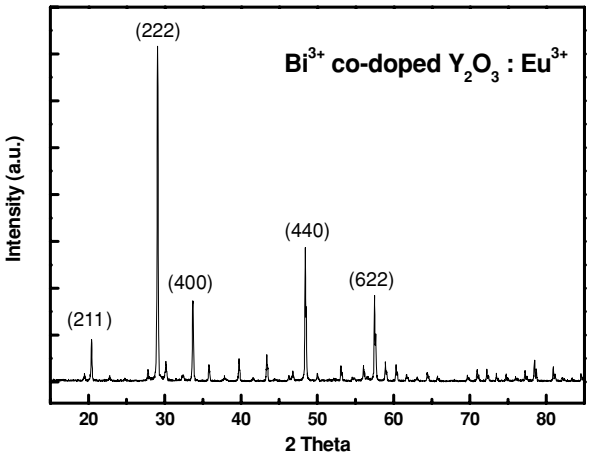

Fig. 1 X-ray diffraction pattern of bismuth co-doped Y_2O_3: Eu fired at 1100°C for 3 h in air

3 Results and discussion

The XRD pattern of Y_2O_3 sample co-doped with Eu and Bi is presented in Fig. 1. According to JCPDS card 41-1105, pure Y_2O_3 has a cubic crystal structure with the Ia3(206) space group, and its lattice parameter is 1.641 nm. Only a single cubic phase was identified from XRD measurement without having any extraneous phase and the doped Eu and Bi ions had little influence on the host Y_2O_3 structure. It was concluded that the co-doping with Eu and Bi increased the lattice parameters of the phosphor, due to the fact that the ionic radius of Y^{3+} (0.088 nm) is slightly lower than those of Eu^{3+} (0.109 nm) and Bi^{3+} (0.196 nm). Eu^{3+} and Bi^{3+} ions were expected to occupy the Y^{3+} sites in this phosphor. It is believed that this single phase was successfully developed through our preparation procedure.

Figure 2 shows the emission and excitation spectra of Y_2O_3 co-doped with Eu^{3+}, Bi^{3+} measured at room temperature. The emission spectrum exhibited a narrow band (600–650 nm) having sharp peaks at about 610–620 nm due to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}. In addition, the excitation spectrum exhibited a broad band between 250 and 550 nm with peaks occurring about 310–400 nm and a sharp peak at 465.5 nm. Conventional Y_2O_3: Eu was not absorbed near UV efficiently. Y_2O_3: Bi exhibited absorption band at 375 nm and emission band around 410 nm because of $^1S_0 \rightarrow {}^3P_1$ transition of Bi^{3+}[5–9]. When incorporated in Y_2O_3: Eu phosphors, Bi^{3+} ions act as a sensitizer for Eu^{3+} ions under 350 nm radiation. The energy transferring from Bi^{3+} ions to Eu^{3+} ions by no radiation process resulted in the final emission from excited Eu^{3+} ions. Bi^{3+} ion was introduced into the Y_2O_3 red phosphors, excitation spectra were enhanced significantly and a new band located at 350–390 because of 6 $s^2 \rightarrow$ 6s6p transition of Bi^{3+}. Figure 3 shows the emission spectra (λ_{ex} = 390 nm, λ_{em} = 614 nm) of the Eu^{3+} and Bi^{3+} co-doped yttrium oxide (with a fixed Eu concentration of 3.0 mol% and variable Bi concentration or vice versa) measured at room temperature as a function of the Eu^{3+} and Bi^{3+} concentrations.

With increasing Eu^{3+} concentration, the relative intensity of the red emission was continuously increased. However, with increasing Bi^{3+} concentration, the intensity of the red emission was increased and reached a maximum at a Bi^{3+} concentration of 3.5 mol %. Above this concentration, the intensity of the red emission decreased. Because of the energy transferred from the Eu^{3+} to the Bi^{3+} ions, the emission intensity of the Bi^{3+} ions increased, while that of the Eu^{3+} ions decreased in the Eu^{3+} and Bi^{3+} co-doped Y_2O_3. However, in the case where Y_2O_3: Eu was co-doped with Bi, all of the samples exhibited a strong absorption band in the near UV region because of the $^1S_0 \rightarrow {}^3P_1$ transition of Bi^{3+},while the strong 610–620 nm emission due to Eu^{3+} was retained.

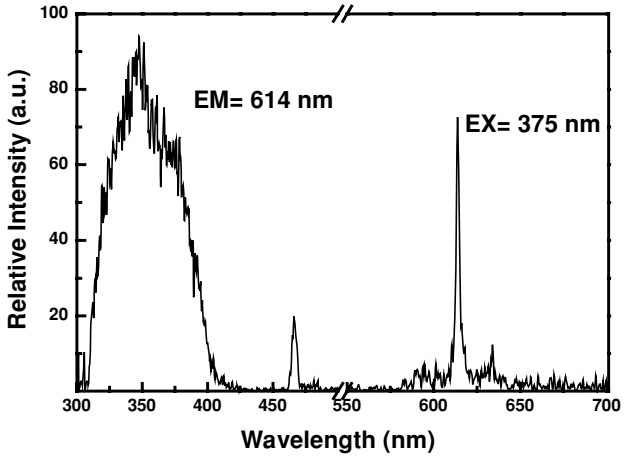

Fig. 2 Emission (λ_{ex} = 375 nm) and excitation (λ_{em} = 614 nm) spectra of Y_2O_3: Eu^{3+}, Bi^{3+}

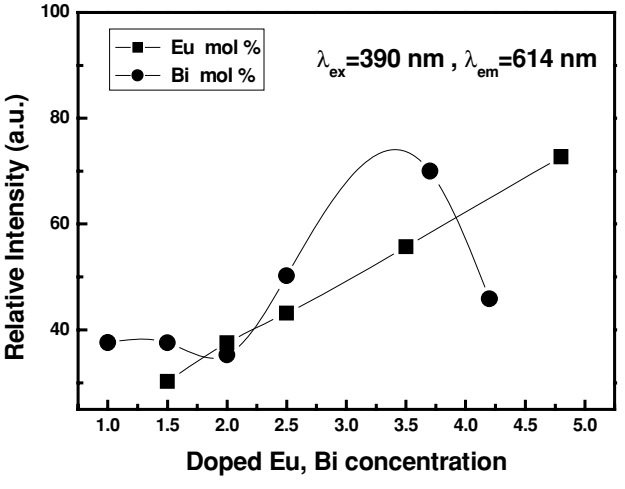

Fig. 3 Emission relative intensity (λ_{ex} = 390 nm, λ_{em} = 614 nm) of Eu^{3+}, Bi^{3+} co-doped yttrium oxide (with a fixed Eu concentration of 3.0 mol% and variable Bi concentration or vice versa) as a function of the Eu^{3+} and Bi^{3+} concentrations

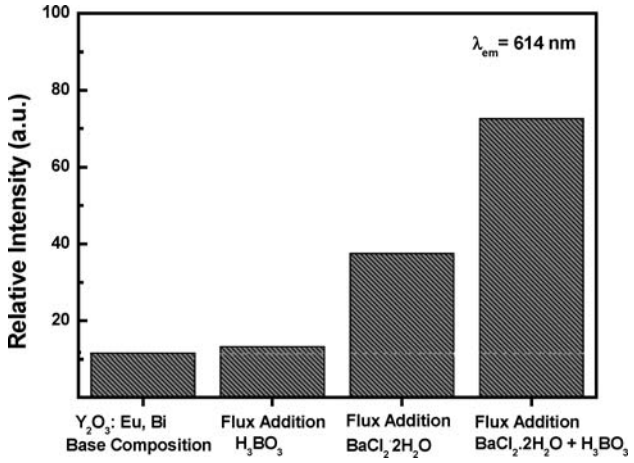

Fig. 4 Relative emission intensity of Y_2O_3:Eu^{3+}, Bi^{3+} at 614 nm with and without the H_3BO_3 and $BaCl_2 \cdot 2H_2O$ fluxes

Figure 4 shows the relative emission intensity of Y_2O_3:Eu^{3+}, Bi^{3+} with or without H_3BO_3 and $BaCl_2 \cdot 2H_2O$ flux at 614 nm. The relative emission intensity of Y_2O_3: Eu^{3+}, Bi^{3+}containing 0.43 mol% $H_3BO_3$was slightly higher than that of the base composition sample. The relative emission intensity of Bi^{3+}co-doped Y_2O_3:Eu^{3+}, containing 2.08 mol% $BaCl_2 \cdot 2H_2O$ was approximately 3.3 times higher than that of the base composition sample. Furthermore, H_3BO_3 was added to the Bi^{3+}co-doped Y_2O_3:Eu^{3+} 2.08 mol% $BaCl_2 \cdot 2H_2O$ sample in order to improve the emission intensity. The relative emission intensity of Y_2O_3:Eu^{3+}, Bi^{3+} containing 0.43 mol% H_3BO_3 and 2.08 mol% $BaCl_2 \cdot 2H_2O$ was approximately 6.4 times higher than that of the base composition sample. This improvement in the emission intensity associated with the Eu^{3+} and Bi^{3+} ions in the Y_2O_3 samples was attributed to the synergetic effect afforded by the H_3BO_3 and $BaCl_2 \cdot 2H_2O$ fluxes.

Figure 5(a) shows the SEM image of the Y_2O_3: Eu^{3+}, Bi^{3+} base composition samples. Spherically shaped crystals with diameters of less than 300 nm grew and became hard and aggregated, having to be partially broken up again in a mortar. The samples were uniform without a visible admixture of any impurity phases. Figure 5(b) shows the SEM image of the sample containing 0.43 mol% H_3BO_3 and 2.08 mol% $BaCl_2 \cdot 2H_2O$. The phosphor particles grew to achieve diameters of 400–800 nm. Also, the Y_2O_3: Eu^{3+}, Bi^{3+} phosphor particles containing the fluxes exhibited no aggregation and had regular morphology characteristics without any visible admixture of any impurity phases. It was observed that the small sized Bi^{3+} co-doped Y_2O_3: Eu^{3+} particles exhibited poor luminescence intensity, but that when the particle size grew due to the addition of the fluxes, the emission intensity increased by approximately 6.4 times.

4 Conclusion

The red emission properties of Bi^{3+} co-doped Y_2O_3: Eu^{3+} prepared by the solid-state reaction were investigated, in order to verify its potential to act as the red emitting phosphor of white LEDs. The emission spectrum consisted of a narrow band at 600–650 nm, with sharp peaks occurring at about 610–620 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+},while the excitation spectrum exhibited a broad band between 250 and 550 nm with peaks occurring in the range of 310–400 nm and a sharp peak being observed at 465.5 nm. In the emission spectra (λ_{ex} = 390 nm) of Eu^{3+}, Bi^{3+}-doped yttrium oxide with a fixed Bi concentration of 3.0 mol% and increasing Eu^{3+} concentration, the relative intensity of the red emission increased continuously. However, in the emission spectra of the Eu^{3+}, Bi^{3+}-doped yttrium oxide with a fixed Eu concentration of 3.0 mol% and increasing Bi^{3+} concentration, the intensity of the red emission intensity increased and reached a maximum at a Bi^{3+} concentration of 3.5 mol%. Above this concentration, the intensity of the red emission decreased. Also, the relative emission intensity of

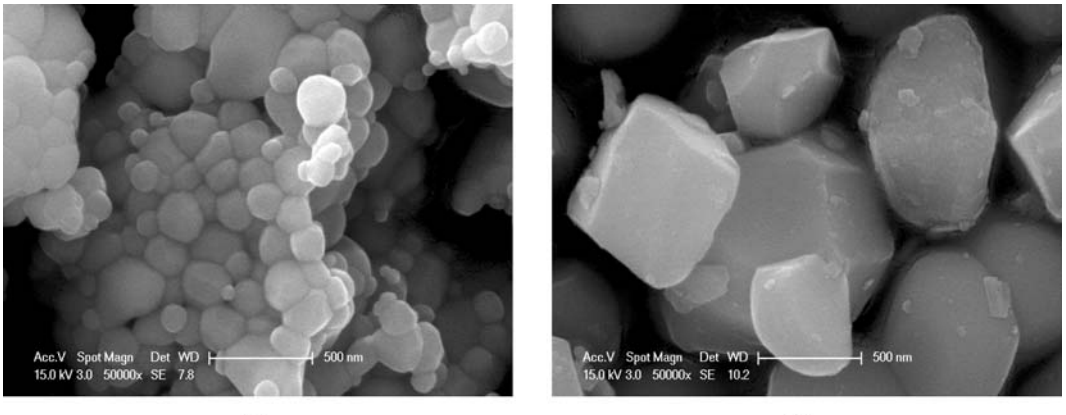

Fig. 5 SEM image of (a) Eu^{3+}, Bi^{3+} co-doped yttrium oxide and (b) Eu^{3+}, Bi^{3+} co-doped yttrium oxide containing 0.43 mol% H_3BO_3 and 2.08 mol% $BaCl_2 \cdot 2H_2O$

the Y_2O_3:Eu^{3+}, Bi^{3+} sample containing 0.43 mol% H_3BO_3 and 2.08 mol% $BaCl_2 \cdot 2H_2O$ was approximately 6.4 times higher than that of the base composition.

References

1. P. Schlotter, R. Schmidt, and J. Schnoider, *Appl. Phys. A: Mater. Sci. Process*, **64**, 417 (1997).
2. Y. Sato, N. Takahashi, and S. Sato, *Jpn. Appl. Phys. Part 2,* **35**, L838 (1996).
3. Y.-D. Hun, J.-H. Shim, Y. Kim, and Y.R. Do, *J. Electrochem. Soc.,* **150**, H57 (2003).
4. K.S. Sohn, J.M. Lee, and N.S. Shim, *Adv. Mater.,* **24**(15), 2081 (2003).
5. G. Blasse and A. Brill, *J. Chem. Phys.,* **48**, 7 (1968).
6. A.M. Srivastava and W. W. Beers, *J. Lumin.*, **81**, 293 (1999).
7. G. Blasse, Prog, *Solid State Chem.,* **18**, 79 (1998).
8. M.Q. Wang, X.P. Fan, and G.H. Xiong, *J. Phys. Chem. Solids,* **56**, 859 (1995).
9. A.O. Wright, M.D. Seltzer, J.B. Gruber, and B.H.T. Chai, *J. Appl. Phys.,* **78**, 2456 (1995).