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Short communication

Characteristics of Bi-based glass powders with various glass transition temperatures prepared by spray pyrolysis

Hye Young Koo, Jang Heui Yi, Yun Chan Kang *

Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea

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Abstract

Spherical shape, submicron, and non-aggregated bismuth-based glass powders were prepared. Glass powders with low glass transition temperature melted the silver powders at firing temperatures of as low as 400 °C. After firing at 400 °C, the specific resistances of the silver conducting films obtained from glass powders with glass transition temperatures of 498 and 373 °C were 21.6 and 5.8 μΩ cm, respectively. After firing at 450 and 500 °C, the specific resistances of the silver conducting films obtained from glass powders with glass transition temperature of 425 °C were the lowest, i.e., 3.0 and 3.1 μΩ cm, respectively.

Keywords: A. Powders-gas phase reaction; A. Powders-chemical preparation

1. Introduction

Thick silver films used for making electrical contacts in devices such as solar cells and hybrid circuits are developed from a conducting paste containing silver particles, glass powders, and organic binders [1–3]. Although glass frit is used in minimal amounts in conducting pastes (1–5 wt%), it plays an important role in the formation of a silver conducting film [4]. The glass powders act as permanent binders and also promote sintering of the metal powders during the firing process and enable binding of the functional film to the substrate [4–8].

The softening and glass transition temperatures of glass powders are affected by the composition of glass materials. Lead and bismuth-based glass materials with different compositions are used as permanent binders in silver conducting films. Zhang et al. studied the influences of softening temperature (T_f) of lead–boron–silicate glasses on the microstructures of silver grid and the performances of silicon solar cells [4]. The properties of glass are also affected by the mean size and morphology of the powders [9–11]. Glass powders prepared by the conventional melting process are mainly used as permanent binders. Nonetheless, glass powders prepared by spray pyrolysis having an average size and morphology similar to those of silver powders also act as good permanent binders.

In this study, we prepared Bi-based glass powders with different glass transition temperatures by spray pyrolysis and determined the optimum preparation temperatures for the powders according to the glass transition temperatures. The effect of glass transition temperatures on the firing characteristics of silver conducting films was also investigated.

2. Experimental method

Bi-based glass powders with glass transition temperatures between 373 and 498 °C were directly prepared by spray pyrolysis using an equipment consisting of 6 ultrasonic spray generators that could be operated at 1.7 MHz, a 1000-mm-long tubular alumina reactor with an internal diameter of 50 mm, and a bag filter. The preparation temperatures ranged from 1300 to 1500 °C. The flow rate of the carrier gas was maintained at 20 L min^{-1}. The overall concentration of the solution of glass components was maintained at 0.5 M.

The crystal structures of the prepared glass powders were analyzed by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) using Cu Kα radiation (λ = 1.5418 Å). The morphological

* Corresponding author. Tel.: +82 2 2049 6010; fax: +82 2 458 3504.
E-mail address: yckang@konkuk.ac.kr (Y.C. Kang).

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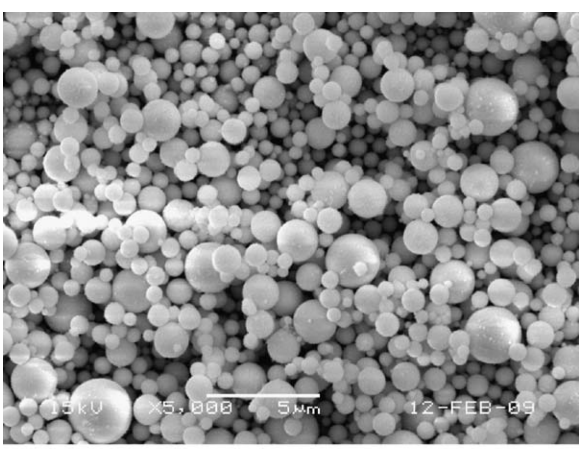
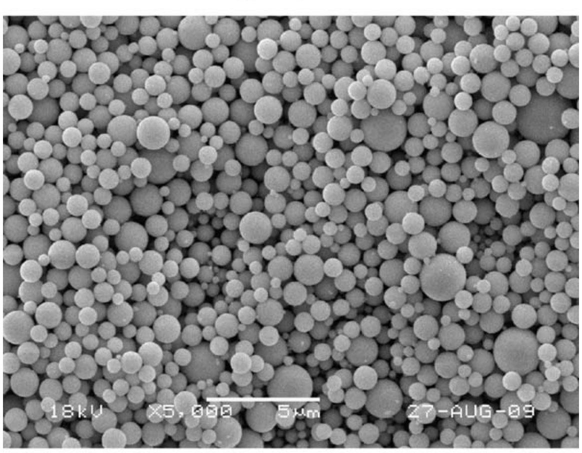
characteristics of the prepared glass powders and fired electrodes were analyzed by scanning electron microscopy (SEM, JEOL, JSM-6060). Dot-mapping was conducted using a field-emission-type scanning electron microscope (FE-SEM; Hitachi, S-4300) equipped with an electron dispersion spectrometer. The specific resistances of the silver electrodes were measured using the 4-point probe method (CMT-SR 1000N, Advanced Instrument Technology).

3. Results and discussion

The melting and quenching processes carried out inside a hot-wall reactor maintained at high temperature led to the formation of glass powders. At low preparation temperatures, the glass powders had hollow structures owing to their incomplete melting; this was because the powders remained in the hot-wall reactor for a shorter time. On the other hand, at high preparation temperatures, glass powders of nanometer and submicron sizes with bimodal size distribution were obtained. At the optimum preparation temperature, the glass powders had a spherical shape, submicron sizes, and non-aggregation characteristics, as shown in Fig. 1. The optimum preparation temperatures of the glass powders varied according to their compositions on the basis of their morphology and crystal structures; these values are presented in Table 1.



(a) Sample 1



(b) Sample 5

Fig. 1. SEM images of the glass powders with various glass transition temperatures.

Table 1
Properties of the glass powders with various glass transition temperatures (T_g).

	Composition	Prep. Temp. (°C)	T_g (°C)
Sample 1	Bi_2O_3–BaO–SiO_2–ZnO–B_2O_3	1400	498
Sample 2	Bi_2O_3–SiO_2–BaO–ZnO–B_2O_3	1400	485
Sample 3	Bi_2O_3–SiO_2–ZnO–BaO–B_2O_3–Al_2O_3	1300	472
Sample 4	Bi_2O_3–SiO_2–B_2O_3–BaO–Al_2O_3	1300	425
Sample 5	Bi_2O_3–ZnO–B_2O_3–SiO_2–Al_2O_3–BaO	1300	373

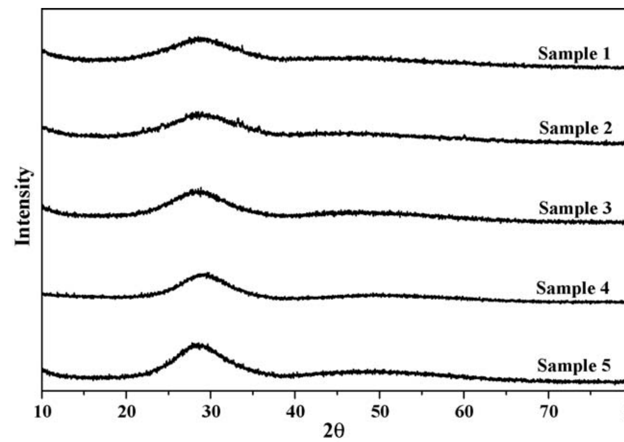


Fig. 2. XRD patterns of the glass powders with various glass transition temperatures.

As shown in Fig. 2, irrespective of their compositions, the glass powders exhibited broad peaks at around 28° in the XRD patterns, which is a characteristic feature of glass materials. Fig. 3 shows the thermogravimetric and differential scanning

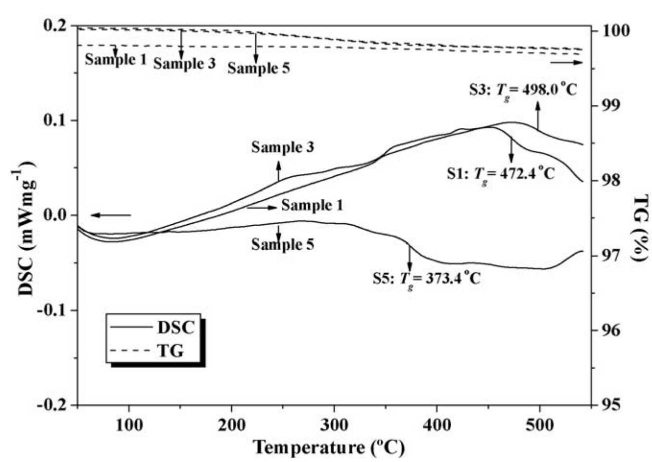


Fig. 3. TG/DSC curves of the glass powders with various glass transition temperatures.

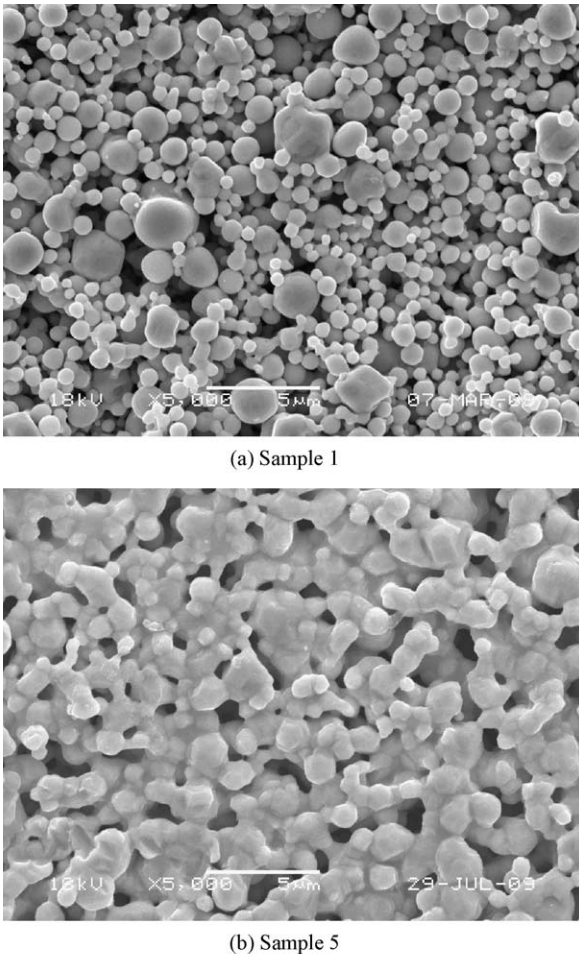


Fig. 4. SEM images of the surfaces of the silver conducting films fired at 400 °C.

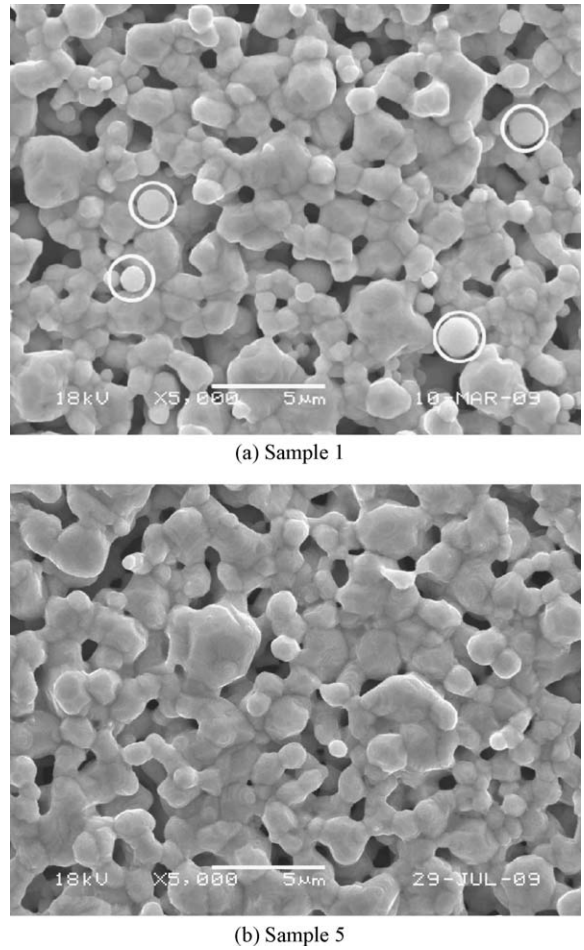


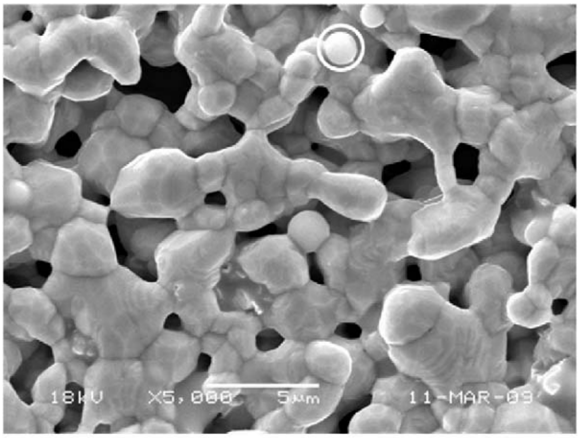
Fig. 5. SEM images of the surfaces of the silver conducting films fired at 450 °C.

calorimetric (TG/DSC) curves of the glass powders. The glass transition temperatures of samples 1, 3, and 5 were 498, 472, and 373 °C, respectively. High-purity glass powders were obtained by spray pyrolysis by the complete decomposition of precursors. Hence, the weight losses of the glass powders at temperatures below 550 °C were low, i.e., about 0.3 wt%, irrespective of the compositions of the glass materials.

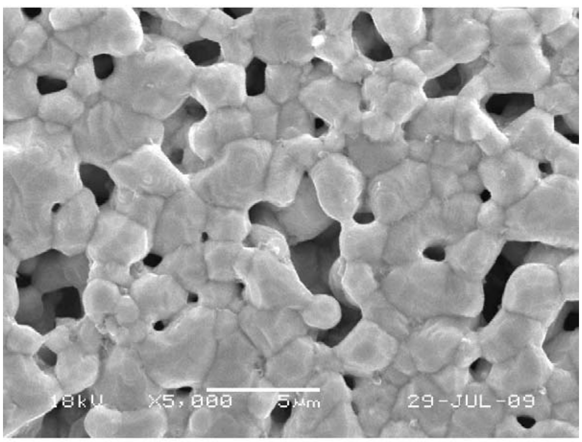
The characteristics of the Bi-based glass powders with different glass transition temperatures as inorganic binders were investigated. The silver powders prepared by spray pyrolysis were used as conducting materials. The printed, soda-lime glass substrate was fired for 20 min at 400, 450, and 500 °C. Fig. 4 shows the SEM images of the silver conducting films fired at 400 °C. The spherical shapes of the glass powders were maintained in the silver films containing glass powders with high glass transition temperatures. Necking between the silver powders occurred with the decrease in the glass transition temperatures of the glass powders. However, the glass powders with low glass transition temperature melted the silver powders at a firing temperature as low as 400 °C. Figs. 5 and 6 show the morphologies of the silver conducting films fired at 450 and 500 °C. At these temperatures, melting of the silver conducting films occurred irrespective of the glass transition temperatures. However, the glass powders with high glass transition temperatures did not melt, as shown in Figs. 5 and 6 (encircled areas). The glass powders with high glass transition temperature remained spherical in the silver conducting films, as shown in the dot-mapping image (Fig. 7(a)). On the other hand, the shape of the glass particles in the silver conducting film formed from glass powders with low glass transition temperature was non-spherical, as shown in the dot-mapping image (Fig. 7(b)).

Fig. 8 shows the SEM images of the cross-sections of the silver conducting films fired at 450 °C. The films formed from the silver paste containing glass powders with low glass transition temperature were denser than those formed from the silver paste containing glass powders with high transition temperature. The thicknesses of the silver conducting films shown in Fig. 8(a) and (b) were 5.9 and 3.8 μm, respectively.

After firing at 400 °C, the specific resistances of the silver conducting films formed from the glass powders with glass transition temperatures of 498 and 373 °C were 21.6 and 5.8 μΩ cm, respectively (Fig. 9). After firing at 450 and 500 °C, the specific resistances of the silver conducting films formed from the glass powders with a glass transition temperature of 425 °C were the lowest, i.e., 3.0 and 3.1 μΩ cm, respectively.

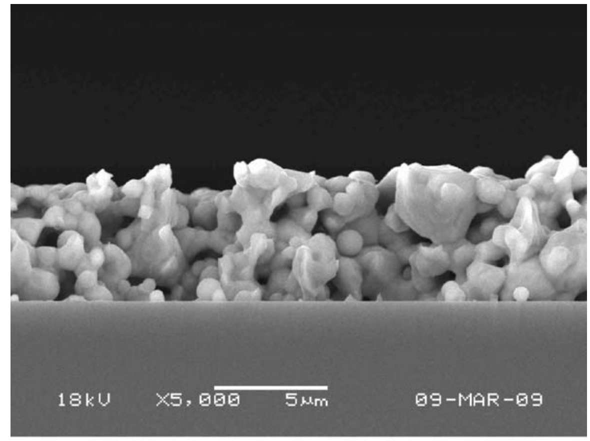


(a) Sample 1

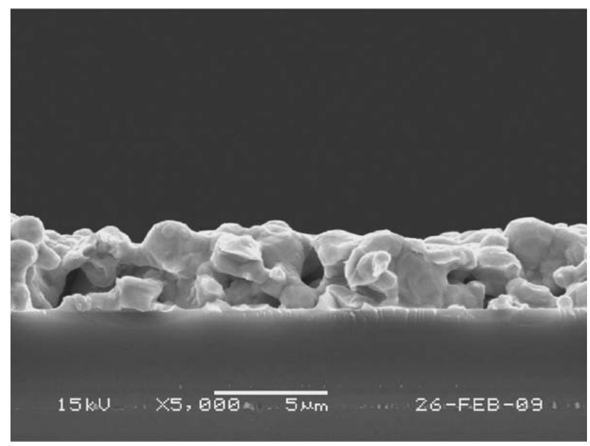


(b) Sample 5

Fig. 6. SEM images of the surfaces of the silver conducting films fired at 500 °C.

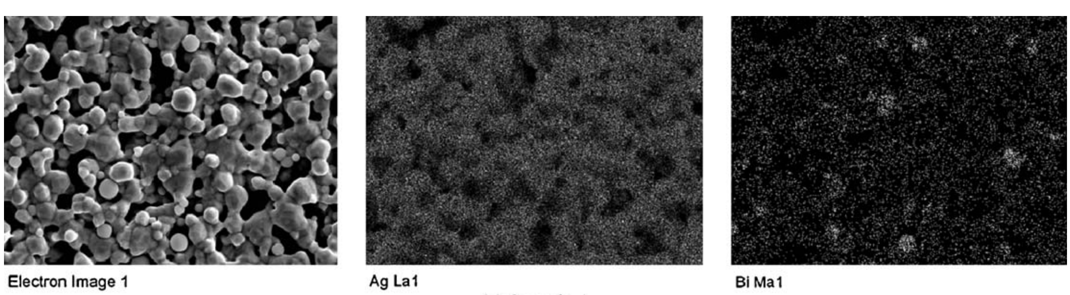


(a) Sample 1

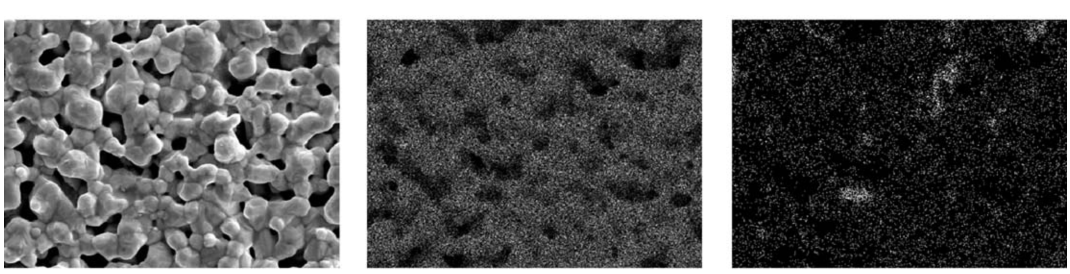


(b) Sample 5

Fig. 8. SEM images of the cross-sections of the silver conducting films fired at 450 °C.



(a) Sample 1



(b) Sample 5

Fig. 7. Results of dot-mapping of the surfaces of the silver conducting films fired at 450 °C.

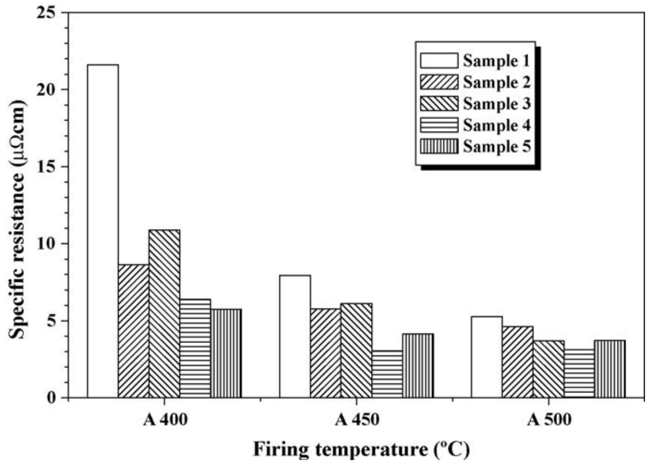


Fig. 9. Specific resistances of the silver conducting films fired at various temperatures.

4. Conclusions

The optimum preparation temperatures of Bi-based glass powders with different glass transition temperatures were determined. The glass transition temperatures of the glass powders affect the morphologies and electrical properties of the silver conducting films. Glass powders with glass transition temperatures of less than 425 °C are suitable to form silver conducting films with dense structures and low specific resistances at firing temperatures below 450 °C.

Acknowledgements

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