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Micrometre-sized zinc silicate phosphor powders prepared using a size-controllable droplet generator from a polyethylene glycol spray solution

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Spherical shape Zn_2SiO_4:Mn,Ba phosphor powders several micrometres in size were prepared by a filter expansion aerosol generator (FEAG) process. The mean size of the Zn_2SiO_4:Mn,Ba phosphor powders prepared by the FEAG process from a spray solution containing polyethylene glycol (PEG) was 1.5 μm. On the other hand, the mean size of the Zn_2SiO_4:Mn,Ba phosphor powders prepared by ultrasonic spray pyrolysis from the same concentration of the spray solution was 0.5 μm. The maximum photoluminescence intensity of the phosphor powders obtained from the spray solution with 8×10^{-4} M PEG was 109% of that of the phosphor powders obtained from the spray solution without PEG. The minimum photoluminescence intensity of the phosphor powders obtained from the spray solution with 1.6×10^{-3} M PEG was 85% of that of the phosphor powders obtained from the spray solution without PEG.

Key Words: spray pyrolysis, gas phase reaction, phosphor, zinc silicate.

Introduction

It is well known that the shape and mean size of powders are important properties in their applications. Currently, a great deal of interest has been focused on the synthesis/processing and characterization of nano-sized powders. However, in some application fields, functional ceramic powders with the mean sizes between 1 and 3 μm are required. In particular, phosphor powders with mean sizes between 1 and 3 μm are usually applied in plasma display panels (PDPs).

Spray pyrolysis has advantages in the preparation of advanced ceramic, metal and glass powders with controlled morphologies and stoichiometries [1-7]. The characteristics of the powders prepared by spray pyrolysis are mainly determined by the type of liquid aerosol generator. An ultrasonic spray generator, which has reasonable production rates of several micrometre droplets, is mainly applied to the preparation of advanced ceramic, metal and glass powders [1-7]. Various types of phosphor powders with a spherical shape have also been prepared by ultrasonic spray pyrolysis. However, the phosphor powders prepared by ultrasonic spray pyrolysis had a mean size of 1 micrometre or submicron sizes. An ultrasonic liquid droplet generator, in which the mean size of droplets is near to 5 micrometres, has a restriction in the preparation of phosphor powders with a size of several micrometres.

The filter expansion aerosol generator (FEAG) process, which is a liquid aerosol generator that produces droplets under low pressure, was also been applied to the preparation of advanced ceramic, metal and glass powders [8-12]. The powders prepared by the FEAG process have similar characteristics to those prepared by ultrasonic spray pyrolysis.

In this study, the new capability of droplet generation by the FEAG process was applied to the preparation of Zn_2SiO_4:Mn,Ba phosphor powders of micrometres size. The mean size of droplets generated by FEAG process was controllable by changing the characteristics of the spray solution such as its surface tension and viscosity. The mean size of the Zn_2SiO_4:Mn,Ba phosphor powders prepared by the FEAG process from a spray solution containing polyethylene glycol (PEG) was 1.5 μm. On the other hand, the mean size of Zn_2SiO_4:Mn,Ba phosphor powders prepared by the ultrasonic spray pyrolysis from the same concentration of spray solution without PEG was 0.5 μm. Polyethylene glycol (PEG) added to the spray solution affected the mean size of droplets generated by the FEAG process. The effects of the concentration of PEG on the morphologies, mean sizes and photoluminescence intensities of the Zn_2SiO_4:Mn,Ba phosphor powders were also investigated.

Experimental Procedure

A schematic diagram of the FEAG process used in this study was shown in Fig. 1. The FEAG process consists of a porous glass filter, an ultrasonic spray generator, a vacuum pump and a bag filter. An ultrasonic spray generator was used as a system to supply the spray solution in a continuous and uniform quantity. The spray solution was supplied through an ultrasonic spray generator using a carrier gas on to a glass filter surface where it forms a thin liquid film. This liquid film is passed through the filter pores by the carrier gas and

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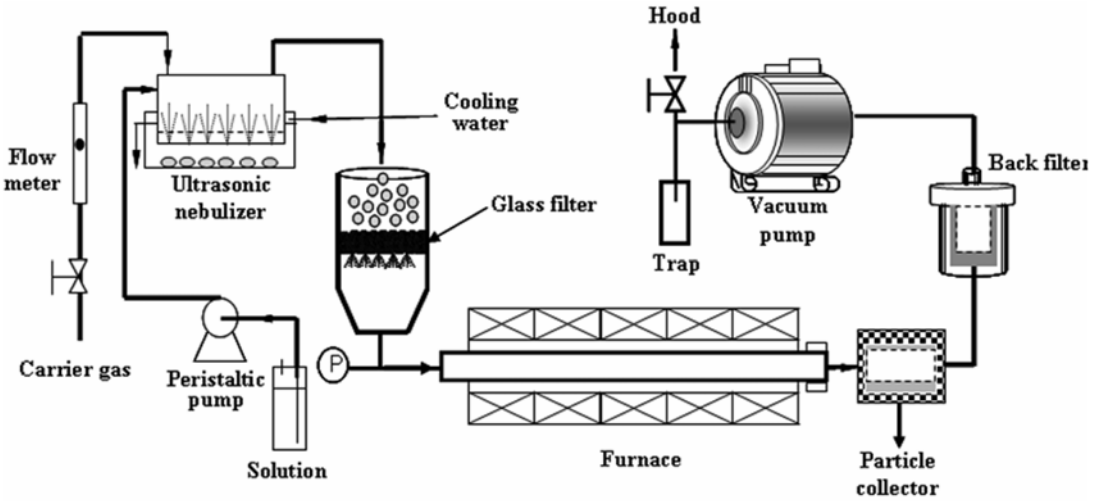

Fig. 1. Schematic diagram of the filter expansion aerosol generator process.

expanded into a low pressure chamber. The droplet formation mechanism in the FEAG process was investigated in our previous paper [8]. A metal salt solution is atomized into droplets and delivered into a hot-wall reactor at 40,000 Pa. As the aerosol stream passes through the reactor, the solvent evaporates and the metal salt decomposes to form product powders. At the end of the reactor, a powder collection filter and vacuum pump of 600 l minute^{-1} are connected in series. The length and diameter of the quartz reactor were 1,200 and 50 mm, respectively.

$Zn_{1.9}SiO_4$:$Mn_{0.1}$,$Ba_{0.001}$ phosphor powders were prepared by spray pyrolysis from aqueous and polymeric precursor solutions. The starting materials were zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, Aldrich], tetraethyl orthosilicate (TEOS) [$Si(OC_2H_5)_4$, Aldrich], manganese acetate tetrahy-drate [$Mn(CH_3COO) \cdot 4H_2O$, Aldrich], barium nitrate [$Ba(NO_3)_2$, Aldrich]. The concentration of the Si component was 117% of the stoichiometric amount for Zn_2SiO_4. The total concentration of metal components was 0.3 M. The polymeric precursor solution was prepared by dissolving polyethylene glycol (PEG 200) into the spray solution. The concentration of polyethylene glycol was altered from 1.6×10^{-4} to 1.6×10^{-3} M. The powders were prepared at 900°C by the FEAG process and post-treated at 1150 °C for 3 h for further crystallization. The reduction of the powders to activate the manganese dopant was conducted at 775 °C for 1 h under a 5% H_2/N_2 mixed gas. The crystal structures of the powders were studied by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation ($\lambda = 1.5418 \times 10^{-10}$ m). The morphologies of powders were investigated by scanning electron microscopy (SEM, JEOL, JSM 6060). The luminescence characteristics of the prepared powders under vacuum ultraviolet (VUV) were measured using a D_2 lamp. Surface area measurements were made by the Brunauer-Emmett-Teller (BET) method using N_2 as the adsorbate gas. The surface tension of spray solutions were measured with a thermostatic 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 mNm^{-1} at 20 °C). Viscosity measurements were made using an Ostwald viscometer immersed in a water bath maintained at a temperature of 20 °C.

Results and Discussion

The morphologies of the precursor powders obtained by the FEAG process from the spray solutions with and without PEG are shown in Fig. 2. The morphologies, mean sizes and size distributions of the precursor powders were affected by the concentration of PEG dissolved in the spray solution. The precursor powders obtained from the spray solution without PEG were several micrometres in size and had a distorted spherical shape. On the other hand, the precursor powders obtained from the spray solutions with PEG had a spherical shape and smooth surfaces irrespective of the concentration of PEG. The difference of morphologies of the precursor powders obtained from the spray solution with and without PEG is due to the change of the drying rate of droplets inside the hot wall reactor. PEG retarded the drying rate of droplets inside the hot wall reactor by forming a viscous gel. Therefore, the mean sizes and size distributions of the precursor powders were affected by the concentration of PEG added to the spray solutions. The precursor powders obtained from the spray solutions with low concentrations of PEG below 8×10^{-4} M had narrow size distributions. On the other hand, the precursor powders obtained from the spray solutions with high concentrations of PEG above 1.1×10^{-3} M had broad size distributions. The mean size of the precursor powders obtained from the spray solutions with concentrations of PEG of 4.8×10^{-4} and 8×10^{-4} M were 0.85 and 1.5 μm. The change of the mean sizes and size distributions of the precursor powders according to the concentrations of PEG added to the spray solutions were caused by the difference

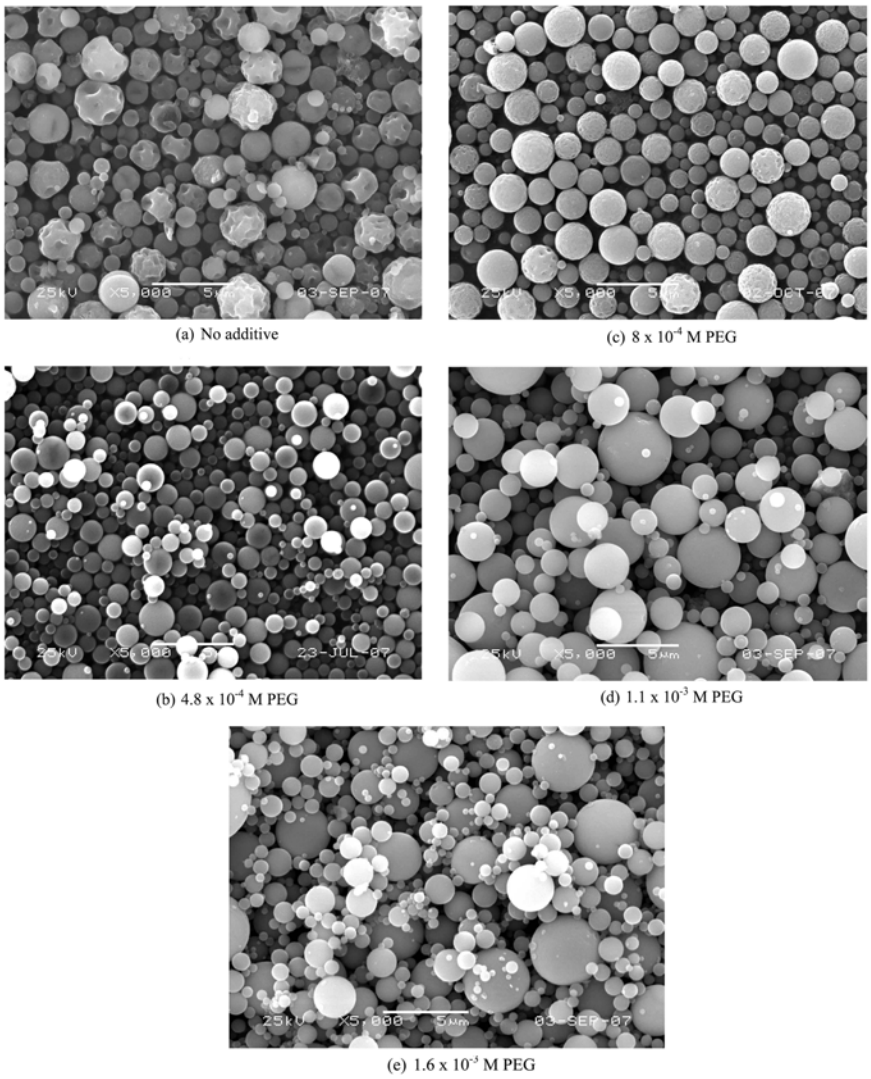

Fig. 2. SEM micrographs of the precursor powders prepared by the FEAG process.

of the size of the droplets produced by the FEAG process. The mean sizes and size distributions of droplets produced by the FEAG process were affected by the properties of the spray solutions such as viscosity and surface tension. The changes of the viscosity and surface tension of the spray solutions according to the concentrations of PEG are shown in Table 1. The surface tension of the spray solution dropped from 65 to 42 mN/m when the concentration of PEG added to the spray solution was 8×10^{-4} M. The viscosity of the spray solution increased with an increase in the concentration of PEG added to the spray solution. The addition of a small amount of PEG to the spray solution decreased the mean size of droplets produced by the FEAG process by decreasing the surface tension of the spray solution. Conversely, the addition of a large amount of PEG to the spray solution increased the mean size of droplets by increasing the viscosity of the spray solution. Therefore, the precursor powders obtained from a spray solution with a low concentration of PEG of 4.8×10^{-4} M had the minimum mean size. A high viscosity of the spray solution increased the size distribution of droplets produced by FEAG process. Therefore, the precursor powders obtained from the spray solution with a high concentration of PEG of 1.6×10^{-3} M had a broad size distribution.

Table 1. Physical properties of the spray solutions.

Concentration of PEG (M)	viscosity ($\times 10^{-3}$ Pa s)	surface tension (mN/m)
0	0.89	65
1.6×10^{-4} M	0.9	54
4.8×10^{-4} M	0.92	45
8×10^{-4} M	0.95	42
1.1×10^{-3} M	0.96	56
1.6×10^{-3} M	1	56

Fig. 3 shows the morphology of the precursor powders prepared by ultrasonic spray pyrolysis from the spray solution without PEG. The flow rate of the carrier gas was

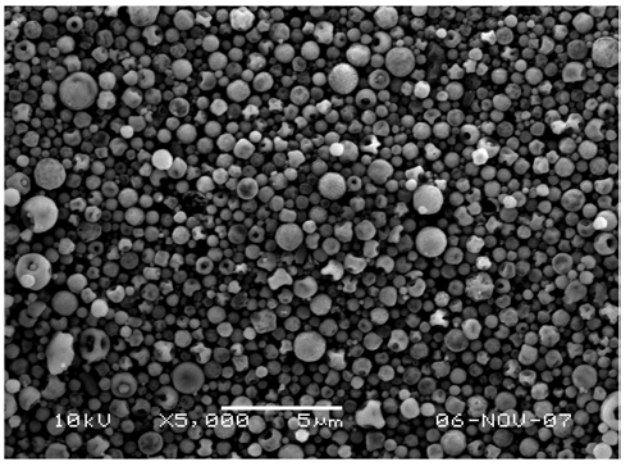

Fig. 3. SEM micrograph of the precursor powders prepared by ultrasonic spray pyrolysis.

20 l minute^{-1}. The precursor powders had a spherical shape and hollow morphology. The mean size of the precursor powders was 0.5 μm. However, the mean size of the precursor powders prepared by the FEAG process from the spray solution with a concentration of PEG of 8×10^{-4} M was 1.5 μm. The mean size of droplets produced by the FEAG process from the PEG spray solution at 40,00 Pa was larger than that of the droplets produced by an ultrasonic spray generator. Therefore, the precursor powders prepared by the FEAG process had a larger size than those prepared by ultrasonic spray pyrolysis.

Fig. 4 shows SEM micrographs of the post-treated Zn_2SiO_4:Mn,Ba powders. The concentration of PEG added to the spray solution affected the morphologies of the post-treated phosphor powders. The phosphor powders maintained a spherical shape and non-aggregation characteristics of the precursor powders after posttreatment

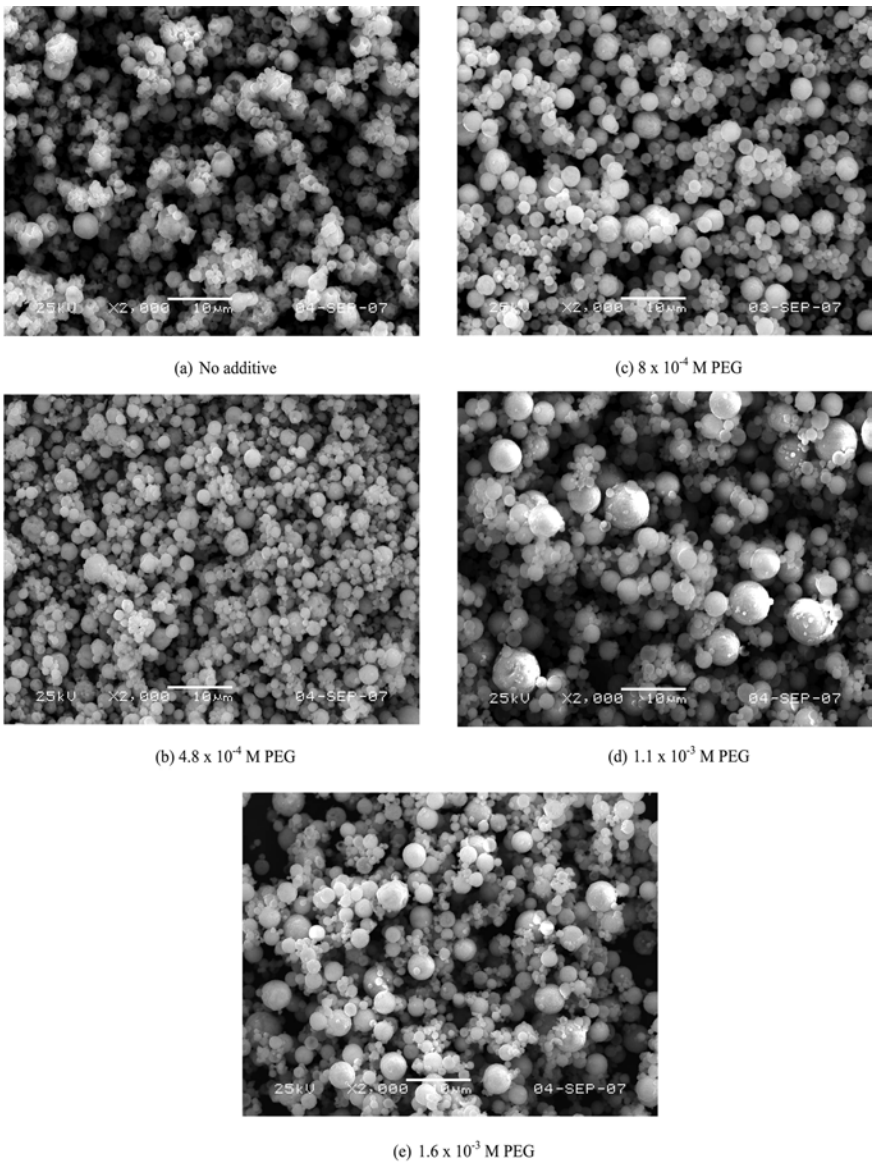

Fig. 4. SEM micrographs of the phosphor powders prepared by the FEAG process.

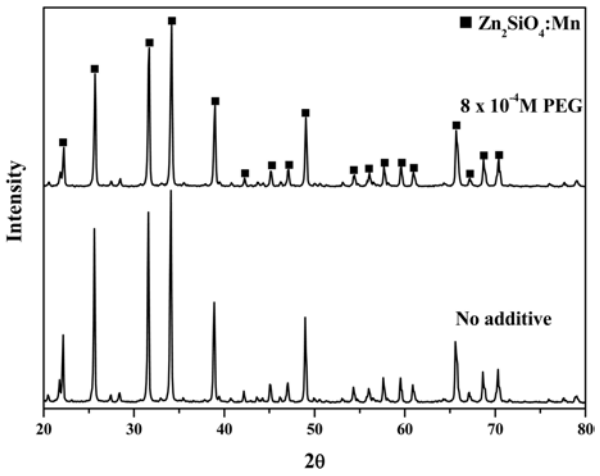

Fig. 5. X-ray diffraction patterns of the phosphor powders prepared by the FEAG process.

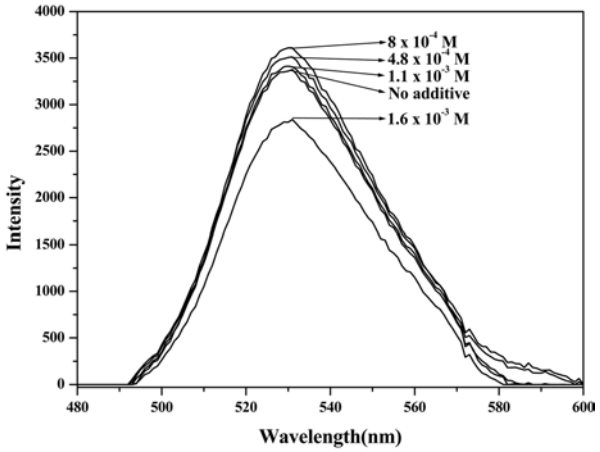

Fig. 6. Photoluminescence spectra of the phosphor powders prepared by the FEAG process.

irrespective of the concentration of PEG. However, the phosphor powders obtained from the spray solution without PEG had a porous and distorted morphology. The addition of PEG to the spray solution improved the sphericity of the phosphor powders. Fig. 5 shows the XRD patterns of the post-treated Zn_2SiO_4:Mn,Ba powders. The post-treated phosphor powders obtained from the spray solutions with and without PEG had a pure Willemite Zn_2SiO_4 crystal phase. The mean crystallite sizes of the phosphor powders obtained from the spray solutions with and without PEG calculated from Scherrer's equation were 42 and 52 nm.

Fig. 6 shows the photoluminescence characteristics of the phosphor powders obtained from the spray solutions with and without PEG. The phosphor powders had the same wavelength showing the maximum peak intensity irrespective of the concentration of PEG added to the spray solution. The maximum photoluminescence intensity of the phosphor powders obtained from the spray solution with 8×10^{-4} M PEG was 109% of that of the phosphor powders obtained from the spray solution without PEG. The minimum photoluminescence intensity of the phosphor powders obtained from the spray solution with 1.6×10^{-3} M PEG was 85% of that of the phosphor powders obtained from the spray solution without PEG. The surface area of the phosphor powders obtained from the spray solution without PEG was 1.7 m^2/g. On the other hand, the surface areas of the phosphor powders obtained from the spray solutions with 8×10^{-4} M and 1.6×10^{-3} M PEG were 1.2 and 2.0 m^2/g. The different morphologies and mean sizes of the powders affected the photoluminescence intensities of Zn_2SiO_4:Mn,Ba phosphor powders prepared by the FEAG process.

Conclusions

The effect of the type of spray generator on the characteristics of Zn_2SiO_4:Mn,Ba phosphor powders prepared by spray pyrolysis was investigated. The mean size of droplets produced by the FEAG process was larger than that of droplets produced by an ultrasonic spray generator. Therefore, the Zn_2SiO_4:Mn,Ba phosphor powders prepared by the FEAG process had a larger mean size than that of the phosphor powders prepared by ultrasonic spray pyrolysis. The change of surface tension and viscosity of the spray solution by adding PEG to the spray solution changed the mean size and morphology of the Zn_2SiO_4:Mn,Ba phosphor powders prepared by the FEAG process. The surface tension of the spray solution dropped from 65 to 42 mN/m when the concentration of PEG added to the spray solution was changed from 0 to 8×10^{-4} M and viscosity of the spray solution changed from 0.89 to 1×10^{-3} Pa·s. The concentration of PEG added to the spray solution affected the photoluminescence intensities of the Zn_2SiO_4:Mn, Ba phosphor powders under vacuum ultraviolet.

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