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Morphology and luminescence of (Y,Gd)BO_3:Eu phosphor particles prepared by urea-assisted spray pyrolysis

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Abstract

Red phosphor of (Y,Gd)BO_3:Eu was prepared by urea-assisted spray pyrolysis through the polymeric reaction. The synthetic route was adopted to enhance optical characteristics of spherical phosphors. In particular, the phosphors synthesized with urea showed quite different morphology and luminous efficiency compared to those without urea. It was certain that precursor with the urea had a positive effect on the particle formation and the surface status of particles. To enhance the luminescence intensity and mechanical characteristics, synthesizing conditions were investigated and optimized, which included the concentration of urea, the synthesis temperature, and the activator concentration. As a result, the red emission intensity of the spherical (Y,Gd)BO_3:Eu phosphor obtained a remarkable improvement by optimal urea-assisted spray pyrolysis, compared to that by conventional solid-state technique.

Keywords: Optical materials; Gas–solid reactions; Luminescence

1. Introduction

Plasma display panels (PDP) are regarded as the most promising candidate for large sized flat panel displays (FTP). Phosphors for PDP application are required for high conversion efficiency by the vacuum UV radiation of 147 nm. At present, Eu-doped yttrium gadolinium borate (Y,Gd)BO_3:Eu phosphor particles are used as a red emitting phosphors for plasma display panels because of their high luminous efficiency under vacuum UV 147 nm excitation [1–3]. Commercial (Y,Gd)BO_3:Eu phosphor particles are mainly prepared by conventional solid-state reaction or liquid solution methods [4–8]. But these conventional processes have disadvantages in controlling the morphology and maintaining the uniformity in composition of phosphor particles, which strongly affected the luminous characteristics of phosphor particles. Therefore, many new processes aiming to eliminate these disadvantages are under investigation.

Among the novel methods of preparing the spherical phosphors, spray pyrolysis is one of the feasible processes for the preparation of improved phosphor particles [9–12]. Phosphor particles prepared by spray pyrolysis have spherical shape, fine size, narrow size distribution, and non-aggregation characteristics because of the special particle formation mechanism [13–15]. However, the hollowness of the particles has been an obstacle, which causes reduction of brightness and long-term stability [16,17].

In this work, aiming to prevent the hollowness of (Y,Gd)BO_3:Eu phosphor particles, we applied the urea as an assistance to the aerosol pyrolysis for preparing (Y,Gd)BO_3:Eu phosphors.

The influence of urea on the mechanical, morphological control and optical properties of phosphor particles in the syhthetic route were examined. Also, the effects of processing parameters such as synthesis temperature and activator concentration on the photoluminescence (PL) characteristics were investigated.

2. Experimental

The spray equipment consisted of an ultrasonic aerosol generator with six vibrators (1.7 MHz), a quartz tube (length,1000 mm and i.d., 50 mm), and a particle collector. The flow rate of air used as a carrier gas was 45 L/min. The residence time of droplets inside the reactor was about 0.6 s.

The starting materials were $Y(NO_3)\cdot 6H_2O$ (99.99%), $Gd(NO_3)\cdot 6H_2O$ (99.99%), $Eu(NO_3)\cdot 6H_2O$ (99.99%) and HBO_3 (99.99%). All of these with stoichiometric ratio were dissolved in distilled water, and certain amount of urea

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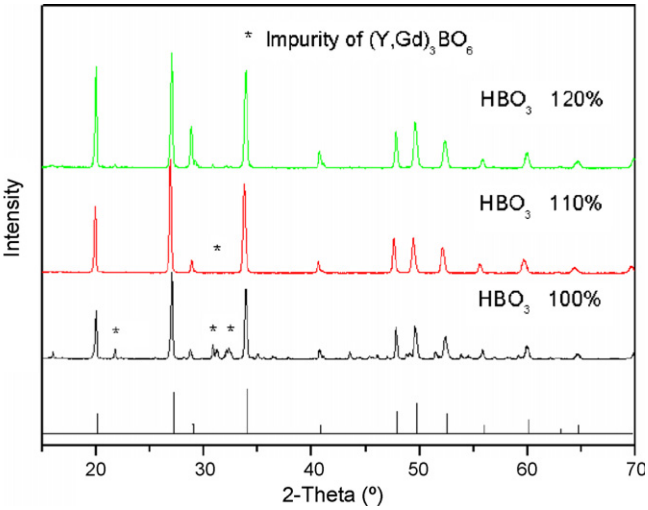

Fig. 1. XRD spectra of particles prepared at different concentrations of boric acid.

was added into this solution. To get a series of $(Y_{1-x-y},Gd_y)BO_3:Eu_x$ phosphor, y value was fixed as 0.3, while x value was varied from 0.01 to 0.12. The ratio of metal ion to urea was changed from 1:5 to 1:20.

The prepared spray solutions were atomized and formed droplets by the ultrasonic nebulizer, which were transferred by carried gas into the quartz tube at 900 °C. The produced (Y,Gd)BO$_3$:Eu phosphor particles were collected by a special collector and post-treated at 1000–1200 °C for 2 h. The crystal structure of produced (Y,Gd)BO$_3$:Eu phosphor was identified by diffractometry (Rigaku D/max 2550 VB$^+$). The morphology was observed by scanning electron microscopy (SEM, JEOL JSM-6360LV). TEM were performed on Tecnai G^{2}20 operated at 200 KV. The photoluminescence measurement was performed with a spectrophotometer using a Xe lamp excitation source.

3. Results and discussion

Fig. 1 shows the XRD spectra of (Y,Gd)BO$_3$:Eu phosphor particles post-treated at 1200 °C, with different concentrations of boric acid. The particles prepared from stoichiometric composition (100% boric acid) have an impurity phase of (Y,Gd)$_3$BO$_6$ because of high volatility of boron component, while the particles prepared from solution with 20% excess boric acid have a pure (Y,Gd)BO$_3$:Eu phase. In the rest of this report, all the samples were prepared from 20% excess boric acid solution. In the XRD spectra shown in Fig. 2, the as-prepared particles at 900 °C by the spray pyrolysis had pure (Y,Gd)BO$_3$:Eu phase, though its crystallinity was not fully developed because of short residence time of particles inside tubular reactor as about 0.6 s. The crystallinity of post-treated particles measured by peak broadening of XRD peaks increased with increasing temperature and well-developed crystallinity at 1200 °C

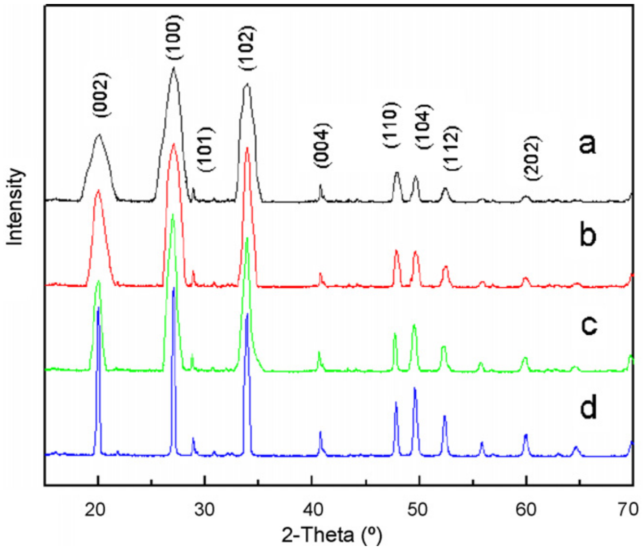

Fig. 2. XRD patterns of (Y,Gd)BO$_3$:Eu phosphor particles (a) as-prepared at 900 °C and after calcinations at (b) 1000 °C, (c) 1100 °C, and (d) 1200 °C for 2 h.

The particles directly prepared by the spray pyrolysis had spherical shape, smooth surface, and hollow particles characteristics. Fig. 3 shows SEM images of the (Y,Gd)BO$_3$:Eu phosphor particles, which were prepared by the spray pyrolysis method with and without urea. The (Y,Gd)BO$_3$:Eu phosphor particles prepared without urea have a hollow structure. Consequently, the particles were fragmented and completely lost their sphericity after heat-treatment. On the contrary, the (Y,Gd)BO$_3$:Eu phosphor particles prepared with urea were a dense and kept their spherical shape perfectly even after heat-treatment. Fig. 4 shows transmission electron microscopy (TEM) images of phosphors prepared from precursor without and with monomers. Though the shape of as-collected particles prepared by general spray pyrolysis method was spherical and hollow, as shown in

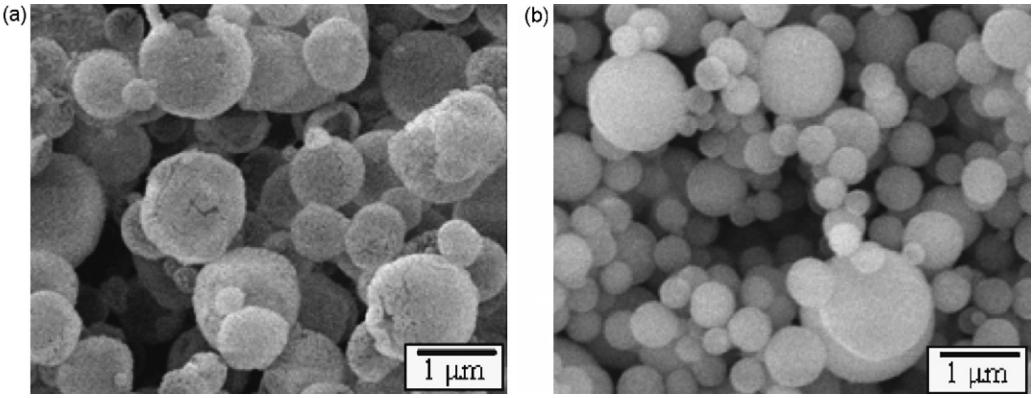

Fig. 3. SEM images of phosphors prepared from precursor (a) without and (b) with monomers.

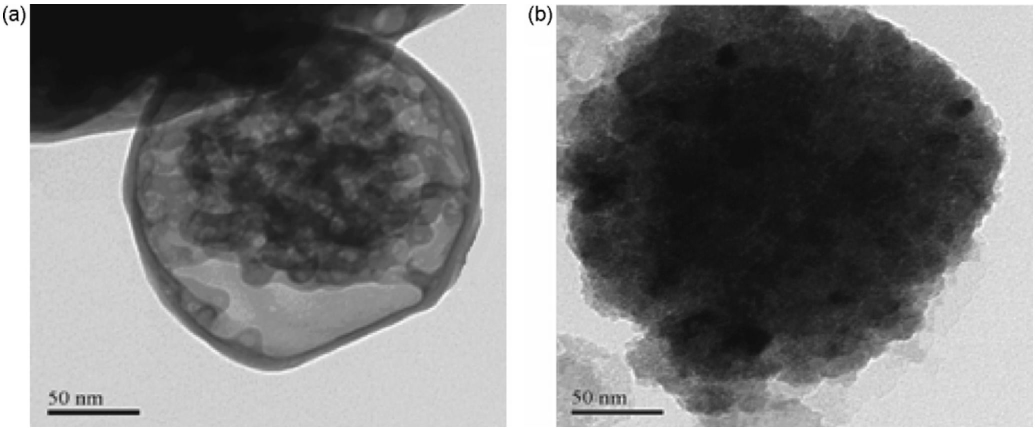

Fig. 4. TEM images of phosphors prepared from precursor (a) without and (b) with monomers.

Figs. 3a and 4a, subsequent heat-treatment for crystallinity of the phosphors always made the particles hollow and cracked. On the other hand, the shape of (Y,Gd)BO_3:Eu phosphor particles prepared with urea-assisted had dense and spherical morphology, as shown in Figs. 3b and 4b. This morphological difference of spherical shape might be due to the different mechanism of the particle formation. When the prepared nitrate solution is chemically modified by adding the urea, the boric acid exists as a hydrolyzed form, $B(OH)_3$ [18]. At an intermediate pH achieved by adding urea, polyborate anions are formed as follows:

$$B(OH)_3 + H_2O \rightarrow BO(OH) + H^+ \quad (1)$$

which makes it possible to produce the volume precipitation [19], the only precondition of the formation of a dense particle [20].

Therefore, the (Y,Gd)BO_3:Eu phosphor particles prepared with urea-assisted can be expected to have a compact and dense morphology. We also observed that the shape of phosphor particles could be controlled by the ratio of the urea to the metal ions. Fig. 5 shows SEM images of (Y,Gd)BO_3:Eu phosphor particles as a function of the ratio of contents in precursor solution. The overall metal ions concentration of precursor solution was 0.05 M, and the as-prepared particles were annealed at 1200 °C for 2 h after the spray pyrolysis at 900 °C. The phosphor particles

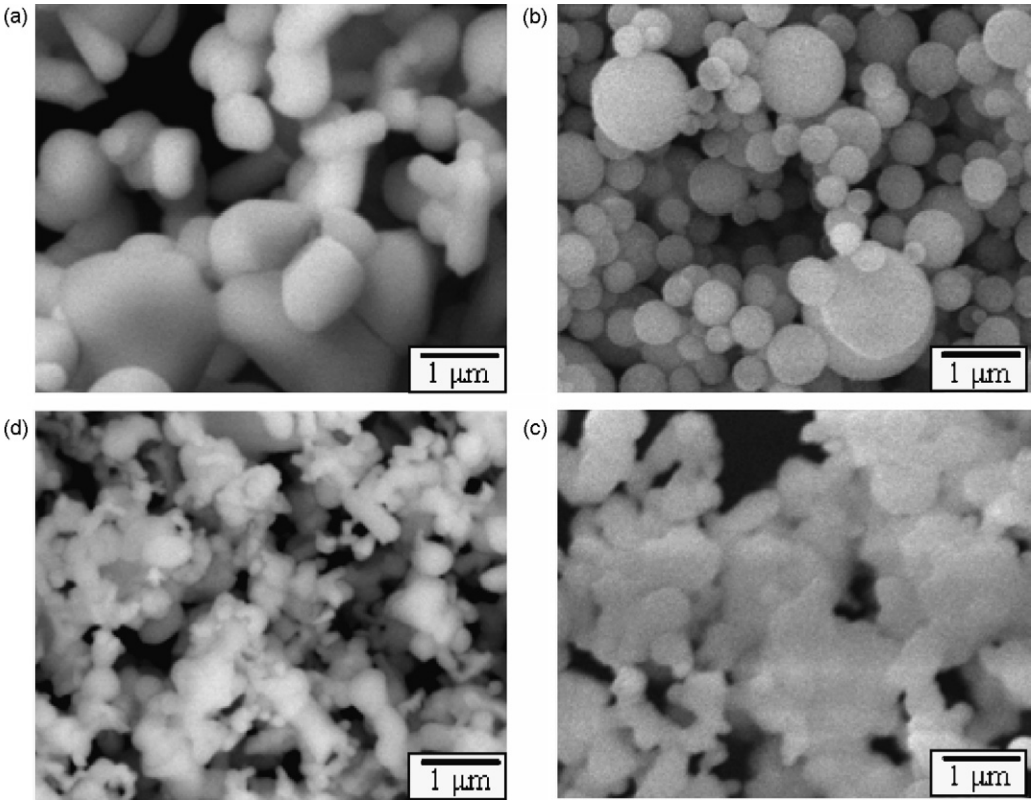

Fig. 5. SEM images of (Y,Gd)BO_3:Eu phosphor particles synthesized as a function of the ratio of adding contents metal ions: urea with (a) 1:5, (b) 1:10, (c) 1:15, and (d) 1:20.

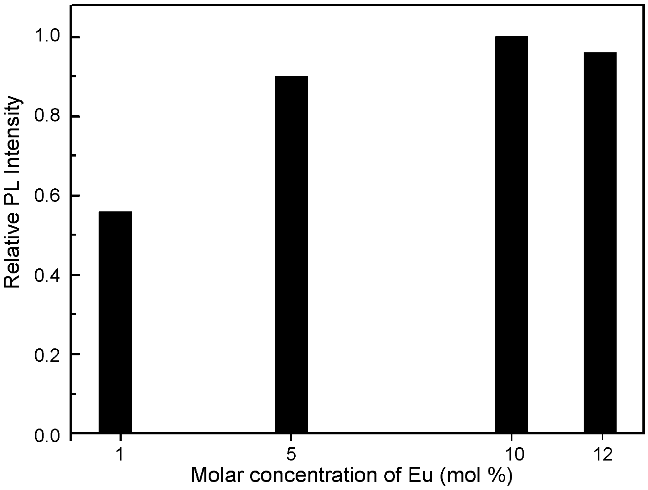

Fig. 6. Relative PL intensity as a function of Eu concentration.

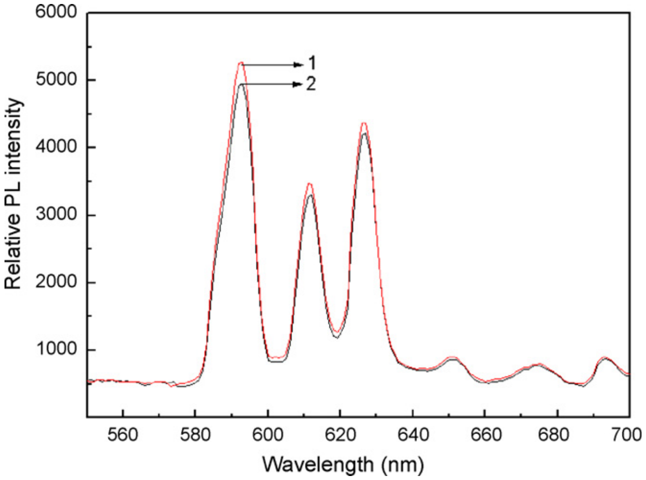

Fig. 8. PL spectra of (Y,Gd)BO$_3$:Eu$_{0.1}$ particles prepared by (1) the solid-state and (2) spray pyrolysis with the ratio of metal ions to urea was 1:10 (λ_{ex} = 147 nm).

were in the spherical shape even after heat–treatment, when the ratio of metal ions to urea was 1:10,as shown in Fig. 5b. When the content of the urea came to up or below the ratio, resultant particles cracked, as shown in Fig. 5a, c and d. They showed that the particles were agglomerated and took a dumbbell shape when the contents of monomers increase. The particle size was also observed to increase.

The relative photoluminescence intensity was shown as a function of Eu concentration in Fig. 6. The photoluminescence intensity increases with the concentration ratio of Eu and that is maximal at 10 mol% concentration. Above this ratio, the photoluminescence intensity decreases with the concentration of Eu in the precursor. It is well known that, because the concentration quenching occurs between activator ions, the excessive doping Eu into the host lattice reduces the luminescence intensity. The photoluminescence intensity of particles was strongly affected by the doping concentrations of Eu. Here the optimum brightness was obtained at a doping concentration of 10 mol%.

Generally, the photoluminescence intensity of phosphor particles is affected by particle morphology. High photoluminescence efficiency requires the phosphor particles to have high crystallinity and a clean surface with few surface defects, which act as a quenching site consuming photoexcited electrons. So the dense and spherical phosphor particles are better than the irregular-shaped ones in terms of obtaining high luminescence efficiency. Fig. 7 shows the emission spectrum of (Y,Gd)BO$_3$:Eu under the VUV (147 nm) excitation with different ratio of metal ions to the urea. When the ratio of metal ions to urea was 1:10, the luminescence intensities became much higher than that of the phosphor particles prepared in the same conditions with different ratio of metal ions to urea. The particles, having a spherical and filled morphology, had the higher photoluminescence intensity than that of the particles having a hollow and irregular shape.

Fig. 8 shows that the photoluminescence intensity measured under the illumination of VUV light for the prepared

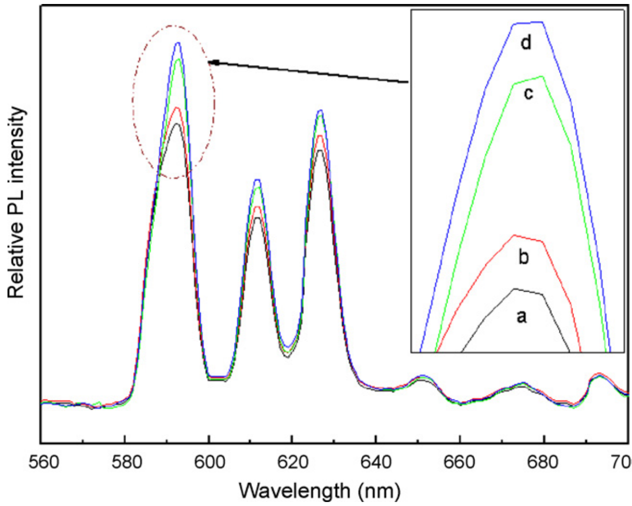

Fig. 7. PL spectrum of (Y,Gd)BO$_3$:Eu phosphor particles as a function of urea contents. Metal ions: urea at (a) 1:5, (b) 1:15, (c) 1:20, and (d) 1:10.

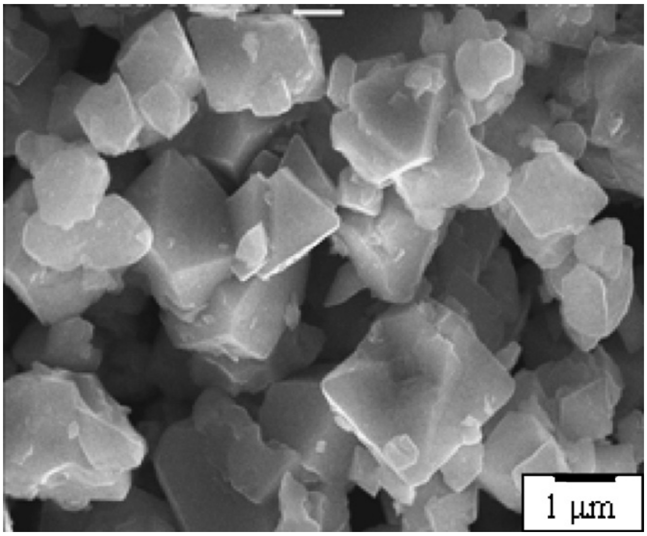

Fig. 9. SEM image of (Y,Gd)BO$_3$:Eu particles prepared by the solid-state method.

(Y,Gd)BO_3:Eu phosphor particles by the pilot-scale spray pyrolysis and the solid-state reaction technique. The dense and spherical (Y,Gd)BO_3:Eu particles prepared by spray pyrolysis with urea showed 106% photoluminescence intensity in comparison with the irregularly -shaped particles prepared by the solid-state reaction technique, whose SEM image was showed in Fig. 9. From the above results, it was proved that the dense and spherical (Y,Gd)BO_3:Eu phosphor particles with an improved photoluminescence intensity could be prepared by adding certain amount of urea in a pilot-scale spray pyrolysis process.

4. Conclusions

Dense and spherical (Y,Gd)BO_3:Eu red phosphor particles were successfully prepared by pilot-scale spray pyrolysis. The as-prepared particles had the enhanced mechanical characteristic compared to those prepared by the solid-state technique. The results are summarized as follows.

The optimal heat-treatment temperature was found to be 1200 °C. The optimal stoichiometric composition of boric acid was 120%. In a pilot-scale spray pyrolysis process, the morphology of particles largely dependened on the ratio of metal ions to urea. The dense and perfect spherical particles were obtained when the ratio of metal ions to urea was 1:10.

It was found that the dense and spherical (Y,Gd)BO_3:Eu phosphor particles prepared by spray pyrolysis with urea have higher photoluminescence intensity than the photoluminescence intensity of the irregularly-shaped ones prepared by the solid-state reaction technique. The emission of phosphors are dependent on the activator contents in the host matrix. The optimal concentration of activator (Eu) ions is 10 mol%.

Therefore, the prepared spherical (Y,Gd)BO_3:Eu phosphor particles in the pilot-scale spray pyrolysis using the spray solution developed in this work can be successfully used as a red phosphor for PDPs.

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