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$LaPO_4$:Tb phosphor powders prepared by spray pyrolysis using two different spray generators

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$LaPO_4$:Tb phosphor powders with a spherical shape and fine size were prepared by the filter expansion aerosol generator (FEAG) and ultrasonic spray pyrolysis processes. The mean size of the phosphor powders prepared by the FEAG process increased from 0.57 to 0.81 μm when the concentration of the spray solution was changed from 0.3 to 1 M. On the other hand, the mean size of the phosphor powders prepared by the ultrasonic spray pyrolysis process increased from 0.82 to 1.16 μm when the concentration of the spray solution was changed from 0.3 to 1 M. The phosphor powders had a pure monoclinic $LaPO_4$ phase after post-treatment at a temperature of 1050 °C irrespective of the type of the spray generator and the concentrations of the spray solution. The photoluminescence intensities of the $LaPO_4$:Tb phosphor powders prepared by the FEAG and ultrasonic spray pyrolysis processes increased with increasing the concentration of the spray solution. The $LaPO_4$:Tb phosphor powders prepared by the FEAG process had lower photoluminescence intensities than those of the phosphor powders prepared by the ultrasonic spray pyrolysis process.

Key words: Phosphor, Spray pyrolysis, Lanthanum phosphate.

Introduction

Terbium-doped phosphate powders have been studied as an alternative green-emitting phosphor [1, 2]. Usually, a solid-state reaction has been used to investigate the possibility of these powders as a new green-emitting phosphor for plasma display panels (PDP) as well as the optimal composition giving a high luminescence and proper decay time for these phosphate phosphor powders. In the PDP application, the phosphor powders, which are characterized by their fine sizes and regular morphologies, are required to give good phosphor layers during conventional printing processes. The new printing processes, such as that involving ink-jet technology, also require phosphor powders that have fine sizes, narrow size distributions, and regular morphologies. Therefore, liquid solution and gas phase reaction methods are under development to prepare phosphor powders with a fine size and regular morphology [3, 4].

Spray pyrolysis is one of the gas phase reaction methods utilizing several micrometre size droplets as the reaction media [4, 5]. The phosphor powders prepared by spray pyrolysis have a fine size and regular morphology. However, the size and morphology of phosphor powders are mainly determined by the type of spray generator in the spray pyrolysis. In this study, $La_{0.83}P_{1.17}O_4$:$Tb_{0.17}$ ($LaPO_4$:Tb) phosphor powders were prepared by spray pyrolysis using two different spray generators. The FEAG process, which generates droplets under a low pressure, was applied to the preparation of $LaPO_4$:Tb phosphor powders. The characteristics of the $LaPO_4$:Tb phosphor powders prepared by the FEAG process were compared with those the phosphor powders prepared by ultrasonic spray pyrolysis.

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Experimental Procedure

Schematic diagrams of the FEAG and ultrasonic spray pyrolysis processes used in this study are given elsewhere [6, 7]. The length and inside diameter of quartz reactor were 1200 mm and 50 mm, respectively. The reactor temperature was maintained at 900 °C. The as-prepared powders obtained by spray pyrolysis were post-treated at a temperature of 1050 °C for 3 h under an air environment. Lantanum nitrate ($La(NO_3)_3 \cdot 6H_2O$), terbium nitrate ($Tb(NO_3)_3 \cdot 5H_2O$), and ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) were used as the precursor of lantanum, terbium, and phosphorous, respectively. These precursors were dissolved in distilled water with a small amount of nitric acid to make a clear solution. The solution concentrations were changed from 0.1 to 1 M.

The surface tension of the spray solutions were measured with a thermostated tensiometer (model K10 Krüss GmbH, Hamburg, Germany), using a platinum-iridium ring and the method of Du Noüy. The measurements were carried out at a room temperature of 20 °C. The tensiometer was calibrated with distilled water (σ = 72.8 mN m^{-1} at 20 °C). Viscosity measurements were made using an Ostwald viscometer immersed in a water bath maintained at a temperature of 20 °C. The crystal structures of phosphor

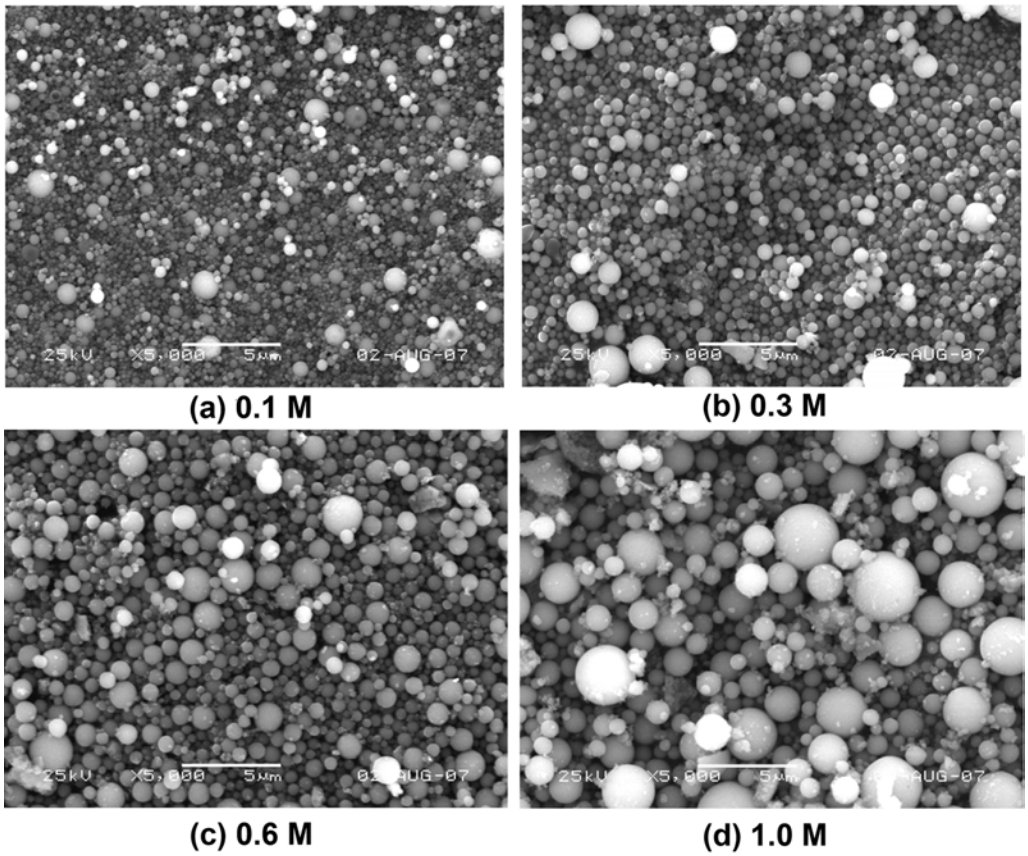

Fig. 1. SEM images of the as-prepared powders obtained by the FEAG process.

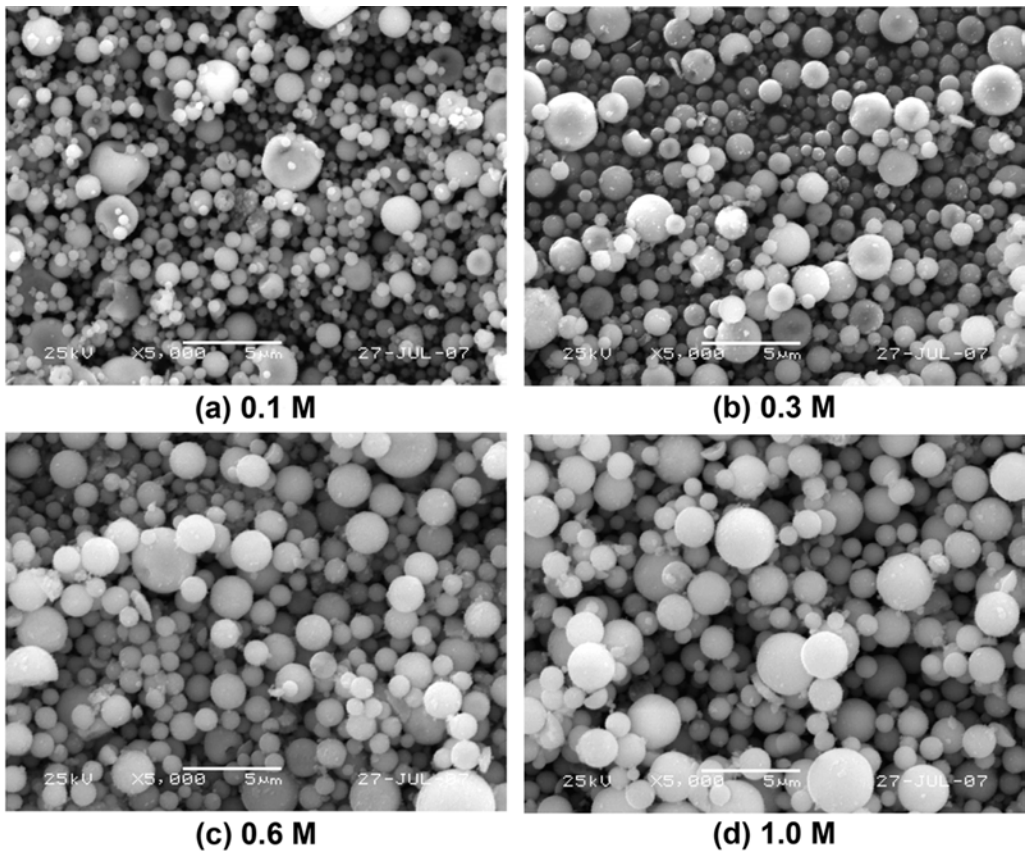

Fig. 2. SEM images of the as-prepared powders obtained by the ultrasonic spray pyrolysis.

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

Results and Discussion

The morphologies of the as-prepared powders obtained by spray pyrolysis from the spray solutions with various concentrations are shown in Figs. 1 and 2. The as-prepared powders obtained by the FEAG and ultrasonic spray generators had a spherical shape and non-aggregated characteristics irrespective of the concentration of the spray solution. The mean sizes of the as-prepared powders are shown in Fig. 3. The mean sizes of the powders were determined from SEM images by counting more than 500 powder particles in each sample in order to minimize errors. The mean size of the as-prepared powders obtained by the FEAG process increased from 0.30 to 0.82 μm when the concentration of the spray solution was changed from 0.1 to 1 M. On the other hand, the mean size of the as-prepared powders obtained by the ultrasonic spray generator increased from 0.68 to 1.12 μm when the concentration of the spray solution was changed from 0.1 to 1 M. In a spray pyrolysis process, one powder particle is formed from one droplet by drying and decomposition processes. Therefore, the mean sizes of the powders prepared by spray pyrolysis were affected by the mean sizes of droplets and the concentrations of the spray solution. The size of droplets formed by the FEAG process was finer than that of the droplets formed by the ultrasonic spray generator. The size distributions of the as-prepared powders obtained by the FEAG process were affected by the concentrations of the spray solution. The size distributions of the as-prepared powders obtained by spray pyrolysis could be changed by a change of the size distribution of droplets generated by the spray generator and different morphologies of the as-prepared powders by altering the concentration of the spray solution. The concentration gradient of precursors inside a large-sized droplet in the drying stage is higher than that inside a small-sized droplet. Therefore, the powders prepared from the large-sized droplets had a more hollow and porous structure than those prepared from the small-sized droplets. The different morphologies of the powders obtained from the small and large-sized droplets increased the size distribution of the powders. In the FEAG process, the mean size of the droplets was affected by the surface tension and viscosity of the spray solution [8]. Figure 4 shows the surface tensions and viscosities of the spray solutions according to the concentration. The surface tensions and viscosities of the spray solutions were slightly changed according to the concentration. Therefore, the mean size and size distribution of droplets generated by the FEAG process were not changed according to the concentration of the spray solution. The morphologies of the powders prepared by spray pyrolysis are also affected by the concentration of the spray solution. The concentration gradients of precursors inside the droplets are affected by the concentration of the spray solution. Therefore, the different morphologies of the as-prepared powders obtained by the FEAG process according to the concentration of the spray solution changed the size distributions of the powders.

Figures 5 and 6 show the SEM images of the post-treated $LaPO_4$:Tb phosphor powders. The as-prepared powders obtained from the FEAG and ultrasonic spray pyrolysis processes were post-treated at a temperature of 1050 ºC for 3 h. The $LaPO_4$:Tb phosphor powders gave the maximum photoluminescence intensities at the post-treatment temperature of 1050 ºC. The morphologies of the phosphor powders obtained by the FEAG process were affected by the concentration of the spray solution. The spherical shape of the as-prepared powders obtained from the spray solution with low concentration of 0.1 M disappeared after post-treatment. On the other hand, the spherical shapes of the as-prepared powders obtained from the spray solutions with concentrations above 0.3 M were

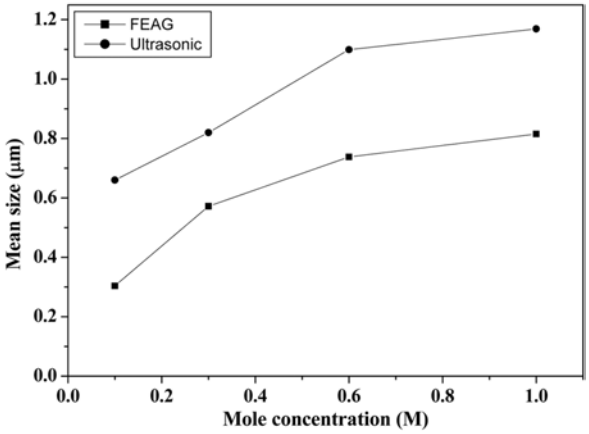

Fig. 3. Mean sizes of the as-prepared powders obtained by the FEAG and ultrasonic spray pyrolysis processes.

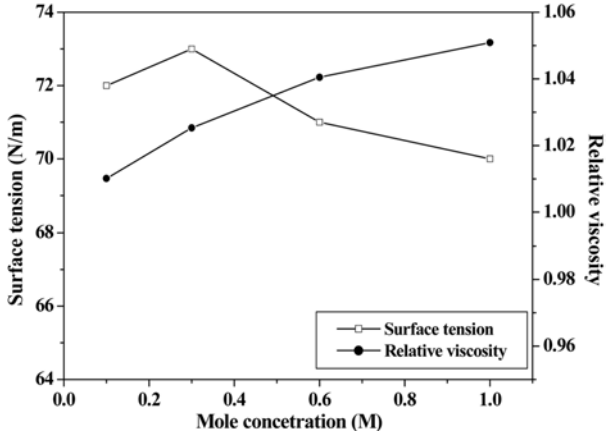

Fig. 4. Surface tensions and relative viscosities of the spray solutions at different concentrations.

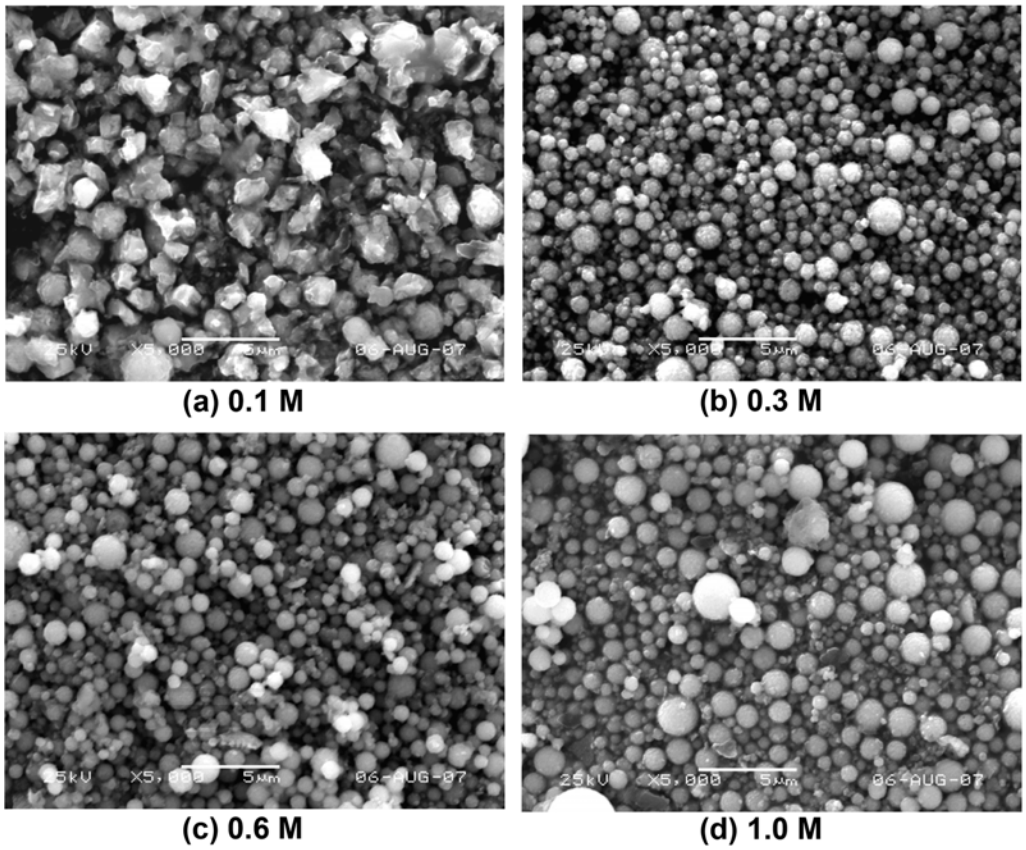

Fig. 5. SEM images of the post-treated $LaPO_4$:Tb phosphor powders obtained by the FEAG process.

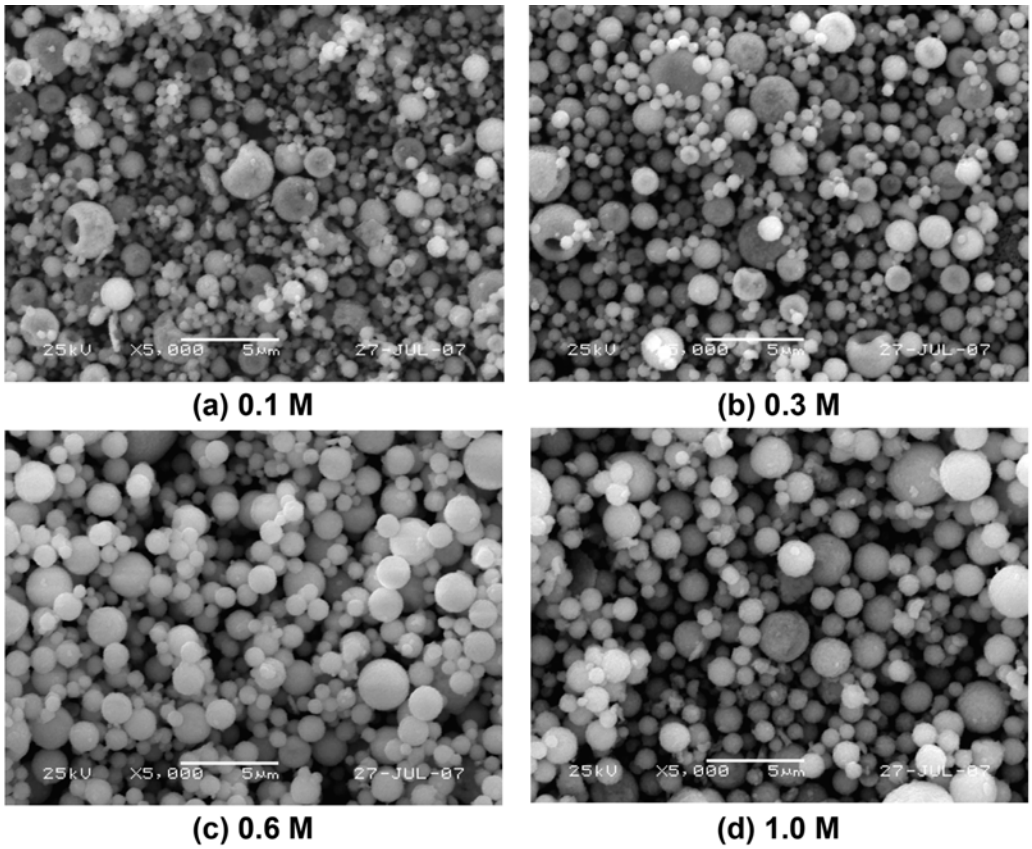

Fig. 6. SEM images of the post-treated $LaPO_4$:Tb phosphor powders obtained by the ultrasonic spray pyrolysis.

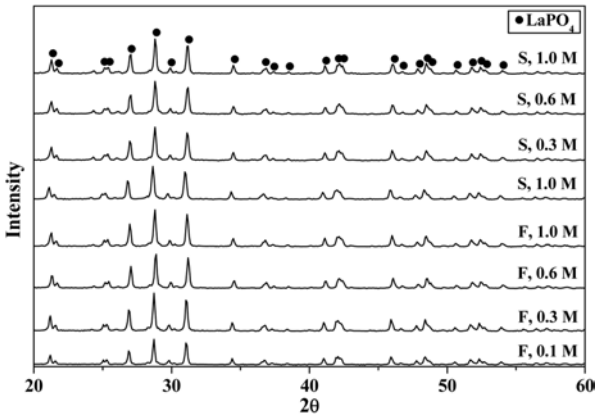

Fig. 7. XRD patterns of the $LaPO_4$:Tb phosphor powders prepared by the FEAG and ultrasonic spray pyrolysis processes after post-treatment at 1050 °C (S: Ultrasonic, F: FEAG).

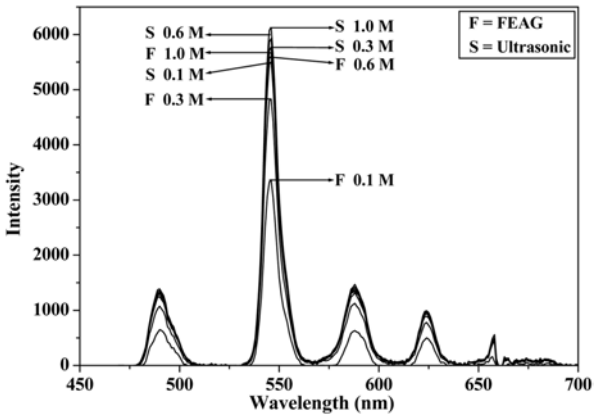

Fig. 8. Photoluminescence spectra of the $LaPO_4$:Tb phosphor powders prepared by the FEAG and ultrasonic spray pyrolysis processes.

maintained after post-treatment. However, the spherical shape of the as-prepared powders obtained by ultrasonic spray pyrolysis was maintained after post-treatment irrespective of the concentration of the spray solution. The low thermal stability of the fine-sized powders obtained by the FEAG process from the spray solution with a low concentration of 0.1 M changed the morphology after post-treatment at a high temperature. The mean size of the phosphor powders prepared by the FEAG process increased from 0.57 to 0.81 μm when the concentration of the spray solution was changed from 0.3 to 1 M. On the other hand, the mean size of the phosphor powders prepared by the ultrasonic spray pyrolysis process increased from 0.82 to 1.16 μm when the concentration of the spray solution was changed from 0.3 to 1 M.

In the XRD patterns, the as-prepared powders contained amorphous phases irrespective of the type of spray generator. However, the phosphor powders prepared by the FEAG and ultrasonic spray pyrolysis processes had a pure monoclinic $LaPO_4$ phase after post-treatment at a temperature of 1050 °C irrespective of the concentrations of the spray solution as shown in Fig. 7. However, the $LaPO_4$:Tb phosphor powders prepared by the FEAG process from the spray solution with a low concentration of 0.1 M had a small mean crystallite size.

Figure 8 shows the photoluminescence spectra of the $LaPO_4$:Tb phosphor powders under an illumination at 147 nm. The prepared $LaPO_4$:Tb phosphor powders had four absolute peaks resulted from the transition from $^5D_4$ to ^7F_j. The photoluminescence intensities of the $LaPO_4$:Tb phosphor powders prepared by the FEAG and ultrasonic spray pyrolysis processes increased with an increase in the concentration of the spray solution. The $LaPO_4$:Tb phosphor powders prepared by the FEAG process had lower photoluminescence intensities than those of the phosphor powders prepared by the ultrasonic spray pyrolysis process. The different mean sizes of the powders prepared by the FEAG and ultrasonic spray pyrolysis processes affected the photoluminescence intensities of the phosphor powders.

Conclusions

Two different spray generators were applied to the preparation of $LaPO_4$:Tb phosphor powders by spray pyrolysis. The mean sizes and morphologies of the prepared $LaPO_4$:Tb phosphor powders were affected by the type of the spray generator and the concentration of the spray solution. The size of droplets formed by the FEAG process was finer than that of the droplets formed by the ultrasonic spray generator. Therefore, the mean sizes of $LaPO_4$:Tb phosphor powders prepared by the FEAG process was finer than those of the powders prepared by the ultrasonic spray pyrolysis process. The different mean sizes of the phosphor powders affected the photoluminescence intensities of the phosphor powders prepared by the FEAG and ultrasonic spray pyrolysis processes.

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