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Effects of NH_4Cl flux on the characteristics of yttrium oxide phosphor particles with a spherical shape

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High brightness Y_2O_3:Eu phosphor particles with a spherical shape and fine size were prepared by spray pyrolysis from spray solutions with polymeric precursors, a drying control chemical additive and ammonium chloride flux. The phosphor particles prepared from the spray solution with the ammonium chloride flux had a hollow and porous structure after post-treatment. However, the phosphor particles prepared from the spray solution with polymeric precursors, a drying control chemical additive and ammonium chloride flux had a spherical shape and filled inner structure after post-treatment. The optimum content of the NH_4Cl flux showing the maximum photoluminescence intensity of the Y_2O_3:Eu phosphor particles was 6 wt%. The improvement of the photoluminescence intensity of the Y_2O_3:Eu phosphor particles by additions of ammonium chloride flux, polymeric precursors and a drying control chemical additive into the spray solution was 37%.

Key words: phosphor, spray pyrolysis, flux material, photoluminescence.

Introduction

Eu-doped yttrium oxide phosphor particles have been used as a red emitting phosphor in plasma display panels (PDP) and fluorescent lamps (FL) because of their high luminescence efficiency under vacuum ultraviolet (VUV) and ultraviolet (UV) excitation [1-4]. In the PDP application, phosphor particles, with fine sizes and regular morphologies, are required to obtain good phosphor layers during conventional printing processes. A newer printing process, such as that involving ink-jet technology, also requires phosphor particles that have fine sizes, narrow size distributions, and regular morphologies.

Spray pyrolysis has been applied to prepare the Y_2O_3:Eu phosphor particles with a fine size and spherical morphology [5-10]. However, the Y_2O_3:Eu phosphor particles prepared by spray pyrolysis from aqueous spray solutions have a hollow structure and low brightness. Polymeric precursor solutions were developed as the spray solutions to improve the morphology of the Y_2O_3:Eu phosphor particles in the spray pyrolysis process [6, 7]. Flux materials with low melting temperatures, such as Li_2CO_3, H_3BO_3, LiCl etc., have been used to improve the brightness of the Y_2O_3:Eu phosphor particles in the spray pyrolysis process [8]. In previous studies of spray pyrolysis, polymeric precursors and flux material were used separately to prepare Y_2O_3:Eu phosphor particles with a fine size and a spherical shape.

In this study, NH_4Cl flux was applied to the preparation of the Y_2O_3:Eu phosphor particles with a submicromtre size and filled morphology in the spray pyrolysis process. A drying control chemical additive (DCCA), citric acid (CA) and ethylene glycol (EG) were dissolved as additives into the spray solution to improve the morphology of the phosphor particles. The photoluminescence characteristics of the prepared Y_2O_3:Eu phosphor particles under vacuum ultraviolet (VUV) illumination were investigated.

Experimental Procedure

The spray pyrolysis system consisted of a droplet generator, a quartz reactor, and a particle collector. A 1.7 MHz ultrasonic spray generator with six vibrators was used to generate large droplets, which were then 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 spray solutions were prepared by dissolving yttrium nitrate, europium nitrate, citric acid (CA), ethylene glycol (EG) and the ammonium chloride (NH_4Cl) flux. The concentration of the CA and EG used as polymeric precursors were 0.2 $molL^{-1}$. N,N-dimethylformamide was used as the DCCA to control the drying rate of droplets inside the hot-wall reactor. The total concentration of the metallic components was 0.5 M. The content of the NH_4Cl flux was fixed at 6 wt% of Y_2O_3:Eu phosphor particles. The spray solutions were atomized into micrometre-sized droplets using an ultrasonic spray generator with six resonators. The flow rate of air used as a carrier gas was 10 $L \cdot minute^{-1}$, and the residence time of the parti-

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cles inside the reactor was 2.4 s. The as-prepared particles were obtained by spray pyrolysis at 900 °C and post-treated at temperatures between 800 and 1200 °C for 3 h in a muffle furnace.

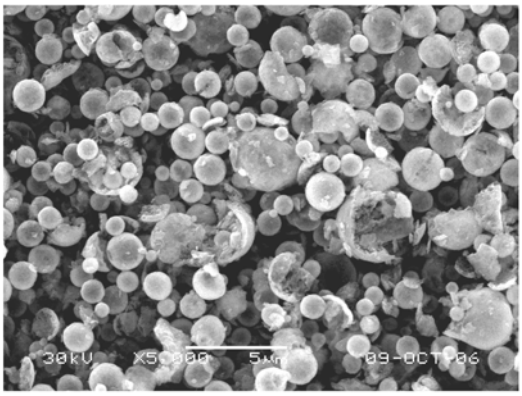
The crystal structures of the particles prepared were analyzed by X-ray diffraction (XRD) using Cu-Kradiation (λ = 1.5418 Å). The morphology of the particles was investigated by scanning electron microscopy (SEM). The luminescence characteristics of the particles prepared under vacuum ultraviolet (VUV) illumination were measured using a D_2 lamp.

Results and Discussions

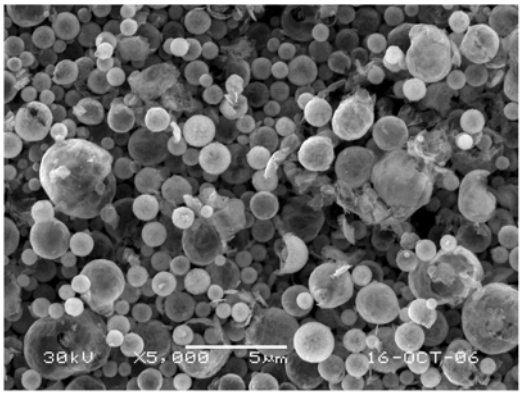
The effects of the types of the spray solution on the morphologies of the precursor particles obtained by spray pyrolysis are shown in Fig. 1. The optimum content of the NH_4Cl flux showing the maximum photoluminescence intensity of the Y_2O_3:Eu phosphor particles was 6 wt%. Therefore, in this study, the content of the NH_4Cl flux was fixed at 6 wt%. The precursor particles obtained from the aqueous spray solution without additives had sizes of several micrometre, hollow and porous morphologies because of the high drying and decomposition rates of the droplets. The precursor particles obtained from the spray solution containing the NH_4Cl flux also had hollow and porous morphologies. The additions of polymeric precursors and DCCA into the spray solution improved the structure of the precursor particles. The precursor particles obtained from the spray solution with polymeric precursors, DCCA and NH_4Cl flux had a fine size and filled inner structure. The controlled drying and decomposition rates of the droplets using the polymeric precursors and DCCA formed precursor particles with a spherical shape and filled morphology in the spray pyrolysis. Citric acid and ethylene glycol formed viscous organic polymers by an esterification reaction during the drying of the droplets. Viscous organic polymers and the DCCA controlled the drying and decomposition rates of the droplets to form precursor particles with a filled inner structure. The mean size of the precursor particles (Fig. 1(c)) measured from the SEM micrographs was 1.2 μm.

Figure 2 shows SEM micrographs of the post-treated Y_2O_3:Eu phosphor particles obtained from the spray solution with the NH_4Cl flux. The precursor particles obtained by spray pyrolysis were post-treated at temperatures between 800 and 1200 °C. The post-treated Y_2O_3:Eu phosphor particles gave some fractured morphologies irrespective of the post-treatment temperature. The precursor particles with hollow and porous morphologies formed the Y_2O_3:Eu phosphor particles with hollow and fractured morphologies.

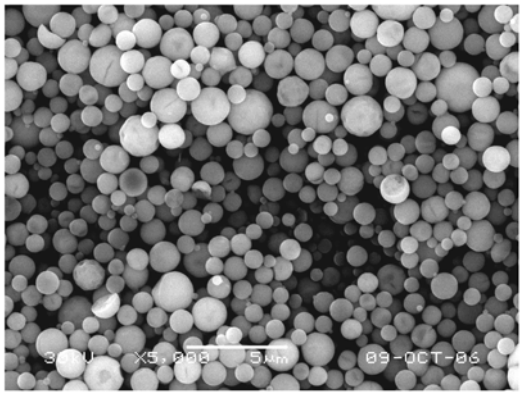
Figure 3 shows the SEM micrographs of the post-treated Y_2O_3:Eu phosphor particles obtained from the spray solution with polymeric precursors, DCCA and the NH_4Cl flux. The post-treated Y_2O_3:Eu phosphor particles were of micrometre, a spherical shape and filled inner structures irrespective of the post-treatment temperatures. The spherical shape of the precursor particles was maintained after post-treatment even at the high temperature of 1200 °C. The mean size of the post-treated Y_2O_3:Eu phosphor particles was similar to that of the precursor particles. In our previous studies, Y_2O_3:Eu phosphor particles prepared from spray solutions with polymeric precursors and a lithium carbonate flux had a nonspherical shape and fine size. The spherical shape of the precursor particles obtained from the spray solutions with polymeric precursors and a



(a) no additive



(b) 6 wt% NH_4Cl



(c) 6 wt% NH_4Cl + Organic additives

Fig. 1. SEM micrographs of the precursor particles obtained by spray pyrolysis.

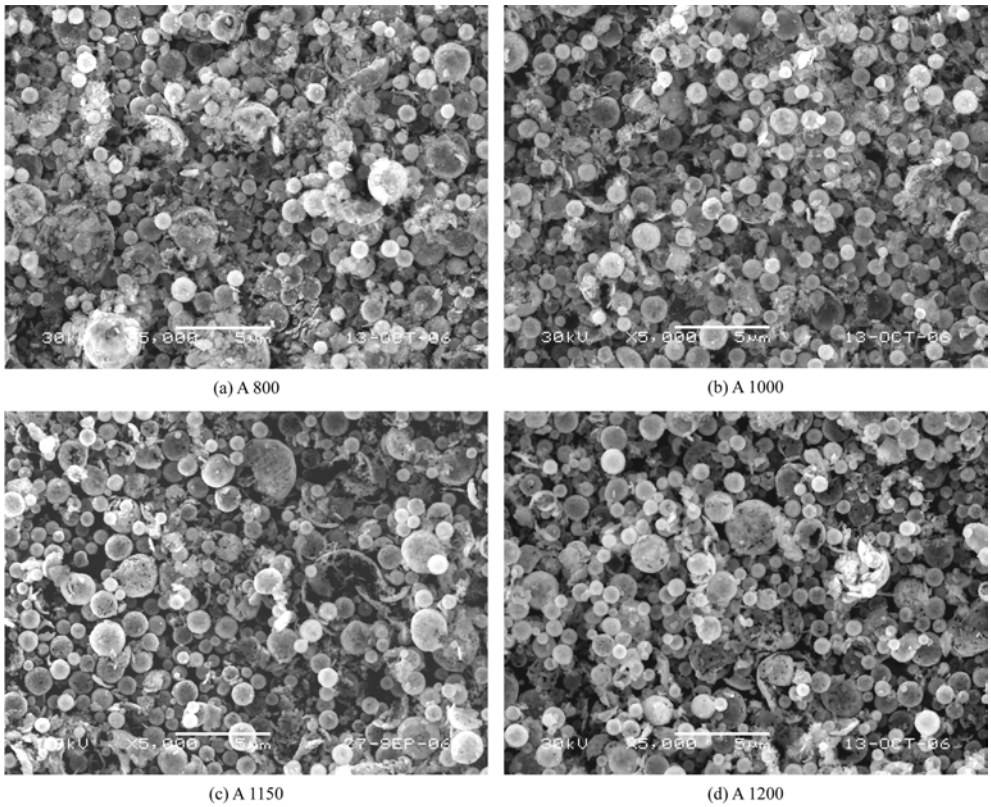


Fig. 2. SEM micrographs of the post-treated phosphor particles obtained from the spray solution with NH_4Cl flux. (A: post-treatment temperature in ^oC)

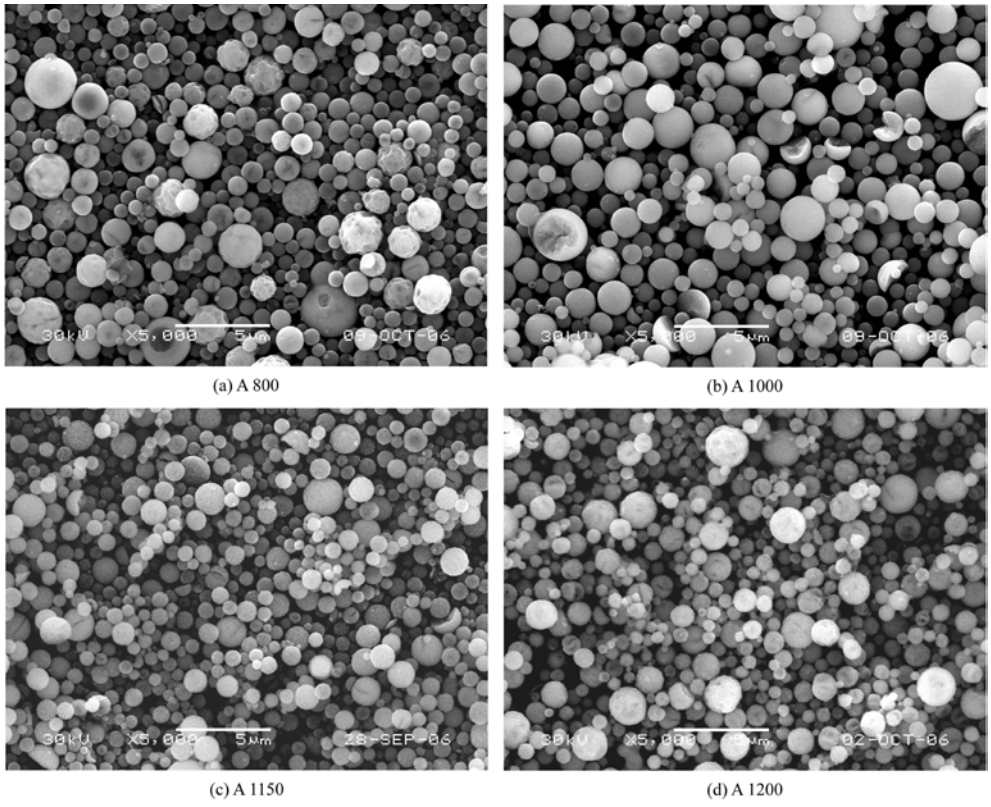


Fig. 3. SEM micrographs of the post-treated phosphor particles obtained from the spray solution with organic additives and the NH_4Cl flux. (A: post-treatment temperature in ^oC)

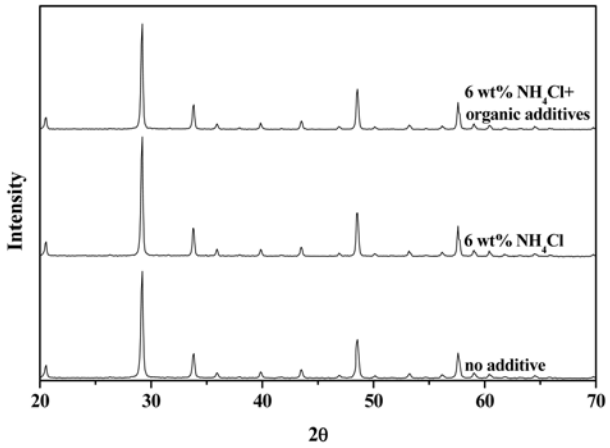


Fig. 4. XRD spectra of the phosphor particles prepared by spray pyrolysis.

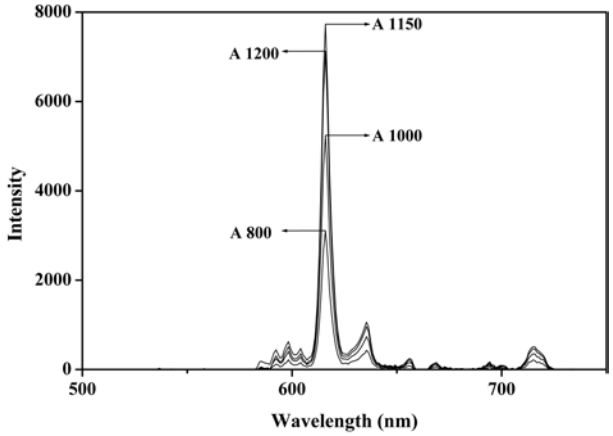


Fig. 6. Photoluminescence spectra of the phosphor particles post-treated at various temperatures. (A: post-treatment temperature in °C)

lithium carbonate flux was destroyed after post-treatment at high temperatures [9, 10]. However, the NH_4Cl flux did not destroy the spherical shape of the Y_2O_3:Eu phosphor particles obtained from the spray solution with polymeric precursors and DCCA. The Y_2O_3:Eu phosphor particles maintained a spherical shape and a filled inner structure after post-treatment at high temperatures because of the high thermal stability of the precursor particles with a filled inner structure.

Figure 4 shows the XRD spectra of the Y_2O_3:Eu phosphor particles prepared from the spray solutions at a post-treatment temperature of 1150 °C. The prepared Y_2O_3:Eu phosphor particles had pure crystal structures and high crystallinities irrespective of the type of spray solution. The mean crystallite size of the phosphor particles was calculated using Scherrer's equation. The mean crystallite sizes of the phosphor particles prepared from the spray solutions with and without NH_4Cl flux were 43 and 39 nm, respectively. However, the additions of the DCCA and polymeric precursors did not increase the mean crystallite size of the phosphor particles.

Figure 5 shows the photoluminescence spectra of the Y_2O_3:Eu phosphor particles obtained from the various types of spray solutions. The precursor particles obtained by spray pyrolysis were post-treated at a temperature of 1150 °C. The NH_4Cl flux was efficient in the improving the photoluminescence intensity of the Y_2O_3:Eu phosphor particles. The addition of NH_4Cl flux into the spray solution improved the photoluminescence intensity of the Y_2O_3:Eu phosphor particles by 27%. The photoluminescence intensity of the phosphor particles was also improved by the additions of DCCA and polymeric precursors to the spray solution containing NH_4Cl flux. Finally, the improvement in the photoluminescence intensity of the Y_2O_3:Eu phosphor particles by the addition of NH_4Cl flux, polymeric precursors and DCCA to the spray solution was 37%. Figure 6 shows the photoluminescence spectra of the phosphor particles obtained from the spray solutions with polymeric precursors, DCCA and NH_4Cl flux at various post-treatment temperatures. The maximum photoluminescence intensity of the Y_2O_3:Eu phosphor particles was obtained at a post-treatment temperature of 1150 °C.

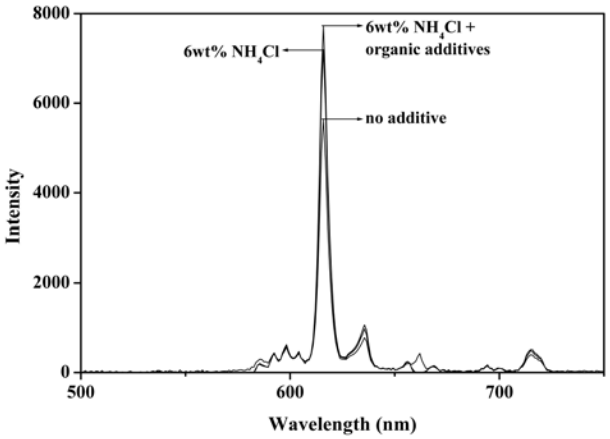


Fig. 5. Photoluminescence spectra of the phosphor particles prepared by spray pyrolysis.

Conclusions

NH_4Cl flux was applied to the preparation of the Y_2O_3:Eu phosphor particles in a spray pyrolysis process. The additions of a drying control chemical additive (DCCA), citric acid (CA) and ethylene glycol (EG) into the spray solution improved the morphology of the Y_2O_3:Eu phosphor particles. The NH_4Cl flux did not destroy the spherical shape of the Y_2O_3:Eu phosphor particles obtained from the spray solution with polymeric precursors and DCCA. The Y_2O_3:Eu phosphor particles prepared from the DCCA, polymeric precursors and NH_4Cl flux had a spherical shape, fine size and high brightness under vacuum ultraviolet illumination.

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