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Fine size (Y,Gd)BO_3:Eu phosphor powders prepared from precursor powders with hollow shape and large size

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ABSTRACT

Fine size (Y,Gd)BO_3:Eu phosphor powders with high photoluminescence intensity under vacuum ultraviolet were prepared by spray pyrolysis. The precursor powders with hollow shape and large size were prepared by spray pyrolysis from the spray solution with citric acid. The precursor powders turned to the (Y,Gd)BO_3:Eu phosphor powders after post-treatment at temperatures between 900 and 1100 °C. The mean sizes of the phosphor powders post-treated at a temperature of 950 °C were 0.37 μm. The photoluminescence intensity of the fine size (Y,Gd)BO_3:Eu phosphor powders was 95% of that of the commercial (Y,Gd)BO_3:Eu phosphor powders with micron sizes.

1. Introduction

The mean size of phosphor powder greatly affects the performance of plasma display panels (PDPs). In the most cases, fine-sized phosphor powders with spherical shape are more effective to form a good phosphor layer within fine-pitch barrier ribs rather than large-sized one. In addition, in novel printing processes, such as those involving dispensing technology, phosphor powders containing fine-sized powders with narrow size distributions are very important for achieving good phosphor layers.

Eu-doped borate phosphor powders have been used as a red-emitting phosphor in PDPs because of its high photoluminescence efficiency under vacuum ultraviolet excitation [1–10]. (Y,Gd)BO_3:Eu phosphor powders are considered as a research target in many ceramic preparation processes. However, fine-sized (Y,Gd)BO_3:Eu phosphor powders could not be well prepared because of high sintering characteristics of borate material at low post-treatment temperature. In spray pyrolysis, which is one of the gas-phase reaction method, (Y,Gd)BO_3:Eu phosphor powders were also studied to improve their morphology and photoluminescence intensity under vacuum ultraviolet excitation [5–9]. The (Y,Gd)BO_3:Eu phosphor powders prepared by spray pyrolysis had micron sizes even at low post-treatment temperature of 1000 °C.

In this study, submicron size (Y,Gd)BO_3:Eu phosphor powders were prepared by spray pyrolysis. The precursor powders with hollow shape and large size were prepared by spray pyrolysis. The precursor powders turned to the (Y,Gd)BO_3:Eu phosphor powders with fine size and high brightness under vacuum ultraviolet excitation.

2. Experimental

The phosphor powders with composition of $(Y_{0.65},Gd_{0.35})_{0.95}BO_3{:}Eu_{0.05}$ were prepared by post-treatment of the precursor powders obtained by spray pyrolysis. Citric acid (CA) was used as the organic additive to prepare the precursor powders with hollow shape and thin wall structure. The preparation equipment consisted of a droplet generator, a quartz reactor, and a powder collector. An ultrasonic aerosol generator with six resonators was used for the mass production of droplets that were carried into the high-temperature tubular reactor by a carrier gas. The length and diameter of the quartz reactor were 1200 and 50 mm, respectively. The temperature of the reactor was fixed at 1000 °C. To prepare the spray solution, $Y(NO_3)_3{\cdot}6H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$, Eu_2O_3, and H_3BO_3 were dissolved in distilled water with the addition of a small amount of nitric acid. The total concentration of the spray solution was 0.1 M. The concentration of boric acid was fixed at 145 mol% of the stoichiometric amount. The concentrations of CA were changed from 0.2 to 1.5 M. The precursor powders obtained by spray pyrolysis were post-treated at temperatures between 850 and 1100 °C.

The crystal structures of the prepared phosphor powders were analyzed by X-ray diffractometry (XRD; RIGAKU, DMAX-33). The morphological characteristics of the powders were analyzed by scanning electron microscopy (SEM; JEOL, JSM 6060). The photoluminescence characteristics of the phosphor powders were measured under excitation using 147 nm vacuum ultraviolet (VUV) evolved from a D_2 lamp.

3. Results and discussions

Fig. 1 shows the SEM images of the precursor and (Y,Gd)BO_3:Eu phosphor powders prepared by spray pyrolysis from the spray solution without CA. The precursor powders prepared by spray pyrolysis at a low flow rate of carrier gas as 10 L min^{-1} had spherical shape and hollow structure. The phosphor powders post-treated at

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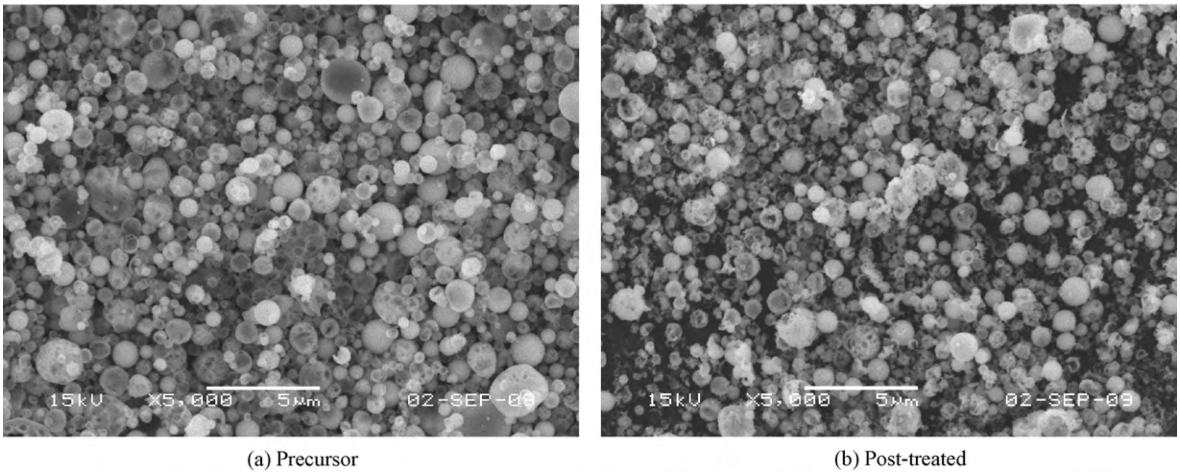
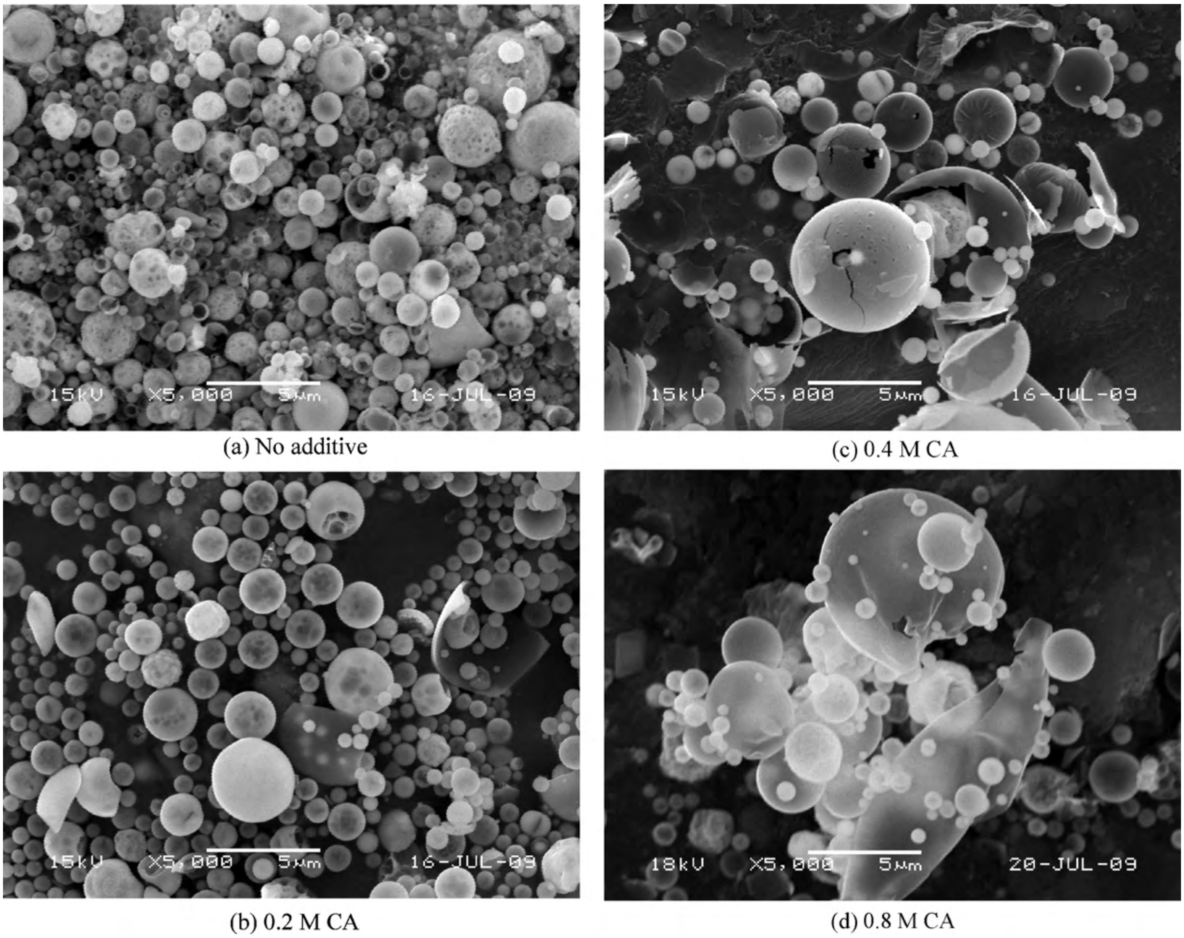


(a) Precursor (b) Post-treated

Fig. 1. SEM images of the precursor and phosphor powders prepared by spray pyrolysis at the low flow rate of the carrier gas as 10 L min^{-1}.

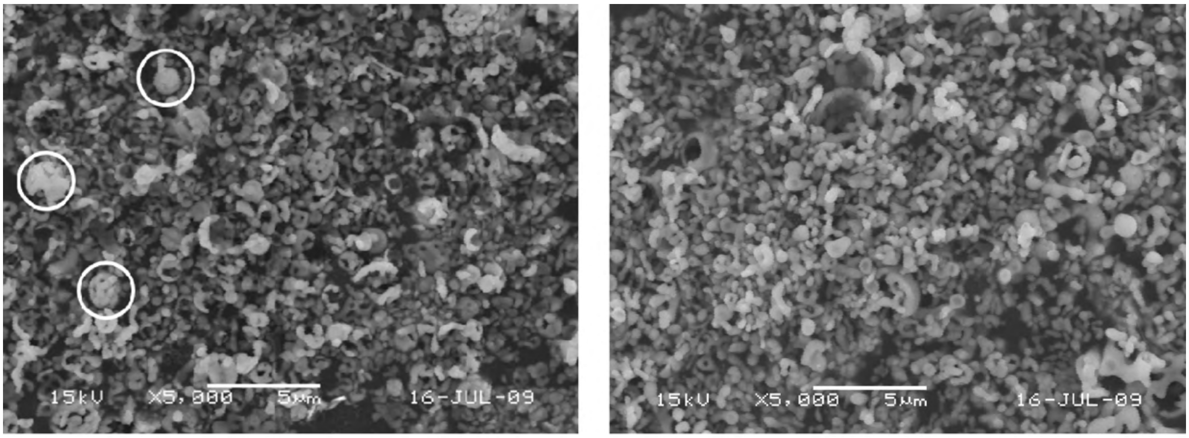
950 °C had spherical shape and micron sizes. One phosphor particle was formed from one droplet.

Fig. 2 shows the precursor powders prepared from the spray solutions with and without CA. The flow rate of air used as the carrier gas was 30 L min^{-1}, and the residence time of the powders inside the reactor was 0.6 s. The precursor powders prepared from the spray solution without CA had hollow structure because of high drying and decomposition rates of the droplets. Addition of CA to the spray solution improved the hollowness of the precursor powders. The morphologies of the powders prepared by spray pyrolysis were affected by the precursor materials used as the source materials of metal components because of different drying and decomposition properties. In the spray pyrolysis, the hollowness of the powders was affected by the gas penetration properties of the dried or decomposed powders. CA is widely used as the chelating agent in the liquid solution methods. In this study, the powders formed from the metal chelates of CA had low gas penetration properties. Additionally, a large amount of gas was evolved

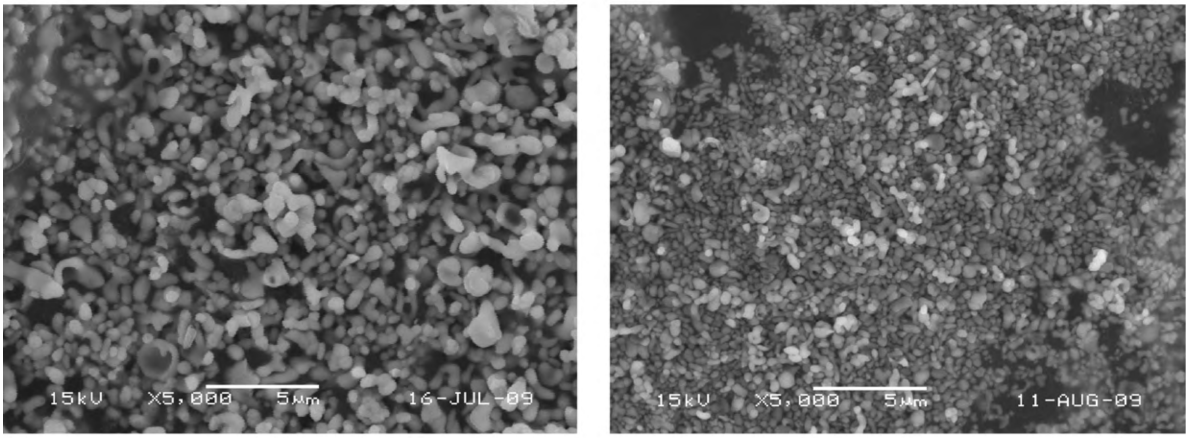


(a) No additive (c) 0.4 M CA (b) 0.2 M CA (d) 0.8 M CA

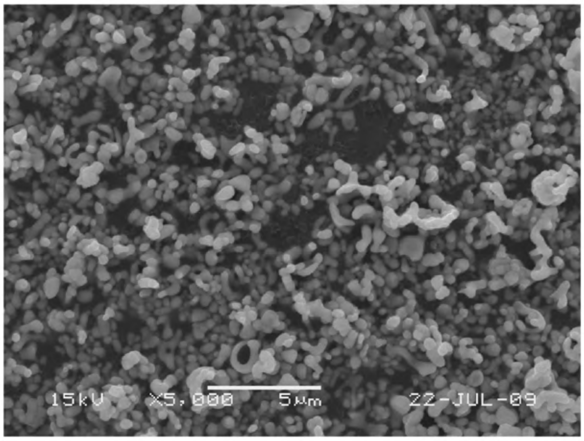
Fig. 2. SEM images of the precursor powders formed from the spray solutions with various concentrations of CA.



(a) No additive (c) 0.4 M CA



(b) 0.2 M CA (d) 0.8 M CA



(e) 1.0 M CA

Fig. 3. SEM images of the (Y,Gd)BO_3:Eu phosphor powders formed from the spray solutions with various concentrations of CA at a post-treatment temperature of 950 °C.

from the decomposition of CA used as the chelating agent. Therefore, the precursor powders prepared from the spray solutions with CA had larger sizes than that of the precursor powders prepared from the spray solution without CA. Gas evolution by decomposition of CA produced the precursor powders with hollow shape and thin wall structure. The hollowness of the precursor powders increased with increasing the concentration of CA.

Fig. 3 shows the SEM images of the (Y,Gd)BO_3:Eu phosphor powders. The precursor powders prepared from the spray solutions with various concentration of CA were post-treated at 950 °C. The phosphor powders had submicron sizes irrespective of the concentrations of CA dissolved to the spray solutions. The spherical shape of the precursor powders disappeared after post-treatment. The precursor powders with several micron sizes turned to the submicron sizes after post-treatment without milling process. The mean sizes and morphologies of the phosphor powders were affected by the concentration of CA. The phosphor powders prepared from the spray solution without CA had aggregated structure of the primary powders. Some of the powders had maintained the spherical-like shape of the precursor powders as shown by circles in Fig. 3(a).

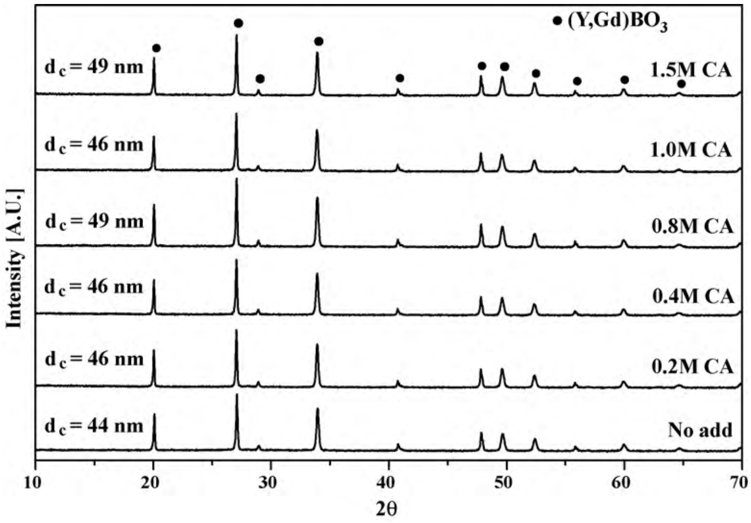


Fig. 4. XRD patterns of the $(Y,Gd)BO_3$:Eu phosphor powders formed from the spray solutions with various concentrations of CA at a post-treatment temperature of 950 °C.

The sphericity of the phosphor powders increased with increasing the concentration of CA dissolved to the spray solution. The phosphor powders prepared from the spray solution with 0.8 M had fine size, spherical-like shape and non-aggregation characteristics. The mean size of the phosphor powders as shown in Fig. 3(d) was 0.37 μm. The hollow shape and thin wall structure of the precursor powders decreased the mean size of the phosphor powders post-treated at 950 °C. The XRD patterns of the phosphor powders prepared from the spray solutions with various concentrations of CA are shown in Fig. 4. The phosphor powders had pure crystal structure of $(Y,Gd)BO_3$ phosphor irrespective of the concentrations of CA dissolved to the spray solutions. The mean crystallite sizes of the phosphor powders calculated by Scherrer's equation were slightly changed from 44 to 49 nm.

Fig. 5 shows the excitation spectra of the phosphor powders prepared from the spray solutions with various concentrations of CA. The excitation spectra closely resemble those of the commercial $(Y,Gd)BO_3$:Eu phosphor powders [11,12]. Two bands banding at 160 and 228 nm were observed.

The emission spectra of the phosphor powders prepared from the spray solutions with various concentrations of CA are shown in Fig. 6. The phosphor powders prepared from the spray solutions with CA had higher photoluminescence intensities than that of the phosphor powders prepared from the spray solution without CA. The maximum photoluminescence intensity prepared from the spray solution with 1 M CA was 149% of that of the phosphor powders prepared from the spray solution without CA. The phosphor powders had similar crystal structures irrespective of the concentration of CA dissolved to the spray solutions. CA is commonly used as the chelating agent in the preparation of multicomponent ceramic powders [13,14]. CA improved the photoluminescence intensities of the phosphor powders by acting as the chelating agent.

The precursor powders prepared from the spray solution with CA of 0.8 M were post-treated at temperatures between 850 and 1100 °C. The morphologies of the phosphor powders are shown in Fig. 7. Some of the phosphor powders maintained the spherical shape of the precursor powders at post-treatment temperatures below 900 °C. On the other hand, the spherical shape of the precursor powders disappeared at post-temperatures above 950 °C in Figs. 3 and 7. The mean sizes of the phosphor powders increased with increasing the post-treatment temperatures. The mean size of the phosphor powders post-treated at 1100 °C was 0.82 μm. Fig. 8 shows the XRD patterns of the phosphor powders post-treated at various temperatures. The phosphor powders had pure crystal

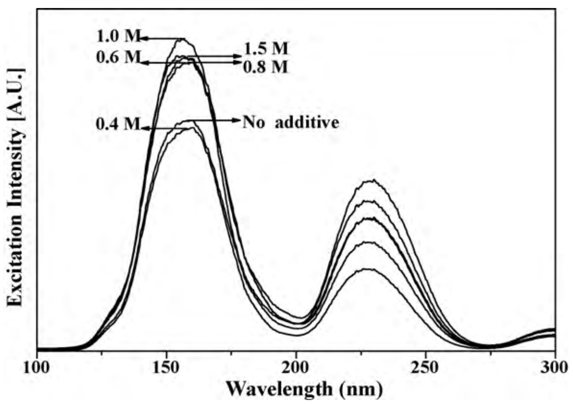


Fig. 5. Excitation spectra of the $(Y,Gd)BO_3$:Eu phosphor powders formed from the spray solutions with various concentrations of CA at a post-treatment temperature of 950 °C.

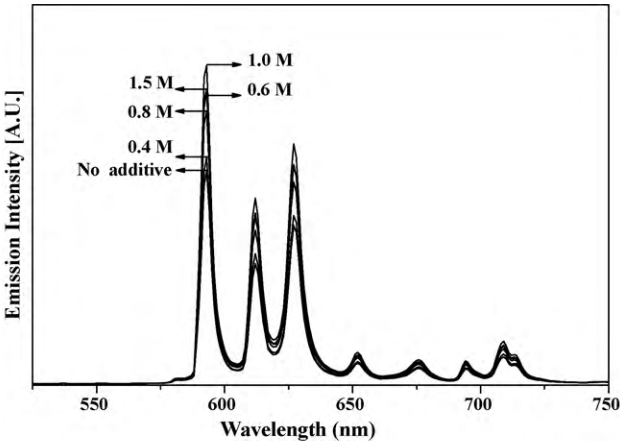
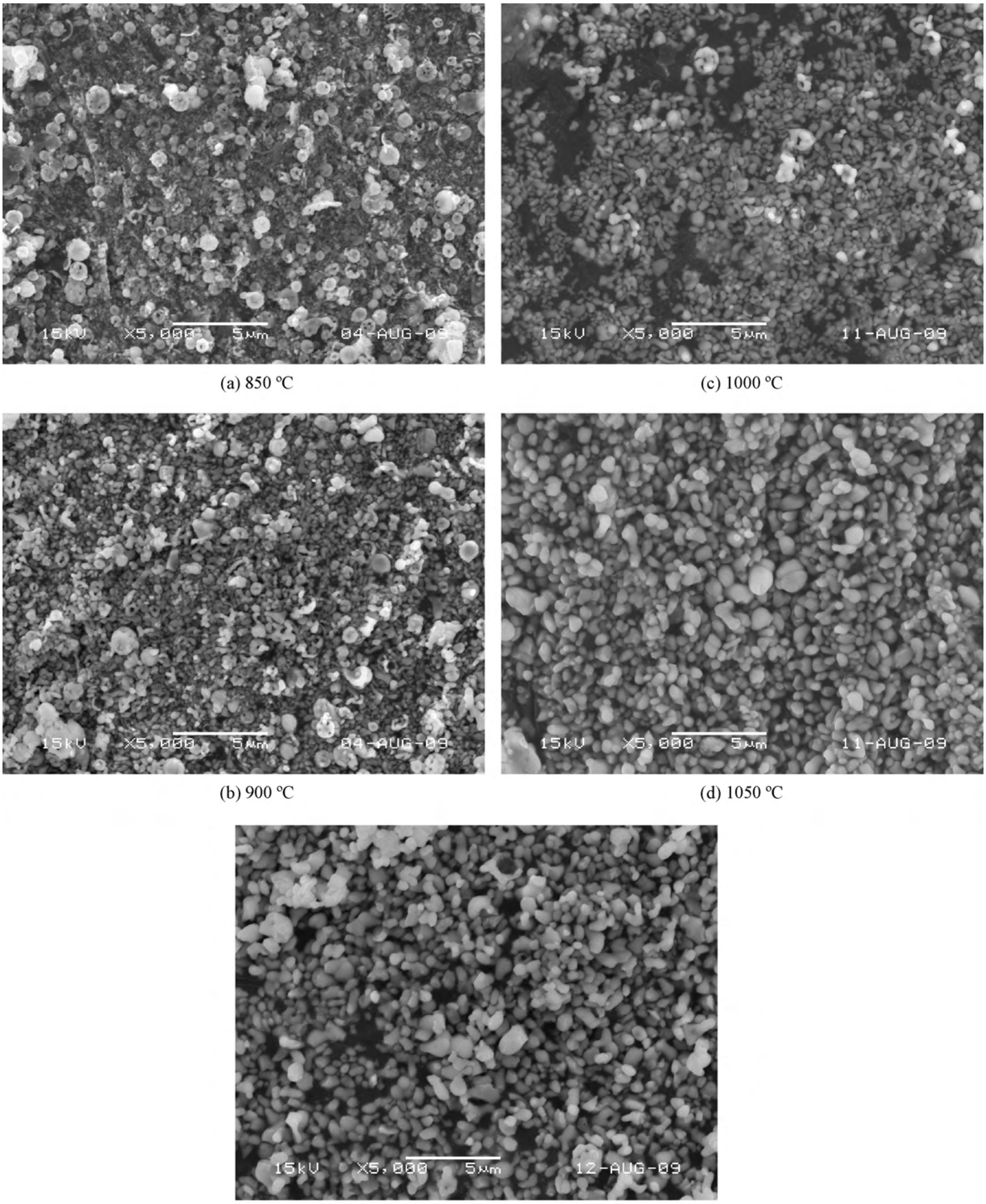


Fig. 6. Emission spectra of the $(Y,Gd)BO_3$:Eu phosphor powders formed from the spray solutions with various concentrations of CA at a post-treatment temperature of 950 °C.



(a) 850 ºC

(c) 1000 ºC

(b) 900 ºC

(d) 1050 ºC

(e) 1100 ºC

Fig. 7. SEM images of the (Y,Gd)BO_3:Eu phosphor powders post-treated at various temperatures.

structure of (Y,Gd)BO_3 phosphor irrespective of the post-treatment temperatures. On the other hand, the mean crystallite sizes of the phosphor powders were changed from 35 to 46 nm according to the post-treatment temperatures. The photoluminescence intensities of the phosphor powders post-treated at various temperatures were measured under vacuum ultraviolet. The phosphor powders post-treated at 850 °C had low photoluminescence intensity because of small mean crystallite size. However, the phosphor powders post-treated at temperatures between 900 and 1100 °C had similar photoluminescence intensities. The maximum photoluminescence intensity of the prepared phosphor powders was 95% of that of the commercial (Y,Gd)BO_3:Eu phosphor powders. The mean size of the commercial phosphor powders prepared by solid state reaction method was 1.2 μm. The fine-sized phosphor powders prepared by conventional solid state reaction method had lower photoluminescence intensities than those with several micron sizes. However, the (Y,Gd)BO_3:Eu phosphor powders prepared by spray pyrolysis from the spray solution with CA had fine size and high photoluminescence intensity under vacuum ultraviolet.

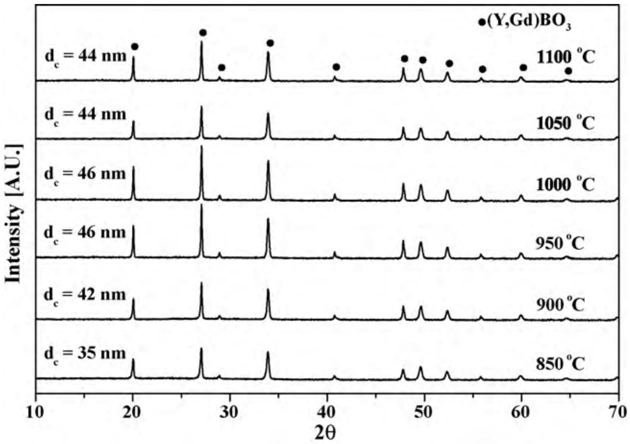


Fig. 8. XRD patterns of the (Y,Gd)BO_3:Eu phosphor powders post-treated at various temperatures.

4. Conclusions

Citric acid was used as organic additive in the preparation of (Y,Gd)BO_3:Eu phosphor powders with fine size by spray pyrolysis. Citric acid enabled the preparation of fine size phosphor powders by forming the precursor powders with hollow shape and thin wall structure. The fine size (Y,Gd)BO_3:Eu phosphor powders had similar photoluminescence intensity to that of the commercial product with several micron sizes.

Acknowledgements

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