J Electroceram (2009) 23:236–241
DOI 10.1007/s10832-007-9406-x

Size control of Pb-based glass powders between 38 and 84 nm in the flame spray pyrolysis

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Received: 31 May 2007 / Accepted: 16 December 2007 / Published online: 29 December 2007

Abstract Nano-sized Pb-based glass powders with different mean size, ranging from 38 to 84 nm were prepared by flame spray pyrolysis. The mean sizes of the glass powders were controlled by changing the concentration of spray solution. The glass powders prepared by flame spray pyrolysis from the spray solutions with different concentration had broad peaks at around 28° in the XRD patterns. The dielectric layers formed from the glass powders with the mean size of 38 nm had dense inner structures at firing temperatures of 480 and 520°C. On the other hand, the dielectric layer formed from the glass powders with the mean size of 84 nm had some voids inside the layer. The transmittances of the dielectric layer formed from the glass powders with the mean sizes of 38 and 84 nm were each 91% and 74% at firing temperature of 480°C.

Keywords Glass powder · Spray pyrolysis · Nano powder · Dielectric material

1 Introduction

The nano-sized glass powders in industries of electronic device and components are under investigation in a variety of applications because of their good processing properties and low softening temperature. The requirement of nano-sized glass powders increased with the development of new printing techniques involving ink-jet technology [1]. Glass materials are mainly prepared by conventional melting and quenching processes. The glass powders with irregular morphology and rough surface were formed by milling process of the glass materials formed by conventional melting and quenching processes [2–4]. Fine-sized glass powders are mainly prepared by wet milling process under liquid media. On the other hand, wet milling process causes the composition problem of the glass powders by leaching of some components to the liquid media. Various types of dry milling process are mainly applied to the preparation of glass powders. However, fine-sized glass powders could not be obtained in the dry milling processes. Liquid solution methods are under developing for the fine-sized glass powders [5]. Glass powders prepared by liquid solution methods are restrict to the applications in many fields of glass industries. For instance, glass powders prepared by liquid solution methods could not be applied for transparent dielectric materials.

Spray pyrolysis was applied to the preparation of glass powders with submicron size and spherical shape [6–8]. In the spray pyrolysis, glass powders were prepared by complete melting and quenching processes like conventional melting process. Therefore, the glass powders prepared by spray pyrolysis had good properties as the source materials for transparent dielectric layers. Flame spray pyrolysis is different from spray pyrolysis in energy source [9–15]. The high temperature diffusion flame causes melting and evaporation of powders to form the nano-sized glass powders. In this study, nano-sized Pb-based glass powders with different mean size, ranging from 38 to 84 nm were prepared by flame spray pyrolysis. The mean sizes of the glass powders were controlled by changing the concentration of spray solution. Optical properties of the dielectric layers formed from the size-controlled Pb-based glass powders were investigated.

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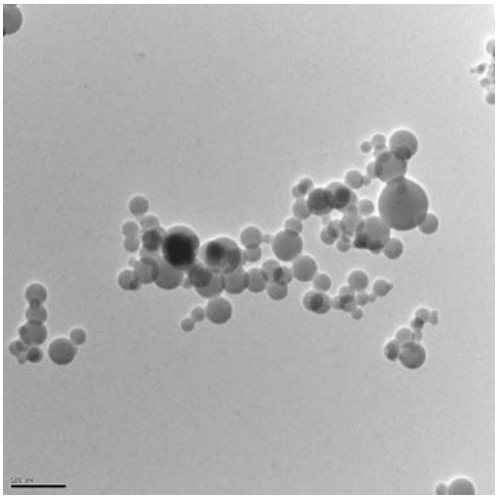
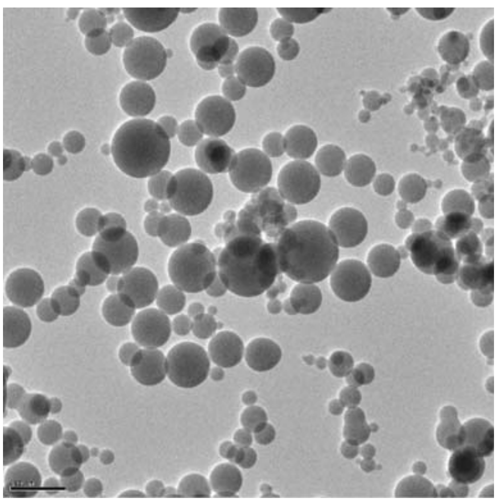
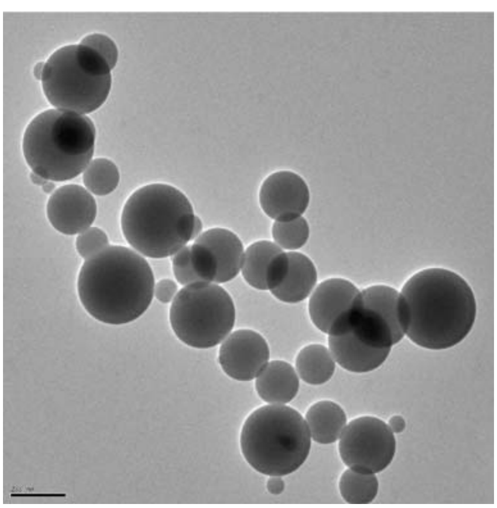


(a) 0.5 M



(b) 1 M



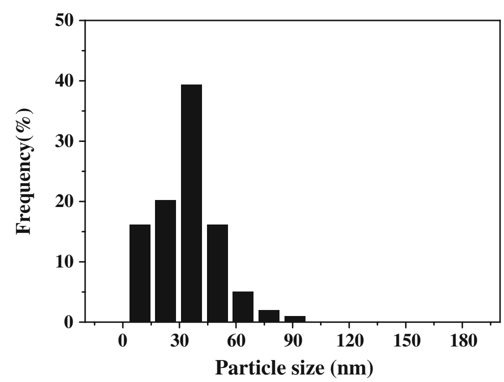
(c) 1.2 M

Fig. 1 (**a**)–(**c**) TEM photographs of the glass powders prepared from the spray solutions with different concentrations

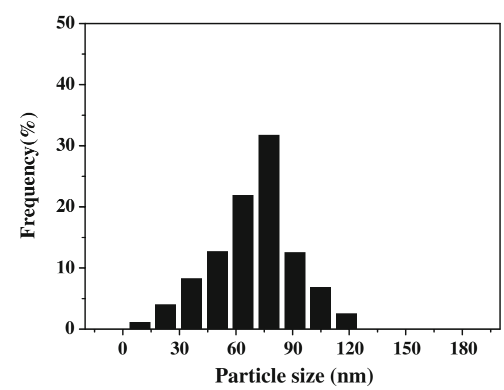
2 Experimental procedure

Size-controlled Pb-based glass powders were prepared by flame spray pyrolysis. Glass powders with a 70 wt% PbO–20 wt% B_2O_3–10 wt% SiO_2 composition were prepared from the aqueous spray solutions. The system of flame spray pyrolysis has a droplet generator, flame nozzle, quartz reactor, powder collector, and blower. A 1.7 MHz ultrasonic spray generator with six resonators is used to generate droplets, which are carried into the high-temperature diffusion flame by oxygen, as the carrier gas. Propane as the fuel and oxygen as the oxidizer create the diffusion flame. The flow rates of fuel, oxidizer and carrier gases were each 4.5, 35, and 10 l/min, in which the length of the diffusion flame was 20 cm. 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%) to distilled water. The overall solution concentrations were changed from 0.5 to 1.2 M.

The thermal properties of the prepared glass powders were measured using a thermo-analyzer (TG-DSC, Netzsch, STA409C, and Germany). X-ray diffraction patterns of glass powders were obtained using x-ray diffractometer (RIGAKU, DMAX-33 X-ray) with Ni filtered Cu Kα radiation (λ=



(a) 0.5 M



(b) 1.2 M

Fig. 2 (**a**) and (**b**) Size distributions of the glass powders prepared from the spray solutions with different concentrations

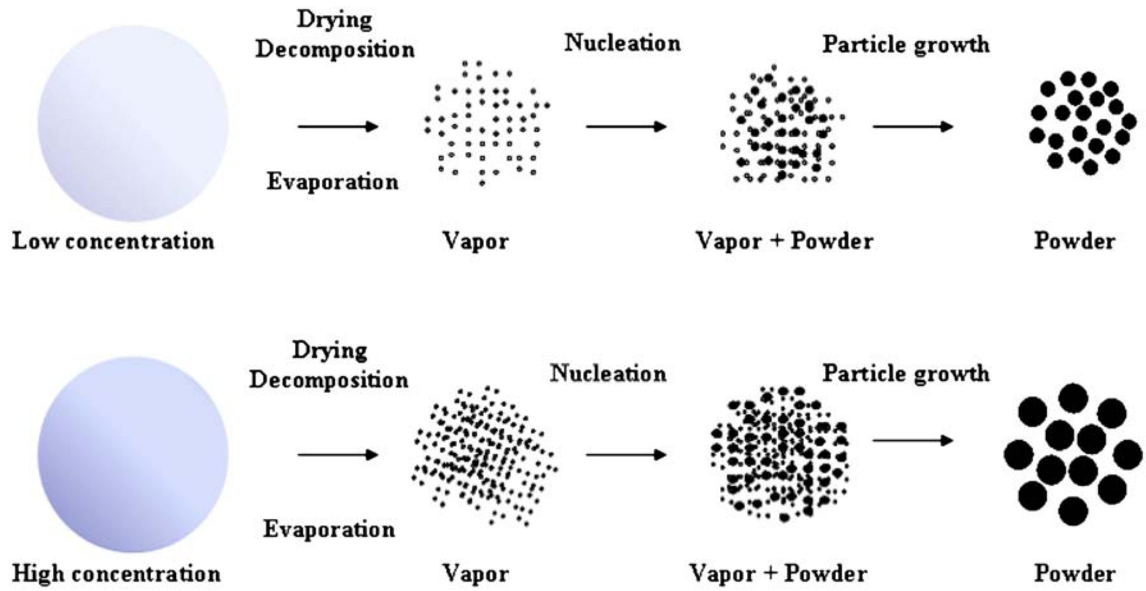


Fig. 3 The formation mechanisms of the nano-sized glass powder in the flame spray pyrolysis

1.5418 Å). Diffraction patterns were taken over the range of $10° \le 2\theta \le 80°$ with scan rate of 5° 2θ/min. The X-ray diffractometer was operated at 40 kV and 45 mA. The morphologies of the powders were investigated using transmission electron microscopy (TEM, FEI, TECHNAI 300K, The Kingdom of the Netherlands). The morphologies of the dielectric layers formed from the nano-sized glass powders were investigated using scanning electron microscopy (SEM, JEOL, JSM-6060, Japan). The transmittance of the dielectric layer was investigated using spectrophotometer within a visible light range (UV–Vis spectrophotometer, Shimadzu, UV-2450, Japan).

3 Results and discussion

The characteristics of the Pb-based glass powders prepared by flame spray pyrolysis are affected by the residence time of the powders and the temperature of diffusion flame. The glass powders prepared at the conditions of low temperature of diffusion flame or short residence time of the powders inside the high temperature diffusion flame had bimodal size distributions with nanometer and micron sizes. In this work, nano-sized glass powders were formed by chemical vapor deposition (CVD) process. Evaporation of the components composing the glass powders occurred at high temperature diffusion flame. Nano-sized glass powders were formed from the evaporated vapors by CVD process. Figure 1 shows the TEM photographs of the Pb-based glass powders prepared by flame spray pyrolysis from the spray solutions with different concentrations. The Pb-based glass powders had a completely spherical shape and a dense structure irrespective of the concentration of spray solution. However, the mean size of the powders prepared by flame spray pyrolysis was affected by the concentration of spray solution. The mean size of the glass powders increased with increasing the concentration of the spray solution. Figure 2 shows the size distributions of the Pb-based glass powders measured from the TEM photographs. The particle size distribution was determined from TEM images by counting more than 500 particles in each sample in order to minimize errors. The overall glass powders prepared from the spray solutions with the concentrations of 0.5 and 1.2 M had nanometer size below 100 nm. The mean sizes of the glass powders prepared from the spray solutions with the concentrations of 0.5 and 1.2 M were each 38 and 84 nm. The mean size of the glass powders prepared from the spray solution with concentration of 1 M was 53 nm. In this work, nano-sized glass powders were formed from the evaporated vapors by CVD process. Therefore, the concentrations of evaporated vapors generated from the droplets affected the mean size of the

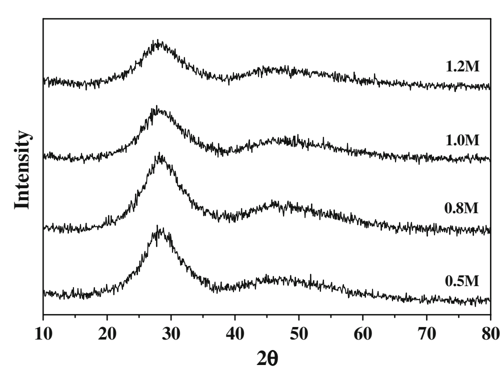


Fig. 4 XRD patterns of the glass powders prepared from the spray solutions with different concentrations

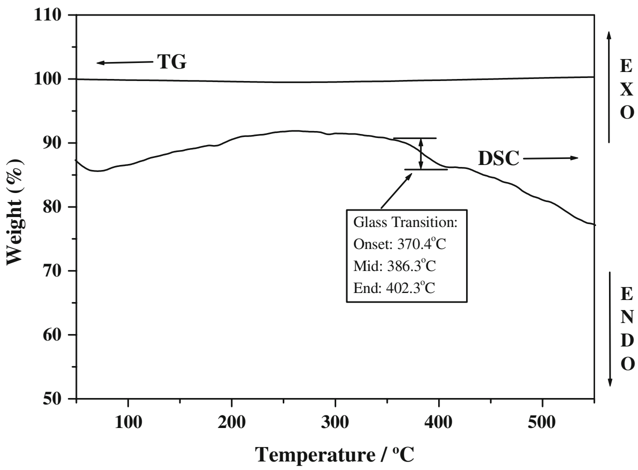
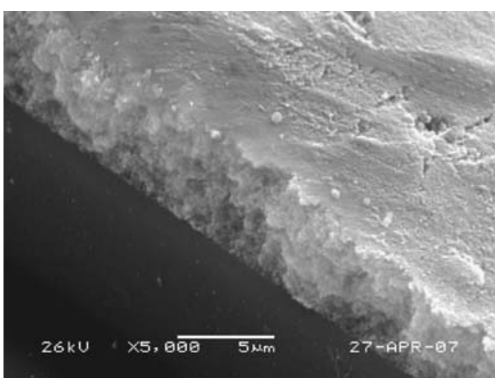


Fig. 5 TG/DSC curves of the nano-sized glass powders prepared by flame spray pyrolysis

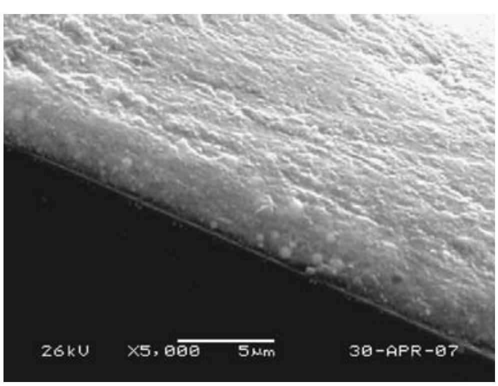
glass powders. Figure 3 shows the schematic diagram of the formation mechanism of nano-sized glass powders in the flame spray pyrolysis from the spray solution with different concentrations. The glass powders obtained from the vapors with high concentration had larger size than that of the glass powders obtained from the vapors with low concentration. In the CVD process, glass powders were formed by surface reaction and coagulation processes. In the surface reaction, the growth of the glass powders occurred by collisions of vapors to the powders. On the other hand, in the coagulation process, the large size glass powders were formed by collisions between the small sized powders. In the preparation of glass powders from the spray solution with high concentration, surface reaction and coagulation processes are actively occurred because of high concentration of evaporated vapors and high number concentration of small size powders formed by nucleation and growth processes. Therefore, the mean size of the glass powders increased with increasing the concentration of the spray solution.

As shown in Fig. 4, the glass powders prepared by flame spray pyrolysis from the spray solutions with different concentration had broad peaks at around 28° in the XRD patterns, which represent the character of glass materials. Nano-sized $PbO–B_2O_3–SiO_2$ powders had glass phase even at short residence time of the powders inside the high temperature diffusion flame.

The thermal properties of the nano-sized glass powders were measured using a thermo-analyzer in the temperature

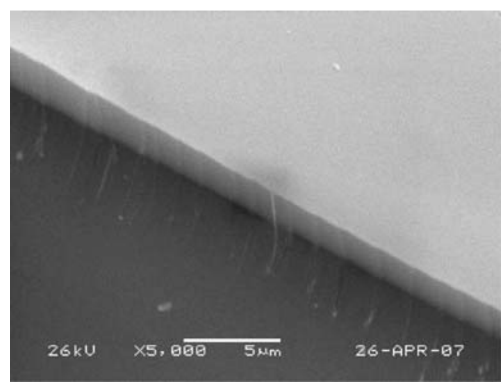


(a) 38 nm

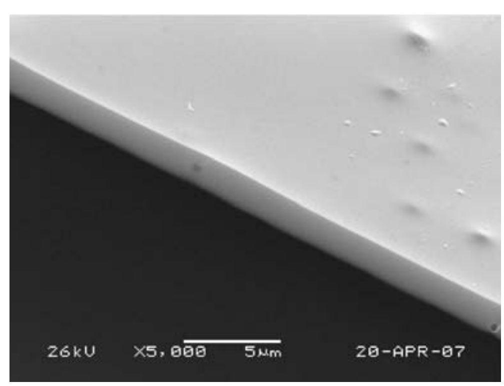


(b) 84 nm

Fig. 6 (**a**) and (**b**) SEM photographs of the cross-sections of the dielectric layers before firing



(a) 38 nm

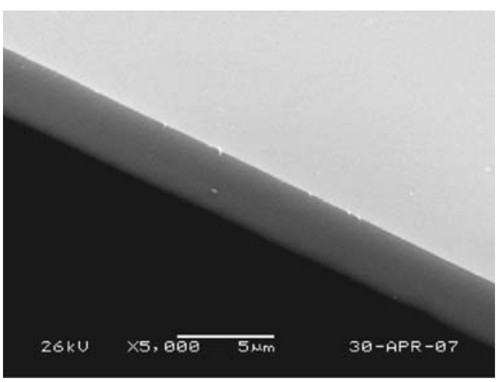


(b) 84 nm

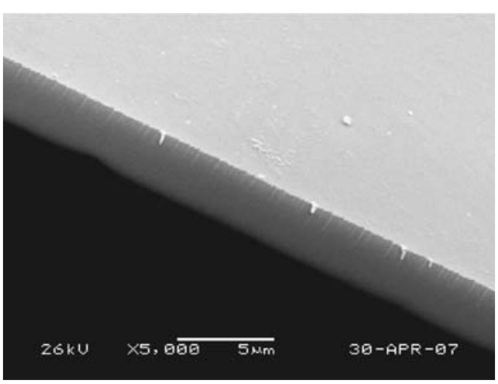
Fig. 7 (**a**) and (**b**) SEM photographs of the cross-sections of the dielectric layers fired at 480°C range from 40 to 600°C at a heating rate of 10°C/min. Figure 5 shows the TG/DSC curves of the nano-sized Pb-based glass powders as shown in Fig. 1(a). In the TG curves, the weight losses of the nano-sized glass powders did not occur in the temperature range from 40 to 500°C. Additionally, the glass powders had no endothermic or exothermic peaks in the DSC curves corresponding to the loss of water molecules and the decomposition of the precursors. The glass transition temperature (T_g) of the nano-sized glass powders was 386.3°C. The decrease of the mean size of the glass powders decreased the glass transition temperature of the glass powders. The T_g of the micron-sized glass powder prepared by ultrasonic spray pyrolysis was 407°C [8].

The nano-sized Pb-based glass powders prepared by flame spray pyrolysis from the spray solution with concentrations of 0.5 and 1.2 M were mixed with an organic vehicle that consisted of ethyl cellulose, α-terpineol, and butyl carbitol acetate (BCA). The glass paste was screen-printed onto the soda-lime glass substrate. The printed glass substrate was dried at 120°C for 30 min. The screen-printed glass substrate was fired by two steps, at first temperature of 400°C for 10 min at a heating rate of 7°C/min and in the second temperatures of 480 and 520°C for 6 min at a heating rate of 7°C/min. Figure 6 shows the SEM photographs of the cross-sections of the dielectric layers formed by screen printing method before firing. The printed layers formed from the nano-sized glass powders had dense structure. Figures 7 and 8 show the SEM photographs of the surfaces and cross-sections of the dielectric layers fired at temperatures of 480 and 520°C. The structures of the dielectric layers fired at low temperature of 480°C were affected by the mean sizes of the nano-sized glass powders. As shown in Fig. 7(b), the dielectric layer formed from the glass powders with the mean size of 84 nm had some voids inside the layer. On the other hand, the dielectric layer formed from the glass powders with the mean size of 38 nm had dense inner structure without voids. The decrease of the mean size of the nano-sized glass powders decreased the softening temperature of the glass powders [8]. However, the dielectric layers fired at temperature of 520°C had similar inner structures irrespective of the mean sizes of the nano-sized glass powders.

Figures 9 and 10 show the transmittances of the dielectric layers fired at temperatures of 480 and 520°C. The transmittances of the dielectric layers fired at temperature of 480°C were affected by the mean sizes of the nano-sized glass powders. The transmittances of the dielectric layer



(a) 38 nm



(b) 84 nm

Fig. 8 (**a**) and (**b**) SEM photographs of the cross-sections of the dielectric layers fired at 520°C

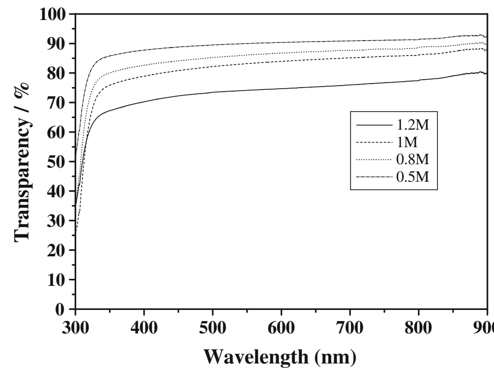


Fig. 9 Transmittance spectra of the dielectric layers fired at 480°C

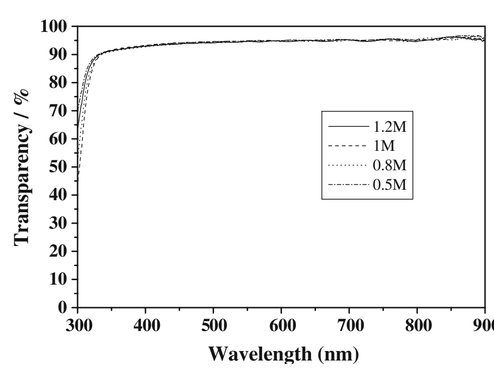


Fig. 10 Transmittance spectra of the dielectric layers fired at 520°C

formed from the glass powders with the mean size of 38 and 84 nm were each 91% and 74% at wavelength of 550 nm. However, the transmittances of the dielectric layers fired at temperature of 520°C were higher than 90% within the visible range irrespective of the mean sizes of the nano-sized glass powders.

4 Conclusion

Pb-based glass powders with nanometer size were prepared by flame spray pyrolysis. Nano-sized glass powders were formed from the evaporated vapors by CVD process. In the CVD process, glass powders were formed by surface reaction and coagulation processes. In the preparation of glass powders from the spray solution with high concentration, surface reaction and coagulation processes are actively occurred because of high concentration of evaporated vapors and high number concentration of small size powders formed by nucleation and growth processes. Therefore, the mean size of the glass powders increased with increasing the concentration of the spray solution. The decrease of the mean size of the nano-sized glass powders decreased the softening temperature of the glass powders. Therefore, the structures of the dielectric layers were affected by the mean size of the nano-sized glass powders at firing temperature of 480°C. The dielectric layers obtained from the nano-sized glass powders had high transmittances within a visible light range.

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