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Characteristics of the glass powders with low Pb content directly prepared by spray pyrolysis

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ABSTRACT

Fine size glass powders with a 21.5 mol% PbO–50.5 mol% B_2O_3–16 mol% SiO_2–12 mol% BaO–0.5 mol% CuO composition were directly prepared by spray pyrolysis. The glass powders prepared at 1000 °C had spherical shape and dense inner structure. The glass transition temperature (T_g) of the glass powders with the mean size of 0.84 μm was 493 °C. The number of voids in fired dielectric layers decreased with increasing the preparation temperature of the glass powders, and the dielectric layer formed from the glass powders prepared by spray pyrolysis at a temperature of 1000 °C had no voids inside the layer. The transmittances of the dielectric layer formed from the glass powders prepared at a temperature of 1000 °C were higher than 70% within the visible range. The mean sizes of the powders were changed from 0.36 to 1.0 μm when the concentrations of the spray solutions were changed from 0.03 to 1 M. The dielectric layers formed from the glass powders with small sizes had higher transmittances than those formed from the glass powders with large sizes.

1. Introduction

Plasma display panels (PDPs) use various types of glass powders for barrier ribs and dielectric layers of front and back panels [1–5]. The dielectric layer of front panel used as protective layer for electrode plays a key role in PDPs. These layers should have a low dielectric constant, a high transparency, a high breakdown voltage, a low firing temperature, and a reasonable thermal expansion coefficient. The characteristics of transparent dielectric layers are affected by the compositions of glass powder. Pb-based glass powders with low Pb content are commercially used as transparent dielectric layers in PDPs. The characteristics of transparent dielectric layers are also affected by the properties of glass powders because the thermal properties of glass changed according to the mean sizes of the powders [6]. The dielectric layers formed from the Bi-based glass powders with fine size had higher transparencies than those of the dielectric layers formed from the Bi-based glass powders with large size.

The glass powders for transparent dielectric layers were mainly prepared by a melting process [7,8]. Therefore, the commercially available glass powders had irregular shape and large size. In the previous studies, spray pyrolysis was applied to the preparation of glass powders with fine size and spherical shape [6,9–11]. Pb-rich glass powders with simple composition of 70 wt% PbO–20 wt% B_2O_3–10 wt% SiO_2 were prepared by spray pyrolysis [9,10].

In this study, glass powders with low Pb content, well known as the material of transparent dielectric layer, were directly prepared by spray pyrolysis. The effects of the preparation temperature, the flow rate of the carrier gas, and the concentration of the spray solution on the characteristics of the glass powders and dielectric layers formed from the prepared glass powders were investigated. The mean sizes of the glass powders in the spray pyrolysis could be controlled by changing the concentrations of spray solution.

2. Experimental procedure

The spray pyrolysis equipment used consisted of six ultrasonic spray generators that operated at 1.7 MHz, a 1000-mm-long tubular alumina reactor of 50-mm ID, and a bag filter. Glass powders with a 21.5 mol% PbO–50.5 mol% B_2O_3–16 mol% SiO_2–12 mol% BaO–0.5 mol% CuO composition were directly prepared by spray pyrolysis. The preparation temperatures were changed from 800 to 1000 °C. The flow rates of the carrier gas were changed from 10 to 30 L/min. The spray solutions were obtained by adding $Pb(NO_3)_2$ (Junsei, 99.5%), H_3BO_3 (Kanto, 99.5%), and tetraethyl orthosilicate (TEOS, Aldrich, 98%)), $Ba(NO_3)_2$ (Junsei, 99%), $Cu(NO_3)_2{\cdot}3H_2O$ (Junsei, 99.5%) to distilled water. The overall solution concentration of the glass components was fixed at 0.33 M.

The crystal structures of the prepared powders were investigated by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation (λ = 1.5418 Å). Measurement of the thermal properties of the prepared powders was performed on a thermo-analyzer (TG-DSC, Netzsch, STA409C) in the temperature range from 40 to 600 °C. The morphological characteristics of the prepared powders and fired

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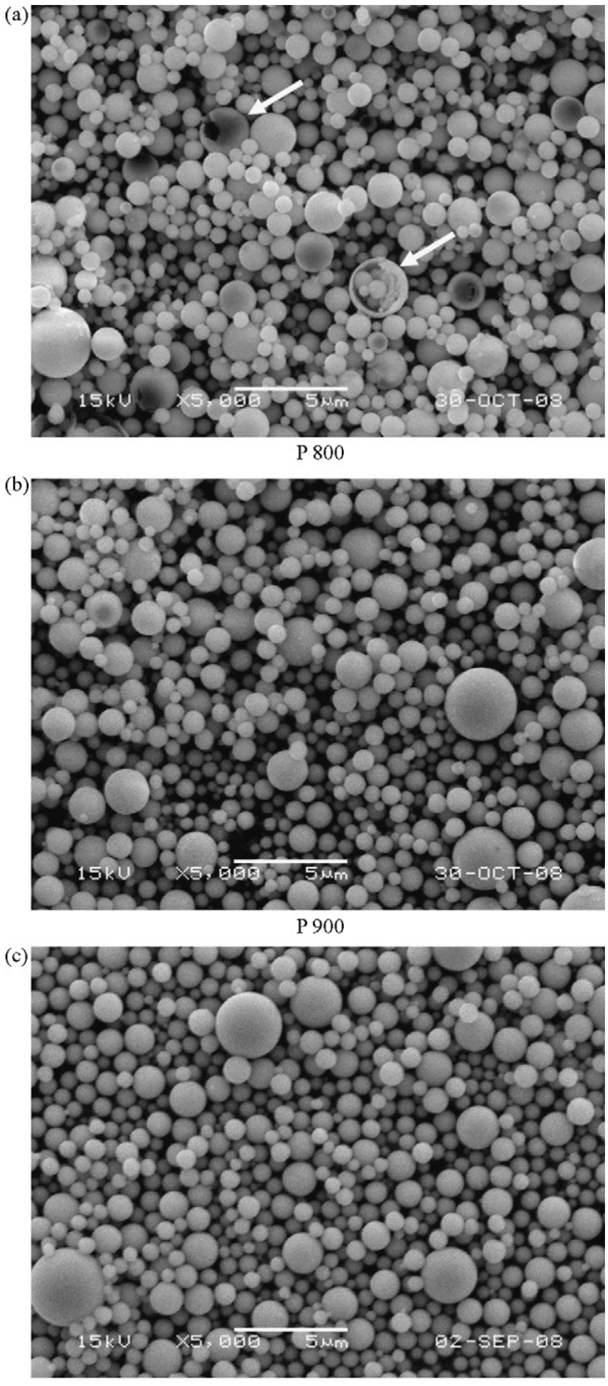


Fig. 1. SEM images of the glass powders prepared by spray pyrolysis at various temperatures.

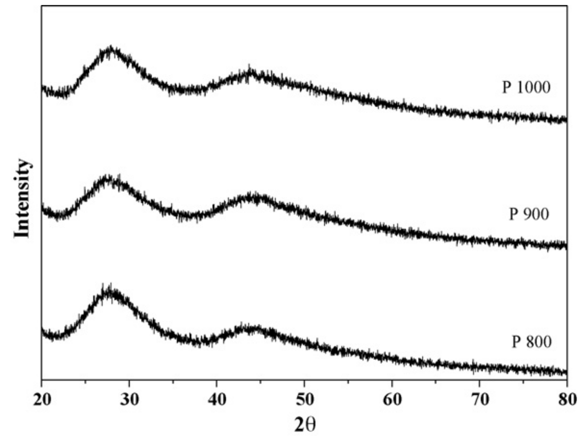


Fig. 2. XRD patterns of the glass powders prepared by spray pyrolysis at various temperatures.

dielectric layers were investigated by scanning electron microscopy (SEM, JEOL, JSM-6060). The transmittance of the dielectric layer was investigated by spectrophotometer within a visible light range (UV–vis spectrophotometer, Shimadzu, UV-2450).

3. Results and discussion

The morphologies of the powders prepared by spray pyrolysis at various temperatures are shown in Fig. 1. The concentration of the spray solution was 0.33 M. The flow rate of the carrier gas was 15 L/min. The powders had spherical shape and non-aggregation characteristics irrespective of the preparation temperatures. However, the inner structures of the powders were affected by the preparation temperatures. The powders prepared at 800 °C had hollow inner structure as shown by arrows in Fig. 1(a). The powders prepared at 900 and 1000 °C had dense inner structures. Fig. 2 shows the XRD patterns of the powders prepared at various temperatures. All the powders prepared by spray pyrolysis had broad peaks in the XRD patterns irrespective of the preparation temperatures. The broad peaks at around 28° in the XRD patterns represent the character of glass materials. Therefore, the prepared powders had glass phases irrespective of the preparation temperatures. In the spray pyrolysis, glass powders were prepared by melting and quenching processes. Partial melting of the powders at a preparation temperature of 800 °C results in the glass powders with hollow inner structure. However, complete melting of the glass powders inside the hot wall reactor maintained at temperatures of 900 and 1000 °C occurred.

Fig. 3 shows the SEM images of the glass powders prepared at 1000 °C according to the flow rate of the carrier gas. The concentration of the spray solution was 0.33 M. The powders prepared at a high flow rate of the carrier gas as 30 L/min had hollow inner structure as shown by arrows in Fig. 3(c). Complete melting of the glass powders did not occur when the flow rate of the carrier was as high as 30 L/min because of short residence time of the glass powders inside the hot wall reactor as 0.3 s. The mean sizes of the glass powders decreased with decrease of the flow rate of the carrier gas. Complete melting of the glass powders decreased the mean size of the powders when the flow rate of the carrier gas was as low as 10 L/min.

Fig. 4 shows the TG/DSC curves of the glass powders prepared by spray pyrolysis at various temperatures. The flow rate of the carrier gas was 15 L/min. In the TG curves, the slight weight losses of the powders due to the evaporation of adsorbed water and the decomposition of some incompletely decomposed precursor occurred at temperatures below 600 °C. The glass transition temperature (T_g) of the glass powders prepared at 1000 °C was 493 °C. The T_g of the glass powders was similar to that of the commercial glass powders with the same composition prepared by conventional melting and quenching process.

The glass powders prepared by spray pyrolysis at various temperatures were mixed with an organic vehicle that consisted of ethyl cellulose, α-terpineol, and butyl carbitol acetate (BCA). The glass powders and organic vehicle were mixed in a 7:3 weight ratio. The glass paste was screen-printed onto the soda-lime glass sub-

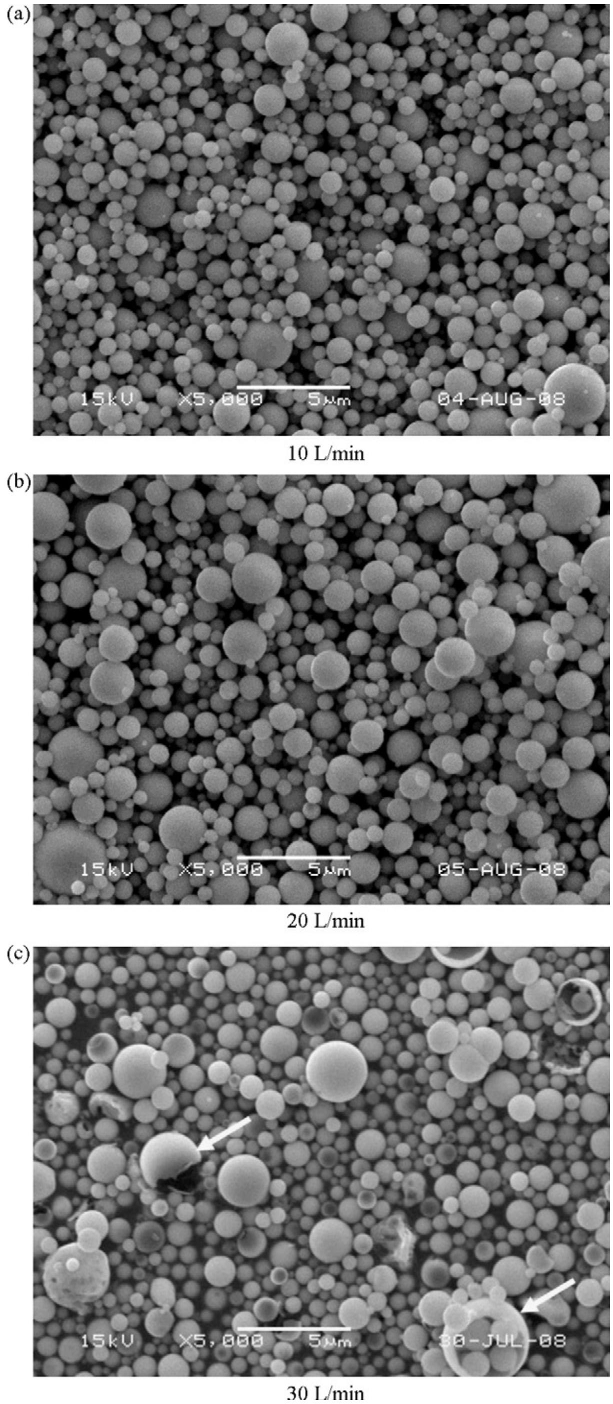


Fig. 3. SEM images of the glass powders prepared by spray pyrolysis at various flow rates of the carrier gas.

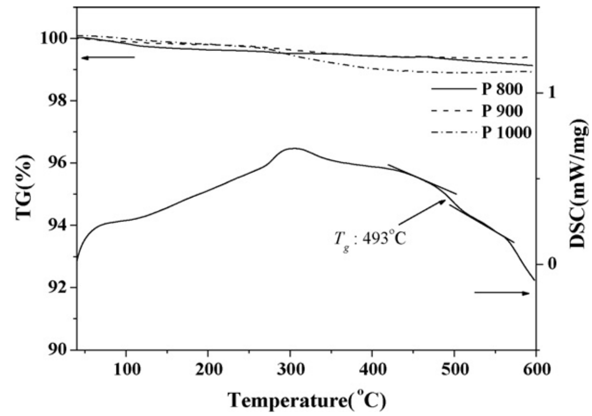


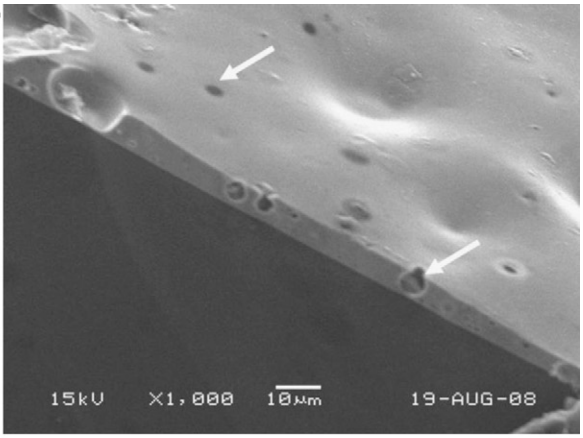
Fig. 4. TG/DSC curves of the glass powder prepared by spray pyrolysis.

strate. The printed glass substrate was dried at 120 °C for 30 min. The screen-printed glass substrate was fired by 2 steps, at first temperature of 400 °C for 10 min at a heating rate of 7 °C/min and in the second temperature of 580 °C for 6 min at a heating rate of 7 °C/min. Fig. 5 shows the cross-sections of the dielectric layers formed from the glass powders prepared at various temperatures. The dielectric layers formed from the glass powders prepared by spray pyrolysis at temperatures of 800 and 900 °C had voids inside the layers as shown by arrows. The number of voids decreased with increase of the preparation temperature of the glass powders, and the dielectric layer formed from the glass powders prepared by spray pyrolysis at a temperature of 1000 °C had no voids inside the layer. Fig. 6 shows the cross-section of the dielectric layer formed from the glass powders as shown in Fig. 3(c). The preparation temperature of the glass powders was 1000 °C. The dielectric layer formed from the glass powders prepared at a high flow rate of the carrier gas as 30 L/min had few voids inside the layer. The glass powders prepared at a high flow rate of the carrier gas as 30 L/min had hollow structure as shown in Fig. 3(c). The dielectric layers formed from the glass powders with hollow structures as shown in Figs. 1(a) and 3(c) had different structures. The hollow structure of the glass powders slightly affected the formation of voids inside the dielectric layers. Therefore, the hollow structure of the glass powders as shown in Fig. 1(a) was not the main reason for the formation of voids inside the layer. Incomplete formation of glass material at low preparation temperatures resulted in the dielectric layer with a number of voids.

Fig. 7 shows the transmittances of the dielectric layers formed from the glass powders prepared at various temperatures. The transmittances of the dielectric layers were strongly affected by the preparation temperatures of the glass powders. The transmittances of the dielectric layer formed from the glass powders prepared at a temperature of 1000 °C were higher than 70% within the visible range. However, the transmittances of the dielectric layer formed from the glass powders prepared at a temperature of 900 °C were as low as 30% within the visible range. The dielectric layer formed from the glass powders prepared at a temperature of 800 °C was opaque in the visible range.

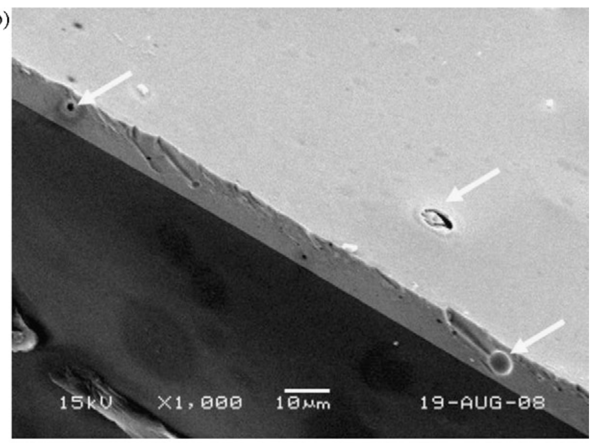
Fig. 8 shows the transmittances of the dielectric layers formed from the glass powders prepared at various flow rates of the carrier gas. The layers formed from the glass powders prepared at a temperature of 1000 °C were fired at a temperature of 580 °C. The dielectric layers formed from the glass powders prepared by spray pyrolysis at flow rates of the carrier gas of 15 and 20 L/min had transmittances higher than 70% within the visible range. However, the dielectric layer formed from the glass powders prepared by spray pyrolysis at a high flow rate of the carrier gas of 30 L/min was opaque in the visible range. Evaporation of some glass component occurred when the flow rate of the carrier gas was low as 10 L/min because of increased residence time of the powders inside the hot wall reactor. Therefore, the dielectric layer formed from the glass powders prepared by spray pyrolysis at a low flow rate of the carrier gas of 10 L/min had low transmittance.

(a)



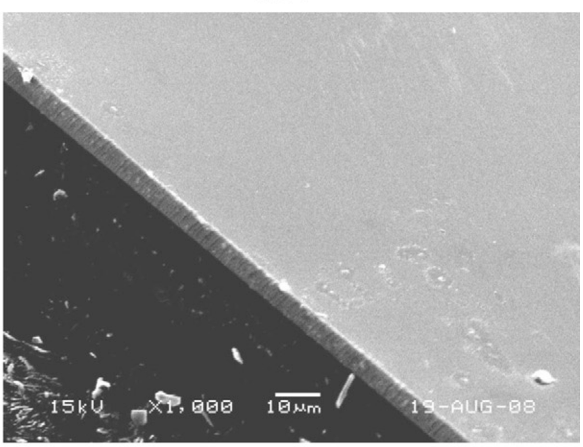
P 800

(b)



P 900

(c)



P 1000

Fig. 5. SEM images of cross-sections of dielectric layers formed from the powders obtained at various temperatures.

Fig. 9 shows the SEM images of the glass powders prepared by spray pyrolysis from the spray solutions with various concentrations at 1000 °C. The flow rate of the carrier gas was 15 L/min. The mean sizes of the powders were changed from 0.36 to 1.0 µm when the concentrations of the spray solutions were changed from 0.03 to 1 M. In this study, one glass particle was formed from one droplet. Therefore, the mean size of the glass powders decreased with decrease of the concentration of the spray solution. The melting characteristics of the glass powders were affected by the mean

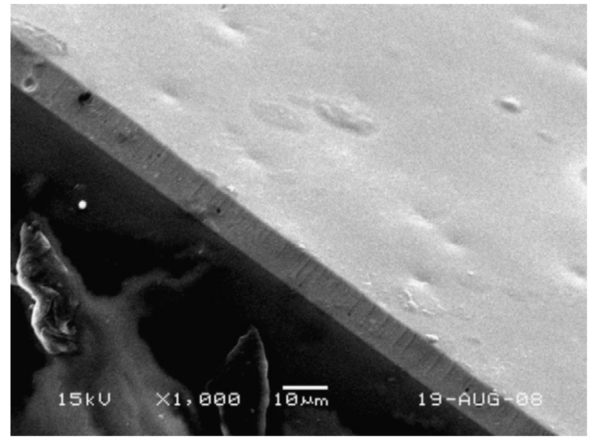


Fig. 6. SEM image of cross-section of dielectric layer formed from the powders prepared at a high flow rate of the carrier gas.

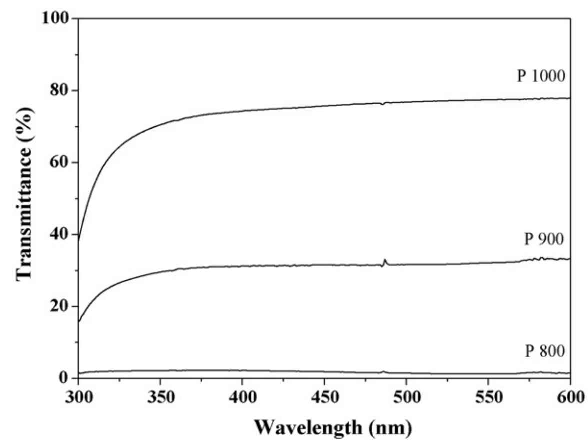


Fig. 7. Transmittances of dielectric layers formed from the powders obtained at various temperatures.

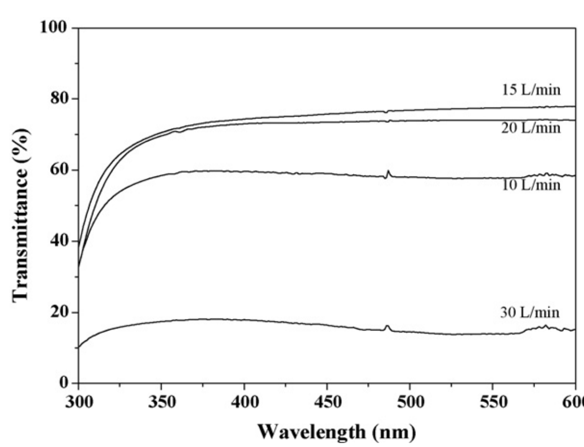


Fig. 8. Transmittances of dielectric layers formed from the powders obtained at various flow rates of the carrier gas.

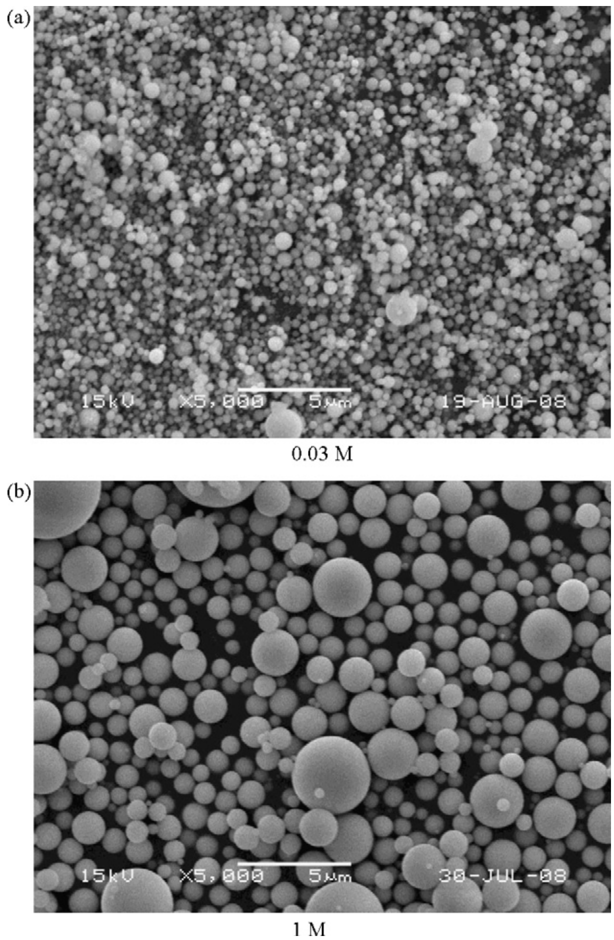


Fig. 9. SEM images of the glass powders prepared by spray pyrolysis from the spray solutions with various concentrations.

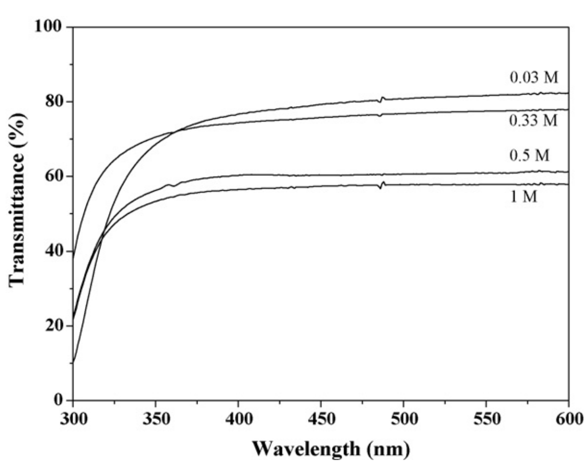


Fig. 10. Transmittances of dielectric layers formed from the powders with various mean sizes.

sizes of the powders. Therefore, the transmittances of the dielectric layers were affected by the mean sizes of the glass powders. Fig. 10 shows the transmittances of the dielectric layers formed from the glass powders with different mean sizes. The dielectric layers formed from the glass powders with small sizes had higher transmittances than those formed from the glass powders with large sizes.

4. Conclusions

Spherical shape glass powders with low Pb content were prepared by spray pyrolysis at various conditions. The optimum preparation temperature and the flow rate of the carrier gas to prepare the glass powders with low Pb content from the spray solution with 0.33 M were 1000 °C and 15 L/min, respectively. The structures and transmittances of the dielectric layers were affected by the preparation conditions of the glass powders. The dielectric layers formed from the glass powders prepared by spray pyrolysis at the optimum preparation conditions had clean surfaces and no voids. The dielectric layers formed from the glass powders with fine sizes had transmittances higher than 70% within the visible range.

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