

## **Terbium-doped lanthanum phosphate phosphor particles with a submicrometre size and spherical shape**

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Submicrometre-sized  $\text{LaPO}_4\text{:Tb}$  phosphor particles with a spherical shape and filled morphology were prepared by spray pyrolysis from a polymeric precursor solution containing citric acid and ethylene glycol. The  $\text{LaPO}_4\text{:Tb}$  phosphor particles obtained from the aqueous spray solution had a hollow morphology and large size because of the high drying and decomposition rates of droplets. The mean sizes of the particles obtained from the aqueous spray and polymeric precursor solutions were each 1 and 0.8  $\mu\text{m}$ , respectively. The optimum post-treatment temperature for the preparation of  $\text{LaPO}_4\text{:Tb}$  phosphor particles with a spherical shape and high brightness was 1100 °C. The prepared  $\text{LaPO}_4\text{:Tb}$  phosphor particles had high photoluminescence intensities under vacuum ultraviolet illumination of 147 nm.

**Key words:** phosphor, spray pyrolysis, phosphate, display material.

### **Introduction**

A new printing process in display applications, such as involving ink-jet technology, requires phosphor particles that have fine sizes, narrow size distributions, and regular morphologies. Conventionally, phosphor particles were prepared by solid-state reaction methods. The phosphor particles prepared by solid-state reaction method have sizes of several micrometre and non-spherical morphologies. Therefore, liquid solution and gas phase reaction methods are under development to prepare the phosphor particles with fine size and regular morphology [1-5].

Terbium-doped phosphate phosphor particles have been studied as an alternative green-emitting phosphor for plasma display panels (PDP) [3, 4]. Various types of liquid solution and gas phase reaction methods are applied to prepare the terbium-doped phosphate phosphor particles with a fine size and regular morphology. Spray pyrolysis is also applied to the preparation of terbium-doped phosphate particles with spherical morphologies [6, 7]. However, in the spray pyrolysis, the morphologies of the phosphor particles were affected by the preparation conditions such as flow rate of the carrier gas, solution concentration, residence time of the particles inside the hot wall reactor, etc [6-13].

In this study, fine-sized  $\text{LaPO}_4\text{:Tb}$  phosphor particles were prepared by an ultrasonic spray pyrolysis method. Polymeric precursors such as citric acid (CA) and ethylene glycol (EG) were added into the spray solution to

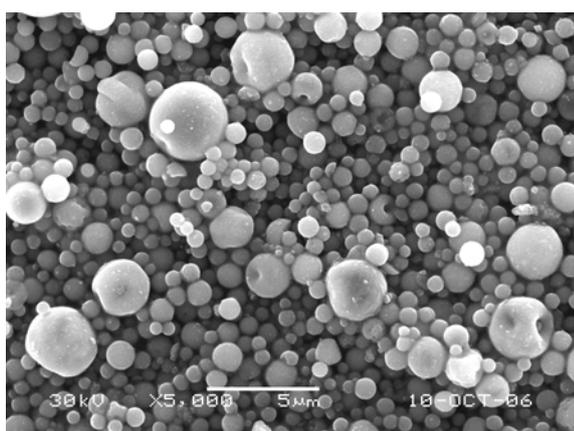
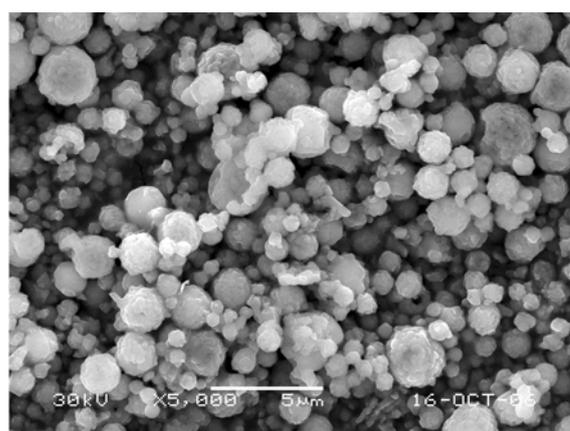
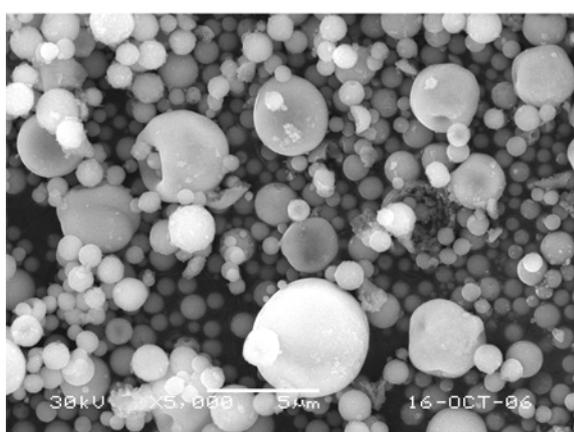
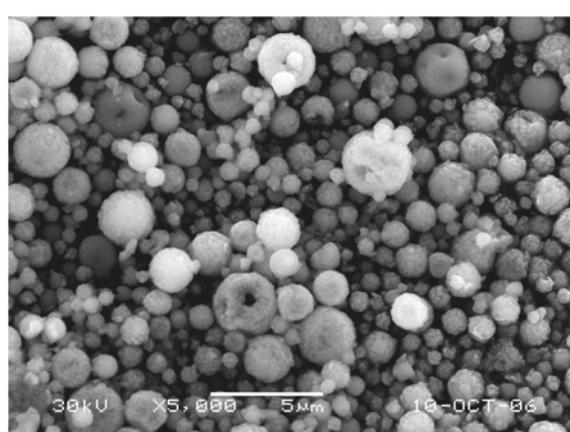
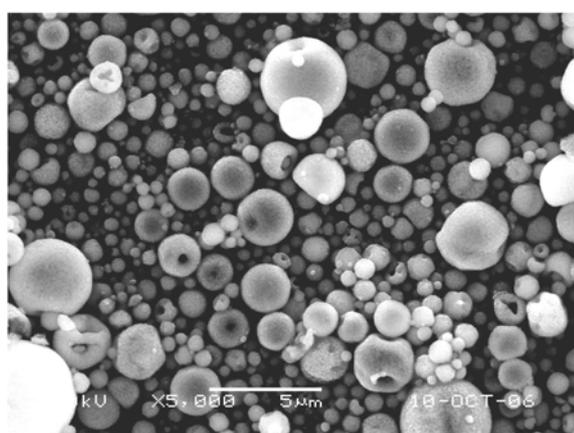
improve the morphology of the fine-sized  $\text{La}_{0.83}\text{PO}_4\text{:Tb}_{0.17}$  ( $\text{LaPO}_4\text{:Tb}$ ) phosphor particles. The photoluminescence characteristics of fine-sized  $\text{LaPO}_4\text{:Tb}$  phosphor particles under vacuum ultraviolet (VUV) illumination were also investigated.

### **Experimental Procedure**

The spray solutions were prepared by dissolving lanthanum nitrate, terbium nitrate and ammonium hydrogen phosphate in distilled water. The overall solution concentration of La, Tb and P components was fixed at 0.3 M. The concentrations of the citric acid (CA) and ethylene glycol (EG) used as polymeric precursors were each changed from 0.1 to 0.6  $\text{mol}\cdot\text{L}^{-1}$ . The length and inside diameter of the quartz reactor were 1200 mm and 50 mm, respectively. The spray solutions were atomized into micrometre-sizes droplets using a 1.7-MHz ultrasonic spray generator having six vibrators. The flow rates of air used as a carrier gas were changed from 20 to 60  $\text{L}\cdot\text{minute}^{-1}$ . The as-prepared particles obtained by spray pyrolysis at 900 °C were post-treated at temperatures between 800 and 1100 °C for 3 h in a muffle furnace.

The crystal structures of the prepared particles were analyzed by X-ray diffraction (XRD) using Cu-K radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The morphology of the particles was investigated by scanning electron microscopy (SEM). The luminescence characteristics of the prepared particles under vacuum ultraviolet (VUV) illumination were measured using a  $\text{D}_2$  lamp.

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(a) 20 L·minute<sup>-1</sup>(a) 20 L·minute<sup>-1</sup>(b) 40 L·minute<sup>-1</sup>(b) 40 L·minute<sup>-1</sup>(c) 60 L·minute<sup>-1</sup>(c) 60 L·minute<sup>-1</sup>

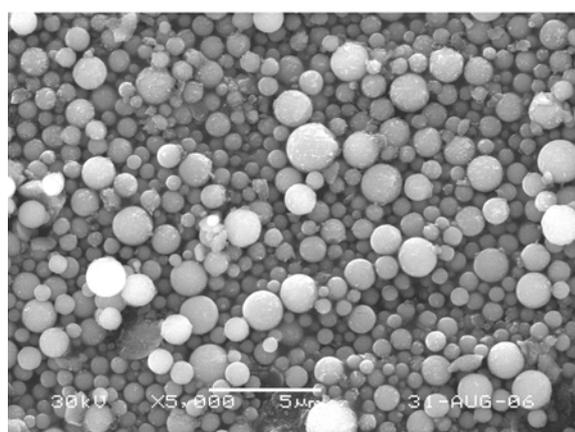
**Fig. 1.** SEM micrographs of the as-prepared particles obtained from the aqueous spray solution.

**Fig. 2.** SEM micrographs of the post-treated particles obtained from the aqueous spray solution.

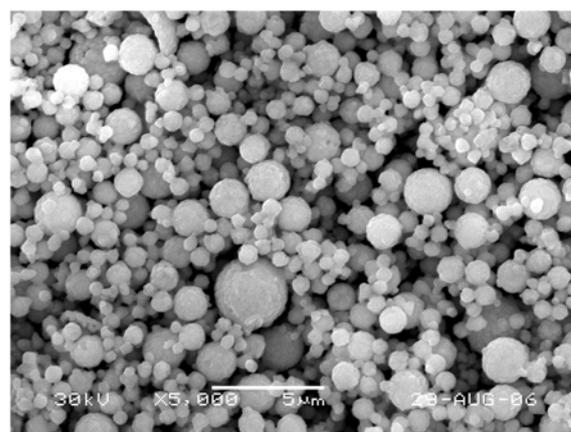
## Results and Discussions

The morphologies of the particles prepared by spray pyrolysis were affected by the flow rates of the carrier gas. Figure 1 shows SEM micrographs of the as-prepared particles obtained by spray pyrolysis from the aqueous spray solutions at different flow rates of the carrier gas. The residence times of the particles inside the hot wall reactor changed from 1.2 to 0.3 s when the

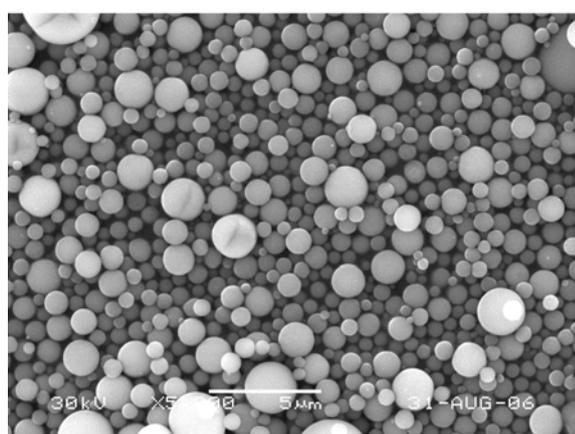
flow rates of the carrier gas changed from 20 to 60 L·minute<sup>-1</sup>. The as-prepared particles had spherical morphologies and sizes of several micrometres irrespective of the flow rate of the carrier gas. However, the as-prepared particles had hollow inner structure because of the high drying and decomposition rates of the droplets inside the hot wall reactor. Figure 2 shows SEM micrographs of the post-treated LaPO<sub>4</sub>:Tb particles at different flow rates of the carrier gas. The as-



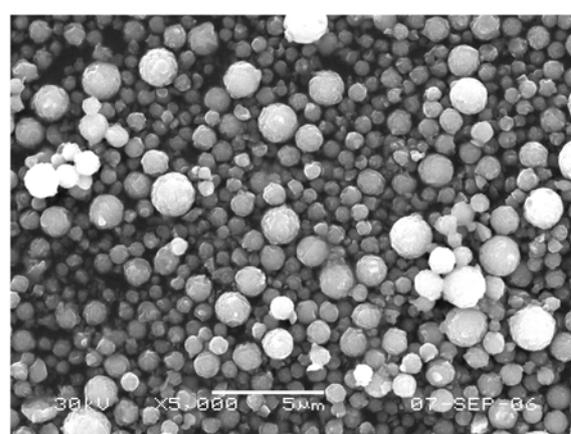
(a) 0.1 M CA/EG



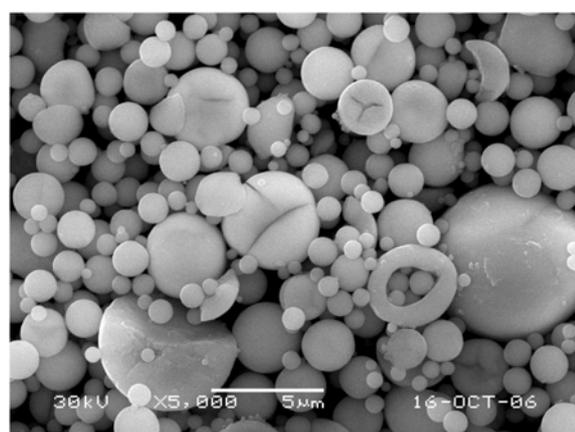
(a) 0.1 M CA/EG



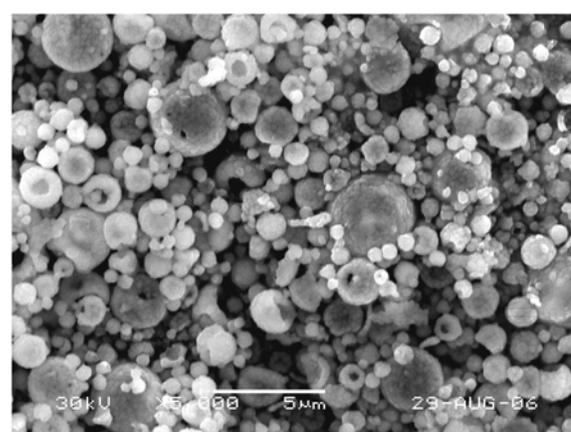
(b) 0.3 M CA/EG



(b) 0.3 M CA/EG



(c) 0.6 M CA/EG



(c) 0.6 M CA/EG

**Fig. 3.** SEM micrographs of the as-prepared particles obtained from polymeric precursor solutions.

prepared particles obtained from the aqueous spray solution were post-treated at a temperature of 1050 °C for 3 h. The post-treated phosphor particles had micrometre sizes, spherical shapes and hollow morphologies irrespective of the flow rate of the carrier gas. The hollowness of the particles increased with an increase in the flow rate of the carrier gas.

Polymeric precursor solutions containing citric acid and ethylene glycol were applied to the preparation of

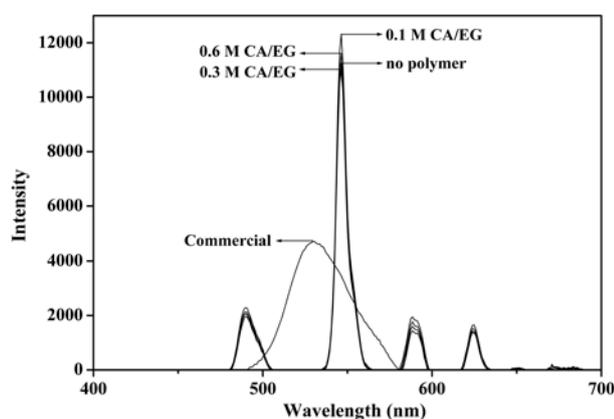
**Fig. 4.** SEM micrographs of the post-treated particles obtained from polymeric precursor solutions.

LaPO<sub>4</sub>:Tb phosphor particles with controlled morphologies. Figures 3 and 4 show SEM micrographs of the as-prepared and post-treated phosphor particles obtained from the polymeric precursor solutions. The flow rate of the carrier gas was 40 L·minute<sup>-1</sup>. The concentrations of citric acid and ethylene glycol were each changed from 0.1 to 0.6 mol·L<sup>-1</sup>. The as-prepared particles (Fig. 3(a), (b)) obtained from the spray solutions with low concentrations of citric acid and ethyl-

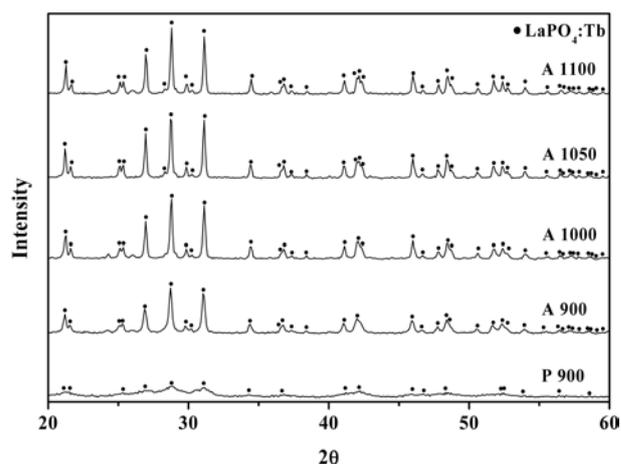
ene glycol had fine sizes, narrow size distributions and regular morphologies. The polymeric chains formed from the esterification reaction between carboxyl and alcohol groups of citric acid and ethylene glycol changed the drying and decomposition stages of droplets. Thus, the as-prepared particles with a spherical shape and filled morphology were prepared by spray pyrolysis from the polymeric precursor solution at a high flow rate of the carrier gas. In Figs. 1 and 3, the as-prepared particles obtained from the polymeric precursor solutions had a finer size than those of the particles obtained from the aqueous spray solutions. The mean size of the as-prepared particles (Fig. 1(b)) obtained from the aqueous spray solution was 1  $\mu\text{m}$ . However, the mean size of the as-prepared particles (Fig. 3(b)) obtained from the polymeric precursor solution was 0.8  $\mu\text{m}$ . On the other hand, the as-prepared particles (Fig. 3(c)) obtained from the spray solution with high concentrations of citric acid and ethylene glycol exhibited some fractured morphologies and a broad size distribution. The high evolution rate of the gases generated from the decomposition of organic polymers formed the as-prepared particles with fractured morphologies and broad size distributions.

In Fig. 4, the concentrations of citric acid and ethylene glycol affected the morphologies of the post-treated  $\text{LaPO}_4:\text{Tb}$  phosphor particles. The post-treated  $\text{LaPO}_4:\text{Tb}$  phosphor particles (Fig. 4(a), (b)) obtained from the low concentrations of citric acid and ethylene glycol had a spherical shape, filled morphology and a narrow size distribution. On the other hand, the  $\text{LaPO}_4:\text{Tb}$  phosphor particles (Fig. 4(c)) obtained from the high concentrations of citric acid and ethylene glycol had a hollow morphology and a broad size distribution. The as-prepared particles obtained from the spray solutions with a optimum concentrations of citric acid and ethylene glycol formed  $\text{LaPO}_4:\text{Tb}$  phosphor particles with a spherical shape, filled structure and a narrow size distribution.

Figure 5 shows the photoluminescence spectra of the

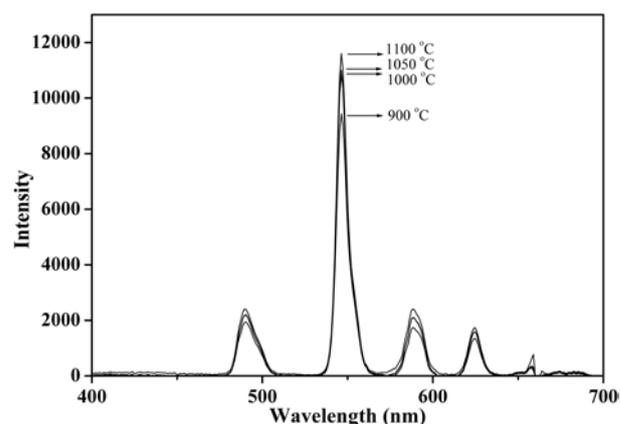


**Fig. 5.** Photoluminescence spectra of the  $\text{LaPO}_4:\text{Tb}$  phosphor particles.

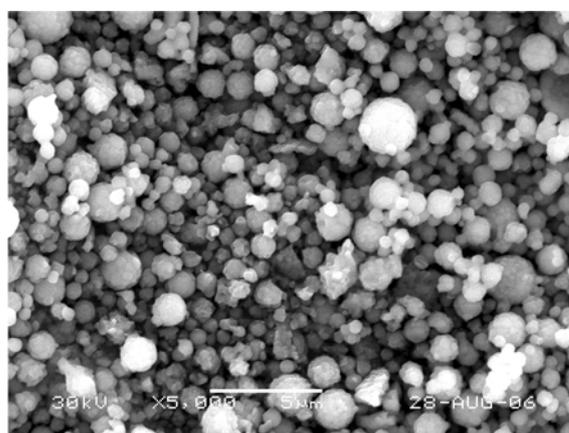


**Fig. 6.** XRD spectra of the as-prepared and post-treated particles. (P : preparation temperature in  $^{\circ}\text{C}$ , A: post-treatment temperature in  $^{\circ}\text{C}$ )

prepared  $\text{LaPO}_4:\text{Tb}$  phosphor particles post-treated at a temperature of 1050  $^{\circ}\text{C}$  under VUV illumination of 147 nm. The photoluminescence characteristics of the prepared  $\text{LaPO}_4:\text{Tb}$  phosphor particles were compared with



**Fig. 7.** Photoluminescence spectra of the phosphor particles post-treated at various temperatures.



**Fig. 8.** SEM micrographs of the phosphor particles post-treated at temperature of 1100  $^{\circ}\text{C}$ .

that of commercial  $\text{Zn}_2\text{SiO}_4:\text{Mn}$  phosphor particles. The commercial  $\text{Zn}_2\text{SiO}_4:\text{Mn}$  phosphor particles prepared by a solid-state reaction method had a high photoluminescence intensity under VUV illumination. The prepared  $\text{LaPO}_4:\text{Tb}$  phosphor particles showed four peaks resulting from the transition from  $^5\text{D}_4$  to  $^7\text{F}_j$ . The photoluminescence intensities of the  $\text{LaPO}_4:\text{Tb}$  phosphor particles changed slightly according to the concentrations of citric acid and ethylene glycol added into the spray solutions.

The effects of the post-treatment temperature on the morphology, crystallinity and photoluminescence intensity of the  $\text{LaPO}_4:\text{Tb}$  phosphor particles obtained from the polymeric precursor solution were investigated and are shown in Figs. 6, 7 and 8. The concentrations of citric acid and ethylene glycol were each  $0.3 \text{ mol}\cdot\text{L}^{-1}$ . Figure 6 shows the XRD spectra of the as-prepared and post-treated particles. The as-prepared  $\text{LaPO}_4:\text{Tb}$  phosphor particles obtained by spray pyrolysis had poor crystal structures because of the short residence time of the particles inside the hot wall reactor which was maintained at temperature of  $900^\circ\text{C}$ . However, the  $\text{LaPO}_4:\text{Tb}$  phosphor particles post-treated at temperatures above  $900^\circ\text{C}$  had a pure crystal structure. The mean crystallite sizes of the phosphor particles were calculated using Scherrer's equation. The mean crystallite size of the as-prepared particles obtained by spray pyrolysis was 17 nm. However, the mean crystallite size of the phosphor particles post-treated at temperatures of  $900$  and  $1050^\circ\text{C}$  were 33 and 44 nm, respectively. Figure 7 shows the photoluminescence spectra of the  $\text{LaPO}_4:\text{Tb}$  phosphor particles post-treated at various temperatures. The phosphor particles post-treated at a temperature of  $1100^\circ\text{C}$  had the maximum photoluminescence intensity. The morphology of the  $\text{LaPO}_4:\text{Tb}$  phosphor particles post-treated at a temperature of  $1100^\circ\text{C}$  is shown in Fig. 8. The  $\text{LaPO}_4:\text{Tb}$  phosphor particles had a spherical shape and non-aggregation characteristics at a post-treatment temperature of  $1100^\circ\text{C}$ .

## Conclusions

Green-emitting  $\text{LaPO}_4:\text{Tb}$  phosphor particles for plasma display panels were prepared by spray pyrolysis. The  $\text{LaPO}_4:\text{Tb}$  phosphor particles obtained from an aqueous spray solution had large sizes and irregular morphologies. However, the  $\text{LaPO}_4:\text{Tb}$  phosphor particles obtained from polymeric precursor solutions were of submicrometre size, had a spherical shape and filled morphology because of the controlled drying and decomposition rates of droplets in the severe preparation conditions. The optimum concentrations of citric acid and ethylene glycol added into the spray solution as polymeric precursors were each  $0.3 \text{ mol}\cdot\text{L}^{-1}$ . The  $\text{LaPO}_4:\text{Tb}$  phosphor particles obtained from the high concentrations of citric acid and ethylene glycol had hollow morphology and a broad size distribution.

## References

1. Y.C. Kang and S.B. Park, *Jpn. J. Appl. Phys.* 38 (1999) L1541-L1543.
2. Y.C. Kang and S.B. Park, *J. Electrochem. Soc.* 147 (2000) 799-802.
3. S. Buddhudu, C.H. Kam, S.L. Ng, Y.L. Lam, B.S. Ooi, Y. Zhou, K.S. Wong, and U. Rambabu, *Mater. Sci. Eng. B* 72 (2000) 27-30.
4. U. Rambabu, D.P. Amalnerkar, B.B. Kale, and S. Buddhudu, *Mater. Chem. Phys.* 70 (2001) 1-6.
5. X. Jing, T. Ireland, C. Gibbons, D. J. Barber, J. Silver, A. Vecht, G. Fern, and P. Trowga, *J. Electrochem. Soc.* 146 (1999) 4654-4658.
6. Y.C. Kang, E.J. Kim, D.Y. Lee, and H.D. Park, *J. Alloy. Compds.* 347 (2002) 266-270.
7. K.K. Lee, Y.C. Kang, K.Y. Jung, and H.D. Park, *Electrochem. Solid-State Lett.* 5[12] (2002) H31-H34.
8. Y.C. Kang, S.B. Park, I.W. Lenggoro, and K. Okuyama, *J. Phys. Chem. Solids* 60 (1999) 379-384.
9. Y. Shimomura and N. Kijima, *J. Electrochem. Soc.* 151 (2004) H86-H92.
10. Y. Shimomura and N. Kijima, *Electrochem. Solid-State Lett.* 7 (2004) H1-H4.
11. J.R. Sohn, Y.C. Kang, and H.D. Park, *Jpn. J. Appl. Phys.* 41 (2002) 3006-3009.
12. Y.C. Kang and S.B. Park, *J. Aerosol Sci.* 26 (1995) 1131-1138.
13. Y.C. Kang, H.S. Roh, and S.B. Park, *J. Am. Ceram. Soc.* 84 (2001) 447-449.