Synthesis of spherical phosphors $(Y,Gd)BO_3$:Eu from Precursors in Polymeric Form by Aerosol Pyrolysis

*Byung Woo Jeoung, Won Tae Yoo, Gun Young Hong, and Jae Soo Yoo**
Department of Chemical Engineering, Chung-Ang University
Huksuk-Dong 221, Dongjak Gu,Seoul 156-756, Korea
Tel:+82-2-820-5274, Fax:+82-824-3495, e-mail:95mailman@hanmail.net

Abstract

The phosphors of high luminous efficiency for PDP application must have high purity, single phase, and dense surface. In this work, the polymeric reaction was applied to preparation of spherical phosphor by aerosol pyrolysis in order to enhance mechanical and optical characteristics. The red phosphor of $(Y,Gd)BO_3$:Eu was prepared from polymeric precursor, in which citric acid and ethylene glycol were used as ion carriers, i.e monomers. For enhancing the luminescence intensity and mechanical characteristics, optimum synthesizing condition were investigated through concentration of monomers, synthetic temperature, doped activator concentrations, and annealing process. The phosphors synthesized with monomers showed quite different morphology from those without monomers. It was observed that polymeric precursor made an effect on particle formation mechanism and status of particles surface. The resultant spherical phosphors show the comparable luminescent properties to the commercial product (product by Nichia co.). Also, they were observed to have the rigid surface.

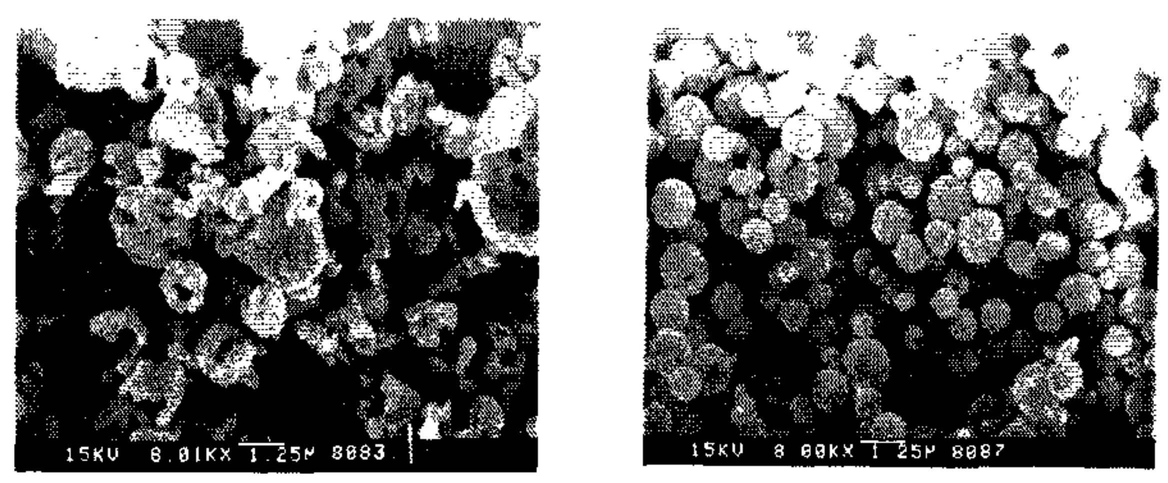
1. Introduction

Among several novel methods to prepare phosphor particles, some have tried to prepare the spherical phosphor by using the aerosol pyrolysis method [1]. As-prepared particles synthesized by aerosol pyrolysis must be annealed to form well-crystallized particles. It is generally known that annealing process causes chemical reaction and crystallization of particles. The monomers are often added to the phosphor for condensation of the particles [2,3].

In this work, we applied the precursor of polymeric form to prepare of $(Y,Gd)BO_3$:Eu phosphors using aerosol pyrolysis. The influences of monomers on properties of particles were investigated to enhance mechanical and optical properties.

2. Experimental

The red phosphor of $(Y,Gd)BO_3$:Eu by aerosol pyrolysis were prepared from polymeric precursor. Here, the citric acid and ethylene glycol were used as ion carriers. The experimental setup was reported elsewhere [4]. The starting materials for precursor solution were $Y(NO_3)_3\ 6H_2O$ (Aldrich,99.9%) and $Eu(NO_3)_3\ 6H_2O$ (Aldrich,99.9%) and $Gd(NO_3)_3\ 6H_2O$ and HBO_3 and citric acid and ethylene glycol. The citric acid and ethylene glycol were added for polymeric reaction. These were dissolved in distilled water. At general formula $(Y_{1-x-y}, Gd_y)BO_3:Eu^{3+}_x$, value of x varied from 0.01 to 0.15 as y is 0.31 and that of y varied from 0.1 to 0.5 as x is 0.05. The ratio of metal and citric acid was changed from 1:0.3 to 1:5 and that of citric acid and ethylene glycol was set to 1:3



(a) without monomers (b) with monomers

Figure 1. The morphology of phosphor according to synthetic routes {(a). without monomers, (b). with monomers}

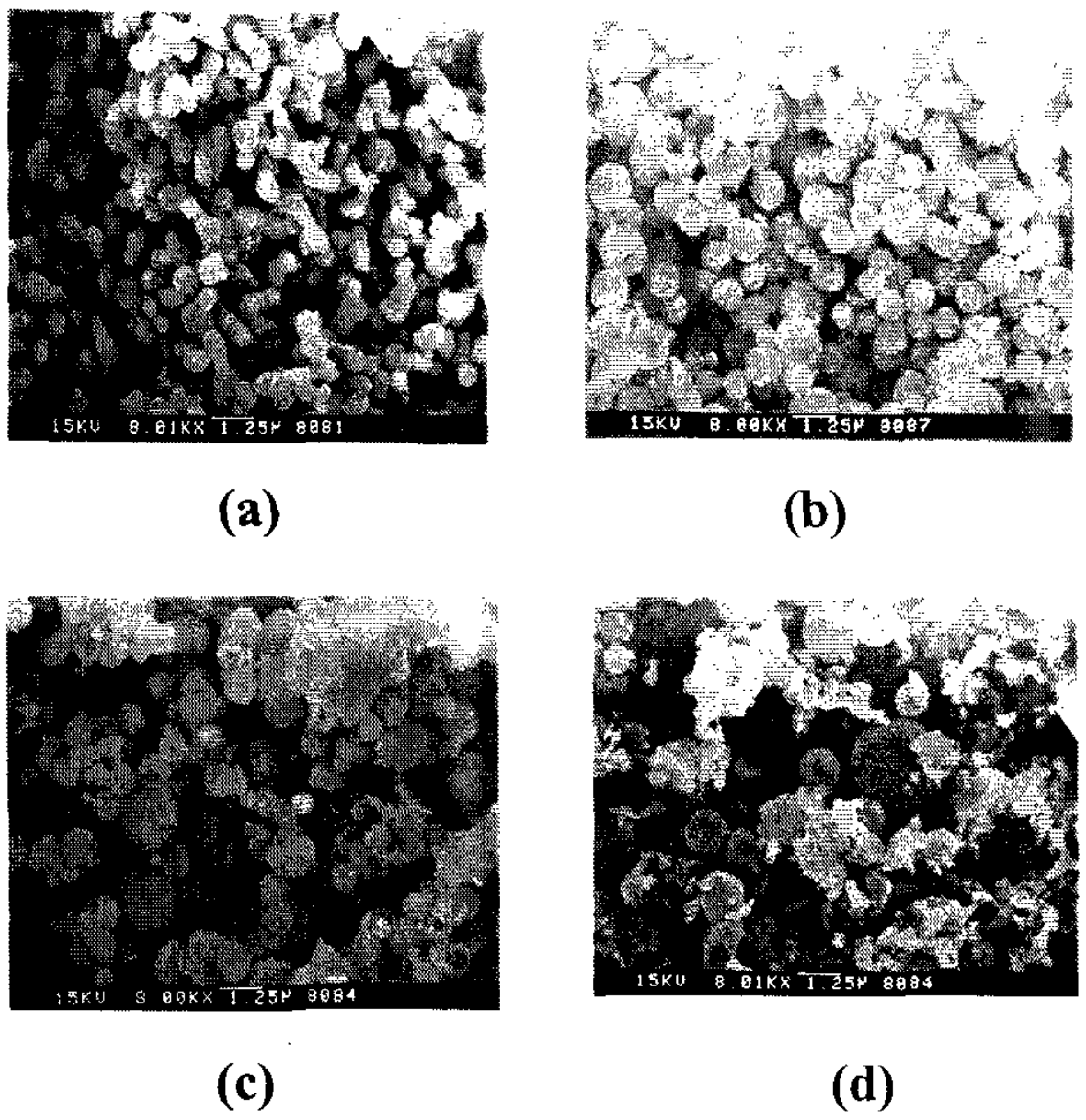


Figure 2. The morphology of $(Y,Gd)BO_3:Eu$ phosphor as a function of the ratio of monomers {metal : citric acid (a) 1 : 5, (b) 1 : 3, (c) 1:1, (d) 1 : 0.3 }

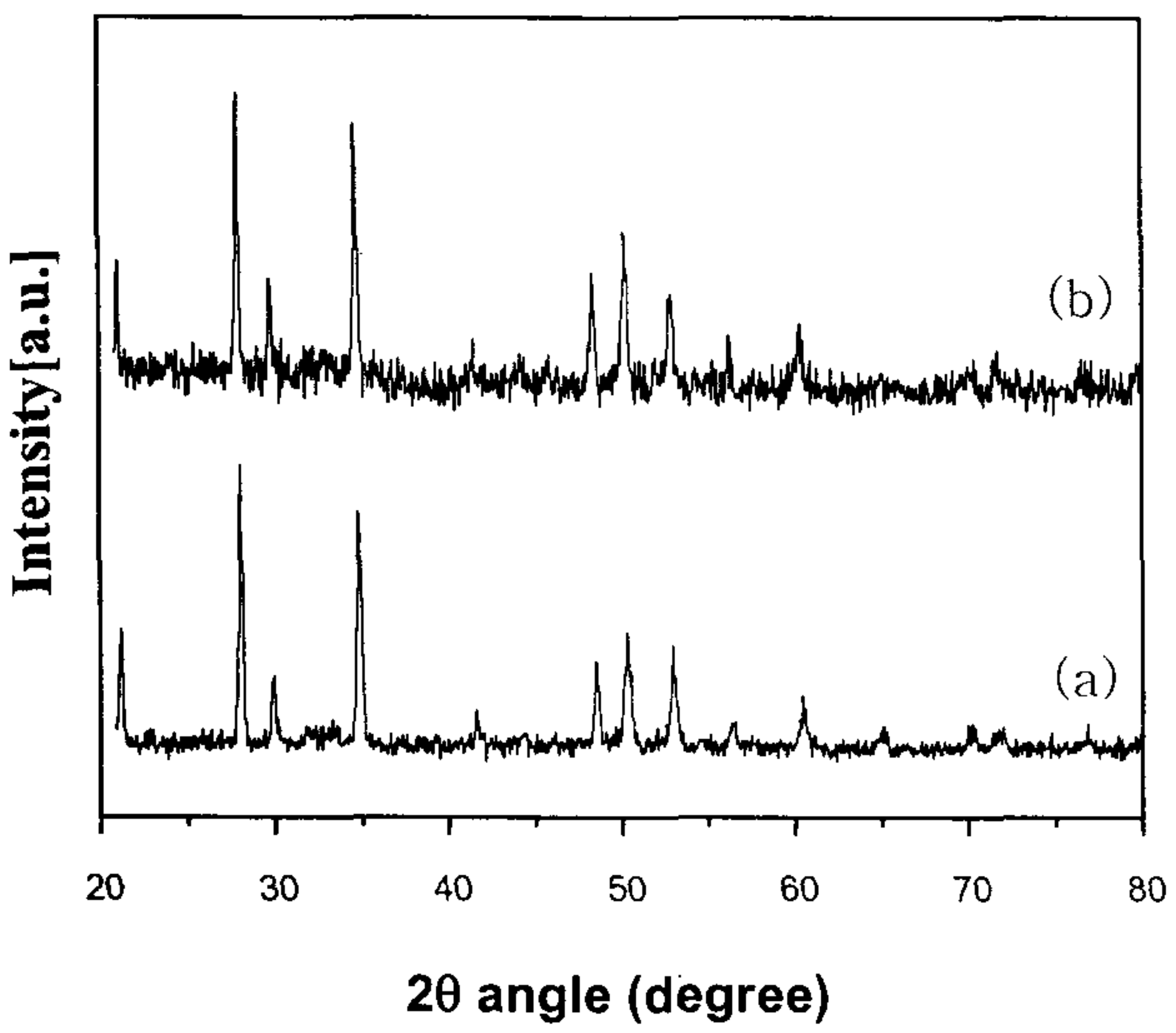


Figure 3. XRD spectra of particles heat-treated at 1050℃ for 3hr as the ratio of adding monomers {metal : citric acid (a) No monomers, (b) 1 : 3 }

The prepared precursor solution with monomers was generated to aerosol by ultrasonic transducer with 1.67 MHz wavelength and then the aerosols were transported to the first furnace reactor keeping on 106℃ by carrier gas, which flow rate was 0.8ℓ/min.. The temperature of second furnace reactor was 800℃ for decomposition of aerosols. The particles decomposed in the reactor were collected by filter paper at the end of second furnace and the as-collected particles were annealed at 1050℃ for 3 hr. The particles were characterized by scanning electron microscopy (Philips co.-515) for morphology of particles and X-ray diffractometry (Scintag, SDS 2000) for crystallinity.

3. Results and Discussion

Figure 1 shows SEM images of the phosphor particles prepared with monomers and without them. It is observed that the particles have different morphologies and the particles prepared with monomers were denser and less cracked compared with those without monomers. In Figure 2, the morphology of particles, which varied with the ratio of monomers in the precursor solution are showed. This shows that the shape of particle is more spherical as the concentration of monomer increases. Especially, the particles prepared with 1:3 ratio of monomer had perfect spherical shape and clean surfaces. Figure 3(b) is XRD peak of phosphors prepared with 1:3 ratio of monomer. This was well in agreement with XRD pattern of phosphors prepared by aerosol pyrolysis in Figure 3(a). The peaks of spherical particles coincided to the XRD pattern in JCPDS card.

As shown in Figure 4, the prepared particles had red emission peaks of 593, 612 and 628nm under 237nm excitation.

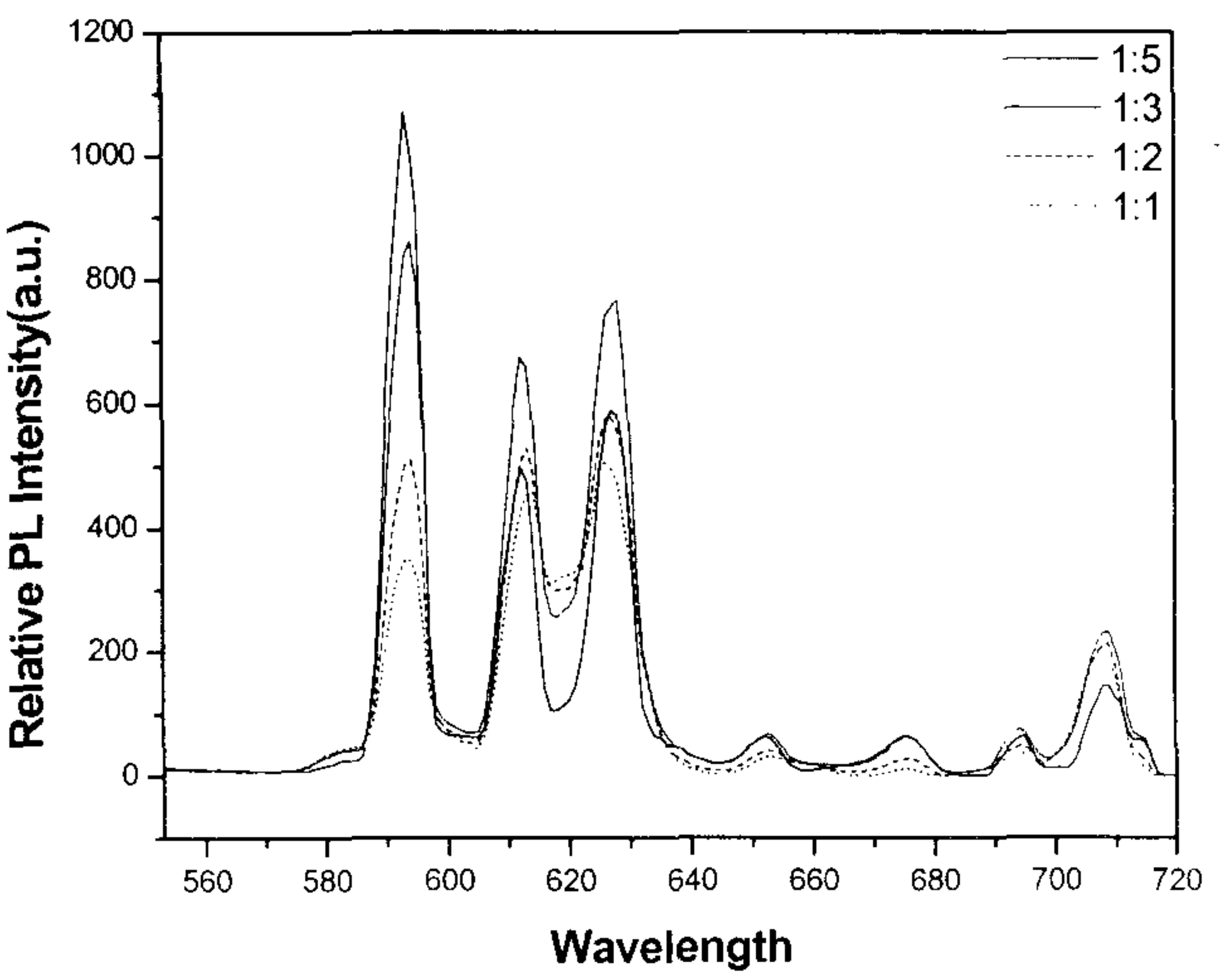


Figure 4. PL spectra of $(Y,Gd)BO_3:Eu$ phosphors as the ratio of monomers

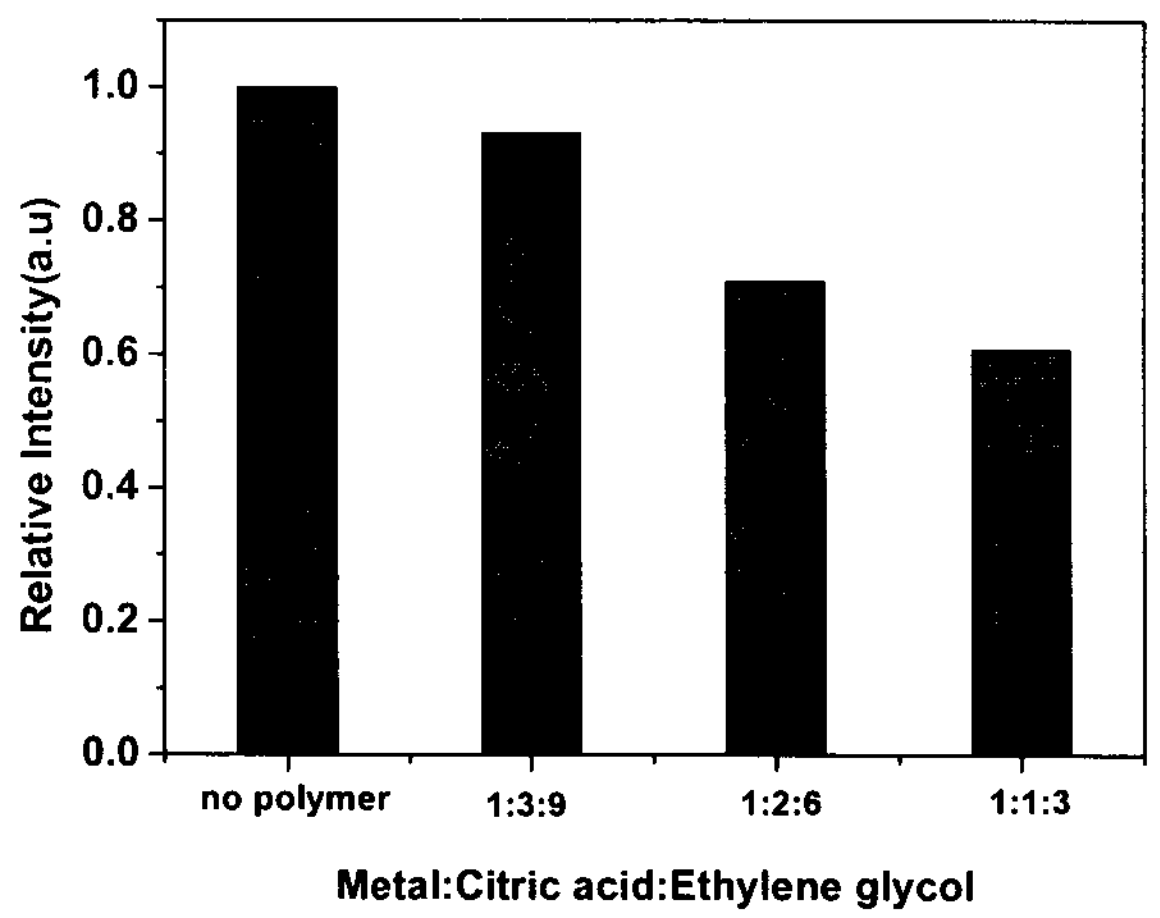


Figure 5 The change of relative intensity as the ratio of monomers

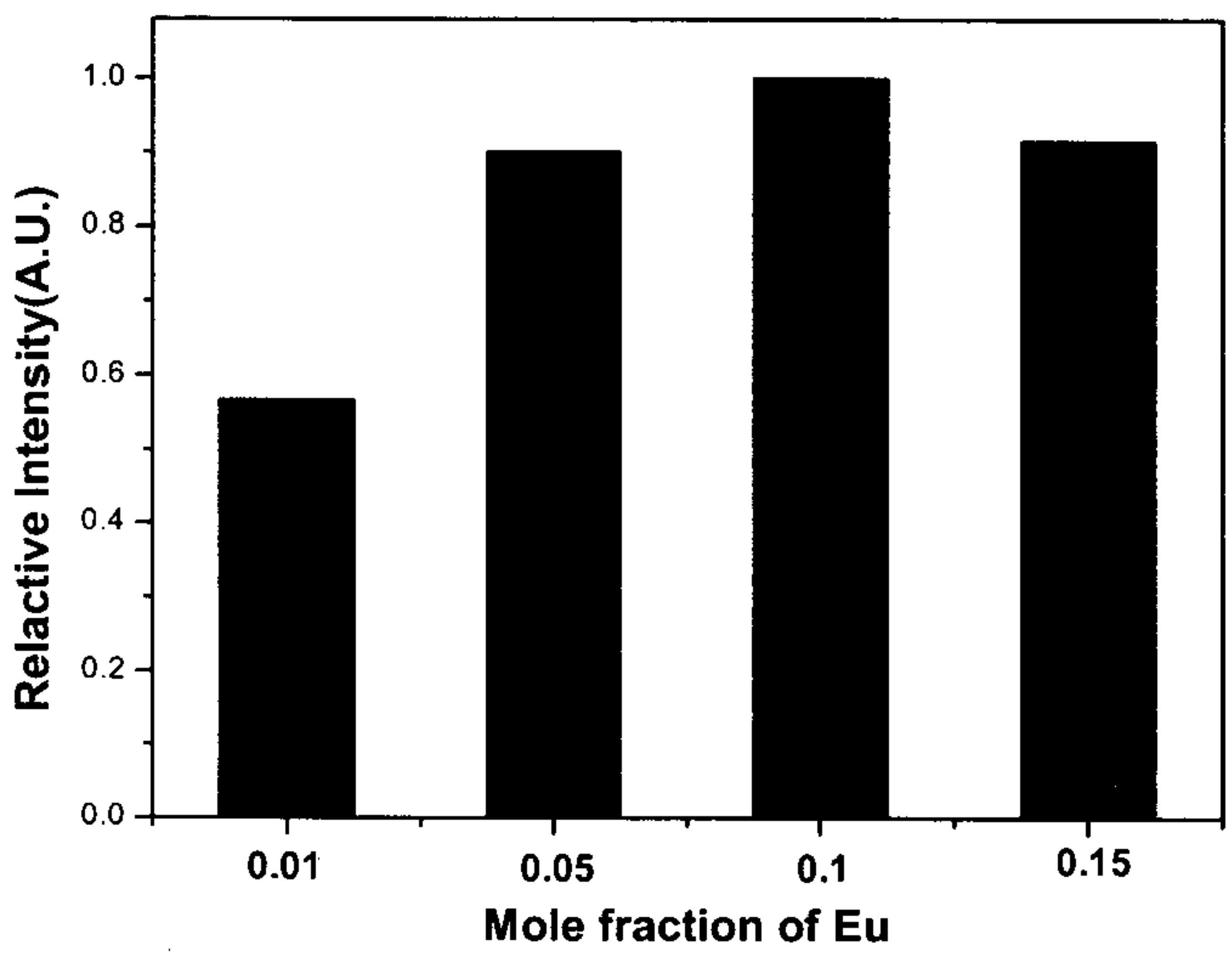
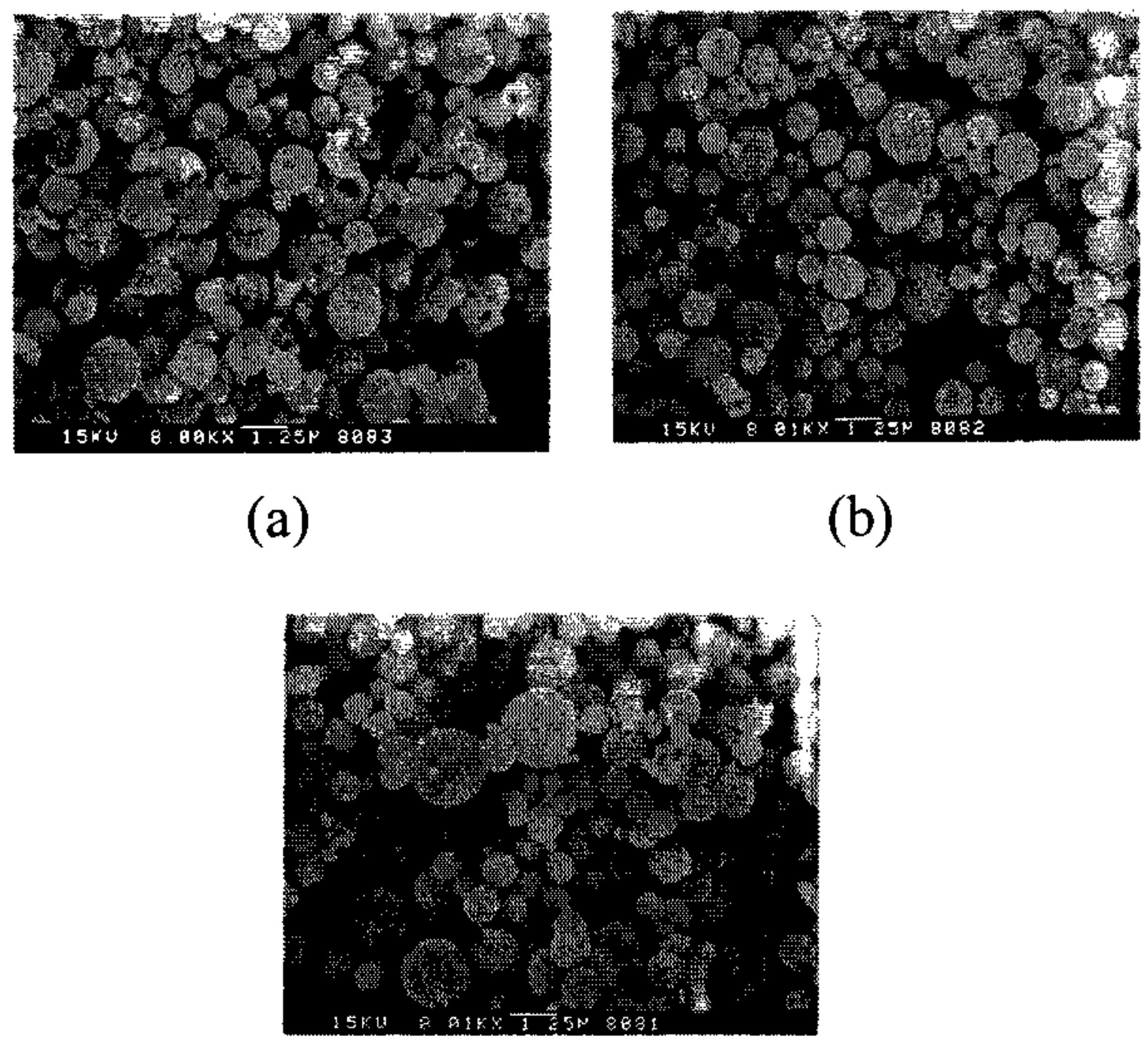


Figure 6. The change of relative intensity with Eu concentration

The intensity of emission was varied according to concentration ratios of citric acid. In the result, Main peak 593nm of $(Y,Gd)BO_3$:Eu tends to increase according to increasing concentration of monomer. Also, the other processes such as concentration of activator, synthetic temperature is expected to seriously affect the properties of $(Y,Gd)BO_3$:Eu phosphor. To optimize the contents of activator in phosphors and to examine the effect of synthetic conditions on luminescent characteristics, the concentration of activator was adjusted over the ratio of 1~15



(a) (b)

(c)

Figure 7. The morphology of $(Y,Gd)BO_3$:Eu the phosphor as the decomposition Temperature {temperature (a) 600℃ (b) 800℃ (c) 900℃}

mol% of the europium to yttrium in the precursor solution with overall concentrations of 0.6M. The synthetic temperature was 800℃ and the ratio of citric acid and ethylene glycol was set to 1:3 and as-synthesized particles were annealed at 1050℃ for 3hr. The relative PL intensities are shown as a function of europium concentration in Figure 6. The PL intensity increase with the concentration ratio of europium and then is maximal at 10 mol%. Above this ratio, the PL intensity decrease with the concentration of europium in the precursor. It is believed that this is due to the concentration quenching between excessive activator. The high thermal energy is needed for decomposition of the aerosols. The synthetic temperatures as source of high energy were varied from 600℃ to 900℃ with 0.8M of precursor solution and 5 mol% of europium and the ratio of citric acid and ethylene glycol was set to 1:3. Figure 7 shows the SEM micrographs of the particles prepared at different synthetic temperature under above process conditions. The particles obtained at 600℃ of synthetic temperature had some holes on the surface of particles. Especially, the particles prepared at 800℃ had perfect spherical shape and clean surfaces.

4. Summary

(Y,Gd)BO_3:Eu for PDP were prepared by using monomer as ion carriers and the morphology of those was investigated. By using monomers such as citric acid and ethylene glycol, the spherical particles with dense and less cracked surface could be obtained. It is expected that the (Y,Gd)BO_3:Eu phosphor with higher optical property and mechanical property might be used for PDP panel.

5. References

[1] Masato Kakihana, Toru Okubo, *J. alloys and compounds*, 266(**1998**) 129~133

[2] Masato Kakihana, Momoko Arima, Masahiro Yoshimura, *J. alloys and compounds*, 283(**1999**) 102~105

[3] Hong-Quan Xie, Jian-Guo Guan, Jun-Shi Guo, *European Polymer J*, 37(**2001**) 1997-2003

[4] G.Y Hong, S.H.Kwon, J.S. Yoo, "*phosphor conference*", pp.187-191(**1999**)

[5] M.P. Pechini, *US Pat. 3 330 697* (**1967**)

[6] J. D. Lee, J. S. Yoo, S. H. Cho, *US Pat 5 885 492* (**1999**)