

Nano-sized Y_2O_3 : Eu phosphor powders prepared by spray pyrolysis from spray solution with ethylenediaminetetraacetic acid, citric acid and boric acid

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Nano-sized Y_2O_3 : Eu phosphor powders were prepared by spray pyrolysis. The precursor powders with a hollow morphology and thin walled structure were obtained from the spray solution with ethylenediaminetetraacetic acid, citric acid and boric acid turned into the Y_2O_3 : Eu phosphor powders with mean sizes of 140 and 450 nm at high post-treatment temperatures of 1050 and 1150 °C. The optimum concentrations of ethylenediaminetetraacetic acid and citric acid to prepare the nano-sized Y_2O_3 : Eu phosphor powders were each 0.1 M. The Y_2O_3 : Eu phosphor powders had regular morphologies and narrow size distributions. The mean crystallite sizes of the phosphor powders post-treated at temperatures of 1050 and 1150 °C were 40 and 44 nm. The phosphor powder post-treated at a temperature of 1050 °C had the highest photoluminescence intensity under vacuum ultraviolet illumination.

Key words: spray pyrolysis, phosphor, nano powder, display material

Introduction

Nano-sized oxide phosphor with a high brightness would enable the production of high-performance solid light-emitting devices and flat-panel devices [1]. In addition, in novel printing processes, such as those involving ink-jet technology, phosphor powders containing nano-sized spherical powders with a narrow size distributions are very important for achieving good luminescent characteristics.

Fine size oxide phosphor powder could be produced by mechanical grinding of aggregate powders formed at high post-treatment temperatures. However, generally, mechanical grinding significantly lowers the luminance of phosphor. Therefore, the establishment of a production process without mechanical grinding is necessary for the production of nano-sized oxide phosphor powder.

Liquid solution methods have been widely applied to the preparation of nano-sized phosphor powders [2-5]. Nano-sized phosphor powders with a high crystallinity and low surface defect concentration have a high brightness under ultraviolet and vacuum ultraviolet illumination. Therefore, nano-sized phosphor powders should be obtained at a high post-treatment temperature. The high post-treatment temperature causes grain growth of the phosphor powder. Therefore, a mechanical milling process should be applied to obtain nano-sized phosphor powders using liquid solution methods.

Precursor powders with a loose structure will produce

the nano-sized phosphor powders at high post-treatment temperatures without a hard milling process. In this study, precursor powders with a hollow and thin walled structure were prepared by spray pyrolysis to obtain nano-sized Y_2O_3 : Eu phosphor powders at a high post-treatment temperature. Y_2O_3 : Eu phosphor powders are used as a red-emitting phosphor in flat-panel displays and fluorescent lamps [6-9]. Spray pyrolysis has also been applied to prepare Y_2O_3 : Eu phosphor powders with a fine size and spherical morphology [10-16]. However, nano-sized Y_2O_3 : Eu phosphor powders produced by spray pyrolysis have not been extensively well studied.

Experimental Procedure

The precursor powders with a hollow and thin walled structure were prepared by ultrasonic spray pyrolysis. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate a large quantity of droplets. The flow rate of air used as carrier gas was 50 Lminute⁻¹. The reactor temperature was maintained at 900 °C. The spray solutions were prepared by mixing yttrium nitrate, europium nitrate, citric acid (CA), ethylenediaminetetraacetic acid (EDTA) and boric acid (H_3BO_3) flux. The total concentration of the metal components was 0.1 M. The content of the boric acid flux was 1 wt% of the Y_2O_3 : Eu phosphor powders. The precursor powders prepared by spray pyrolysis were post-treated at temperatures between 950 and 1250 °C for 3 h in a muffle furnace.

The crystal structures of the powders prepared were analyzed by X-ray diffraction (XRD) using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology of the powders was investigated by scanning electron microscopy (SEM).

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The luminescence characteristics of the powders prepared under vacuum ultraviolet (VUV) illumination were measured using a D_2 lamp.

Results and Discussions

The morphologies of the precursor powders prepared by spray pyrolysis from the spray solutions with and without organic additives are shown in Fig. 1. The precursor powders prepared from the spray solution without an organic additive had a hollow and porous structure because of the high drying and decomposition rate of the droplet and powder. In this study, the residence time of the powders inside the hot wall reactor was as short as 0.5 s because of the high flow rate of the carrier gas. EDTA plus CA as organic additives were dissolved in the spray solution to improve the hollowness of the precursor powders. The addition of EDTA to the spray solution improved the hollowness of the precursor powders. The optimum concentration of EDTA to prepare precursor powders with a hollow structure was 0.1 M. The addition of CA to the EDTA solution also improved the hollowness of the precursor powders. Therefore, the precursor powders prepared from the spray solution with EDTA plus CA had a hollow and thin walled structure.

Fig. 2 shows the SEM images of the $Y_2O_3 : Eu$ phosphor powders obtained from the spray solutions with and without organic additives at a post-treatment temperature of 1150 °C. The phosphor powders prepared from the spray solution without an organic additive maintained the spherical morphology of the precursor powders after post-treatment. On the other hand, the spherical morphologies of the precursor powders prepared from the spray solution with organic additives disappeared after post-treatment. The phosphor powders had submicrometre sizes and loosely aggregated structures even at a high post-treatment temperature of 1150 °C.

Fig. 3 shows the XRD patterns of the $Y_2O_3 : Eu$ phosphor

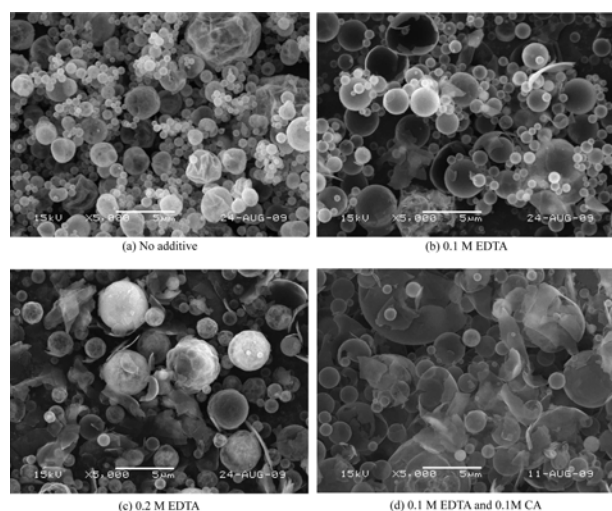


Fig. 1. SEM images of the precursor powders prepared from the spray solutions with and without organic additives.

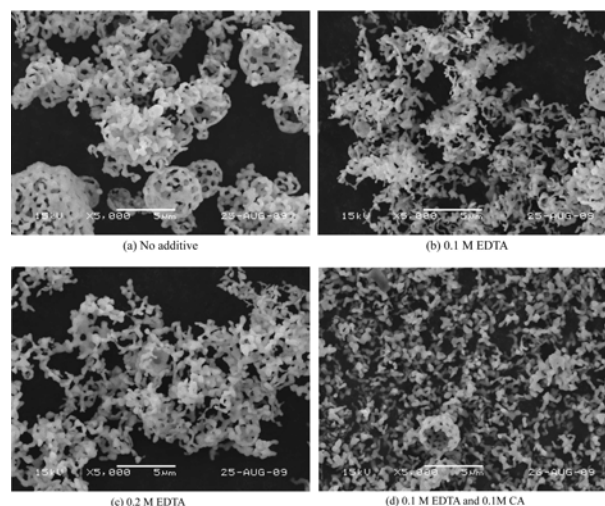


Fig. 2. SEM images of the $Y_2O_3 : Eu$ phosphor powders post-treated at 1150 °C.

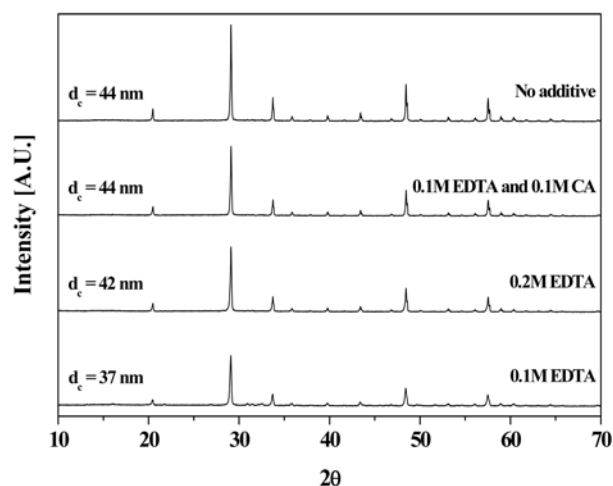


Fig. 3. XRD patterns of the $Y_2O_3 : Eu$ phosphor powders post-treated at 1150 °C.

powders obtained from the spray solutions with and without organic additives at a post-treatment temperature of 1150 °C. The phosphor powders had cubic crystal structures irrespective of the types of spray solution. The mean crystallite size of the phosphor powders was calculated using Scherrer's equation. The mean crystallite sizes of the phosphor powders prepared from the spray solutions without organic additives and with EDTA plus CA were each 44 nm. On the other hand, the mean crystallite size of the phosphor powders prepared from the spray solution with 0.1 M EDTA was 37 nm.

Fig. 4 shows the emission spectra of the $Y_2O_3 : Eu$ phosphor powders obtained from the spray solutions with and without organic additives at a post-treatment temperature of 1150 °C. The phosphor powders prepared from the spray solution with EDTA plus CA had the highest photoluminescence intensity under VUV illumination. The photoluminescence intensity of the phosphor powder obtained from the spray solution with EDTA plus CA was 146% of that

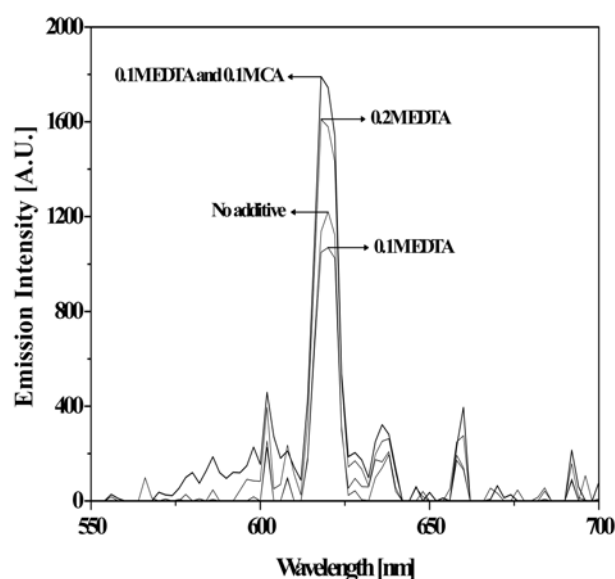


Fig. 4. Photoluminescence spectra of the $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor powders post-treated at 1150°C .

of the phosphor powders obtained from the spray solution without organic additives. On the other hand, the photoluminescence intensity of the phosphor powders obtained from the spray solution with 0.1 MEDTA had a low photoluminescence intensity because of the fine primary powder size and low mean crystallite size.

The precursor powders prepared from the spray solution with EDTA plus CA were post-treated at various temperatures. The concentrations of EDTA and CA dissolved to the spray solution were the same at 0.1 M. The post-treated powders were milled by hand using an agate mortar. Figs. 5 and 6 show the SEM images of the $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor powders before and after the milling process. The phosphor powders prepared at post-treatment temperatures of 950 and 1050°C had slightly aggregated structures of the primary nano-sized powders. However, the phosphor powders post-treated at a temperature of 1250°C had hardly aggregated structure of the micrometre-sized primary powders. The spherical shapes of the post-treated phosphor powders disappeared after the simple milling process as shown in Fig. 6. The mean size of the phosphor powders increased with an increase in the post-treatment temperature. The mean size of the phosphor powders post-treated at a temperature of 950°C was several tens of nanometres. Therefore, the microstructure of the nano-sized phosphor powders was not easy to observe in low resolution SEM images. The phosphor powders post-treated at temperatures of 1050 and 1150°C had regular morphologies and narrow size distributions. The mean sizes of the phosphor powders as shown in Fig. 6(b) and (c) were 140 and 450 nm. On the other hand, the phosphor powders post-treated at a temperature of 1250°C were several micrometres in size after the milling process.

Fig. 7 shows XRD patterns of the $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor powders post-treated at various temperatures. The phosphor

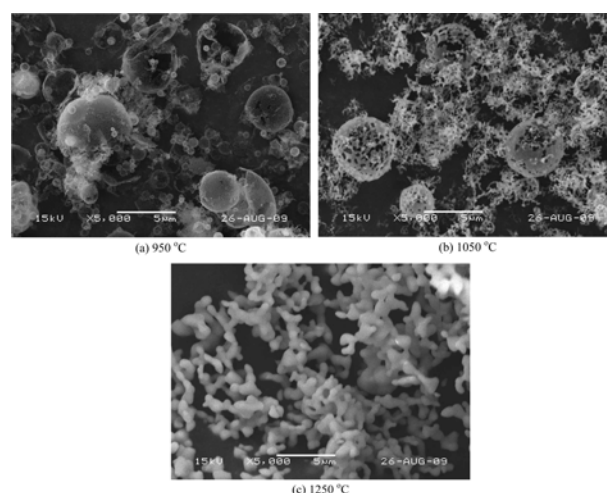


Fig. 5. SEM images of the $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor powders post-treated at various temperatures before milling.

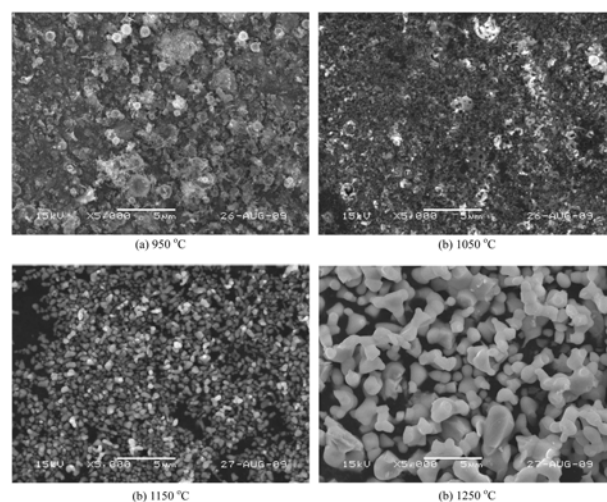


Fig. 6. SEM images of the $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor powders post-treated at various temperatures after milling.

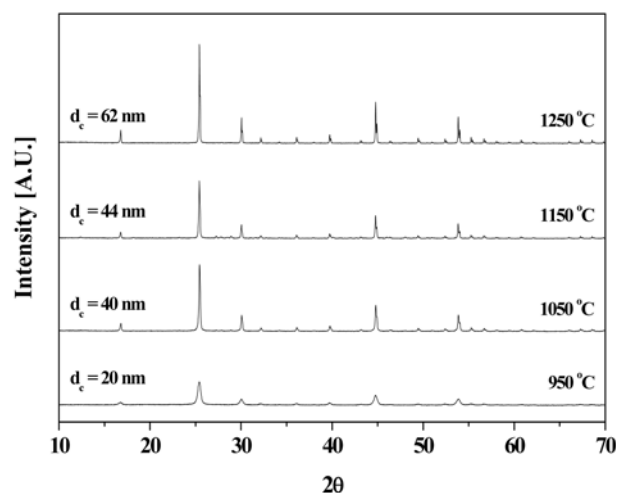


Fig. 7. XRD patterns of the $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor powders post-treated at various temperatures after milling.

powders had cubic crystal structures irrespective of the post-treatment temperatures. The mean crystallite sizes of

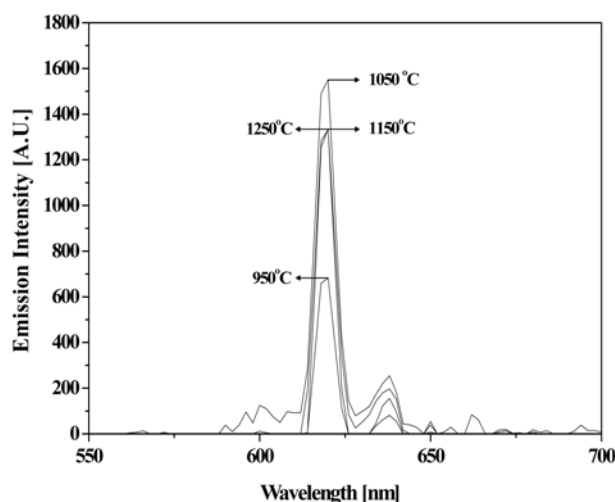


Fig. 8. Photoluminescence spectra of the $\text{Y}_2\text{O}_3 : \text{Eu}$ phosphor powders post-treated at various temperatures.

the phosphor powders post-treated at temperatures of 950, 1050 and 1250 °C were 20, 40 and 62 nm. The post-treatment temperature of 950 °C was too low for crystal growth of the $\text{Y}_2\text{O}_3 : \text{Eu}$ phosphor powders.

Fig. 8 shows the emission spectra of the $\text{Y}_2\text{O}_3 : \text{Eu}$ phosphor powders post-treated at various temperatures. The phosphor powders post-treated at a temperature of 1050 °C had the highest photoluminescence intensity under VUV illumination. The phosphor powders post-treated at a temperature of 950 °C had the lowest photoluminescence intensity because of the ultrafine size and low crystallite size.

Conclusions

Nano-sized $\text{Y}_2\text{O}_3 : \text{Eu}$ phosphor powders were prepared by spray pyrolysis from a spray solution with ethylenediaminetetraacetic acid, citric acid and a boric acid flux. Ethylenediaminetetraacetic acid and citric acid used as organic additives enabled the formation of the precursor

powders with a hollow and thin walled structure. The precursor powders with a hollow morphology and thin walled structure turned into the nano-sized $\text{Y}_2\text{O}_3 : \text{Eu}$ phosphor powders with a regular morphology and narrow size distribution. The nano-sized $\text{Y}_2\text{O}_3 : \text{Eu}$ phosphor powders post-treated at a high temperature of 1050 °C had good photoluminescence intensity under vacuum ultraviolet.

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