Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 687–690
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Characteristics of nanosized Bi-based glass powders prepared by flame spray pyrolysis as transparent dielectric layer material

Jung Hyun Kim [a], Hye Young Koo [a], You Na Ko [a], Dae Soo Jung [a], Yun Chan Kang [a,*], Jong-Heun Lee [b]

[a] Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea
[b] Department of Materials Science and Engineering, Korea University, Anam-dong, Sungbuk-ku, Seoul 136-713, Republic of Korea

Received 7 December 2009; received in revised form 18 January 2010; accepted 1 October 2010
Available online 29 October 2010

Abstract

Bi-based glass powders with particle size of 34 nm were prepared by high-temperature flame spray pyrolysis. The glass transition temperature (T_g) of the powders was 442 °C. Dielectric layers fired at temperatures of 480 and 500 °C contained voids, while those fired at temperatures above 540 °C had clean surfaces and no voids. The dielectric layers sintered at temperatures of 560 and 580 °C had transmittances of 70% in the visible range. Further, it was observed that the dielectric layers formed from the nanosized glass powders obtained from spray solutions containing excess boron had higher transmittances (80% in the visible range at a sintering temperature of 580 °C) than the layers formed from spray solutions containing stoichiometric amounts of boron.

Keywords: Chemical synthesis; Gas–solid reaction

1. Introduction

Various types of glass powders such as Pb-based glass powders are used for the fabrication of transparent dielectric layers in plasma display panels (PDPs). Studies on the development of Pb-free glass powders are being conducted by various research groups, and Bi-based glass powders are attracting considerable attention as raw materials for the fabrication of transparent dielectric layers in PDPs because of their low firing temperature and high transparency [1–3].

Fine glass powders for the fabrication of transparent dielectric layers have been obtained by spray pyrolysis and flame spray pyrolysis [4–9]. Pb-based and Bi-based glass powders prepared by spray pyrolysis have submicron-sized particles and spherical shapes, and the dielectric layers formed from these powders show good optical properties. Nanosized Pb-based glass powders have been prepared by high-temperature flame spray pyrolysis [8,9]. Nanosized glass powders have been formed by chemical vapor deposition (CVD). The conventional CVD process is advantageous when used for the preparation of nanosized powders having simple compositions; however, it is ineffective for the preparation of multicomponent oxide powders, because it is difficult to control the composition of the powders [10].

In this study, nanosized Bi-based glass powders were prepared by flame spray pyrolysis, and the optical properties of the dielectric layers formed from these glass powders were investigated. The effects of excess boron in the spray solution on the properties of the glass powders were investigated.

2. Experimental

Glass powders containing 42 wt% Bi_2O_3, 23 wt% B_2O_3, 19 wt% ZnO, 13 wt% BaO, and 3 wt% SiO_2 were prepared by high-temperature flame spray pyrolysis. The apparatus used for flame spray pyrolysis was similar to the apparatus described in previous literature [9]. A 1.7-MHz ultrasonic spray generator comprising six resonators is used to generate droplets; these droplets are carried to the high-temperature diffusion flame by oxygen, which is the carrier gas. The droplets evaporate, decompose, and melt under the influence of the diffusion flame, which is established using propane as the fuel and oxygen as the

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

0272-8842/$36.00
doi:10.1016/j.ceramint.2010.10.008

oxidizer. The flow rates of the fuel, oxidizer, and carrier gas were 5, 40, and 10 L/min, respectively. The spray solutions were obtained by adding Bi_2O_3, H_3BO_3, $BaCO_3$, ZnO, tetraethyl orthosilicate (TEOS), and nitric acid to a mixture of distilled water and ethyl alcohol (volume ratio: 9:1). Ethyl alcohol was added to the spray solution to increase the temperature of the diffusion flame. The overall solution concentration was 0.5 M.

Bi-based glass powders prepared by flame spray pyrolysis 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 a soda-lime glass substrate. The screen-printed glass substrate was fired in two steps, first at a temperature of 400 °C for 10 min at a heating rate of 7 °C/min and then at temperatures ranging from 480 to 580 °C for 6 min at a heating rate of 7 °C/min.

The crystal structures of the prepared powders were investigated by X-ray diffraction (XRD, Rigaku, D/MAX-RB) with Cu Kα radiation $\lambda = 1.5418$ Å). The thermal properties of the prepared powders were studied using a thermo-analyzer (TG-DSC, Netzsch, STA409C) in the temperature range of 40–550 °C. The morphological characteristics of the prepared powders and the fired dielectric layers were investigated by using a scanning electron microscope (SEM, JEOL, JSM-6060) and a high-resolution transmission electron microscope (TEM, FEI, Technai, 300 K). The transmittances of the dielectric layers were investigated by using a spectrophotometer in the visible light range (UV–vis spectrophotometer, Shimadzu, UV-2450).

3. Results and discussion

The morphology of the nanosized glass powders prepared by flame spray pyrolysis is shown in Fig. 1. The constituents of the glass powders evaporated completely under the influence of the high-temperature diffusion flame. Nanosized powders were formed from the evaporated vapors through a nucleation and growth mechanism. Fig. 2 shows a TEM image and diffraction pattern of the glass powders prepared by flame spray pyrolysis. The diffraction patterns indicate that the glass powders with an average particle size of 34 nm had slightly aggregated and amorphous morphologies. The XRD pattern of the nanosized powders prepared by flame spray pyrolysis (Fig. 3) shows a broad peak at around 28°, which is typical of a glassy material. Fig. 4 shows the TG/DSC curves of the Bi-based glass powders. In the TG curve, the weight loss of the powders was 3.53 wt.% at temperatures below 550 °C. The Bi-based glass powders prepared in the present study had a T_g value (442 °C) lower than that of the Bi-based glass powders prepared by the conventional melting process [1,2]. It was inferred that the decrease in the particle size of the powders to the nanometer range resulted in the decrease in the T_g of the glass material.

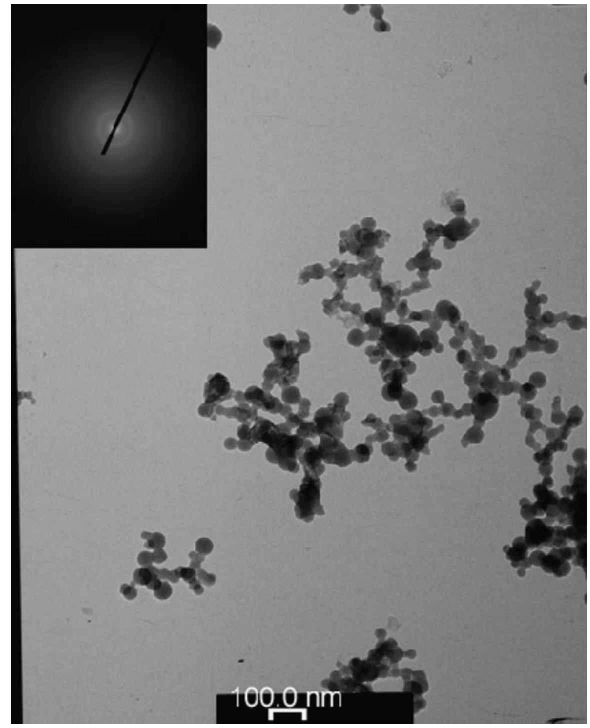

Fig. 2. TEM image and diffraction pattern of the glass powders prepared by flame spray pyrolysis.

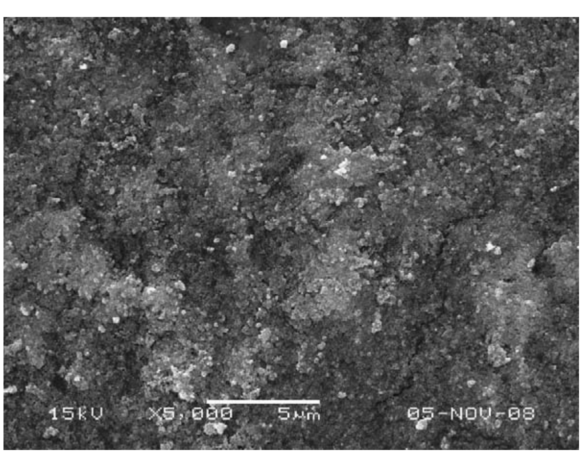

Fig. 1. SEM image of the glass powders prepared by flame spray pyrolysis.

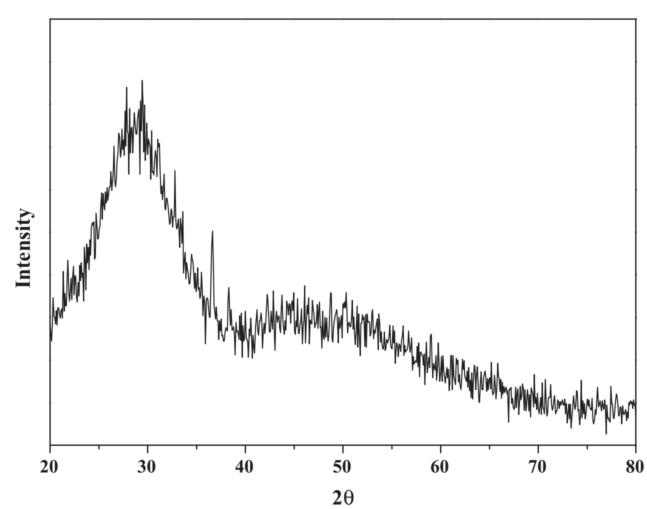

Fig. 3. XRD pattern of the glass powders prepared by flame spray pyrolysis.

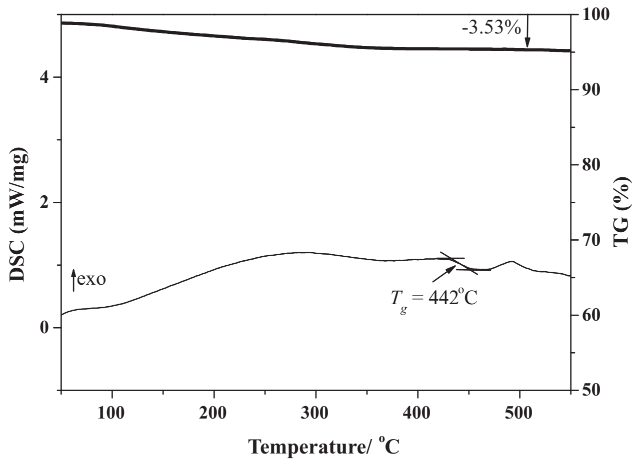

Fig. 4. TG/DSC curves of the glass powders prepared by flame spray pyrolysis.

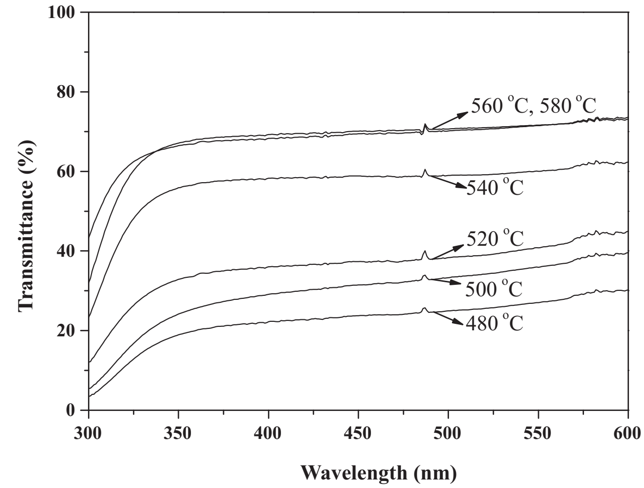

Fig. 6. Transmittances of dielectric layers fired at various temperatures.

Fig. 5 shows SEM images of the dielectric layers. Melting of the glass powders occurred at 480 °C. However, voids were observed in the dielectric layers fired at 480 and 500 °C. The dielectric layers had a small thickness of 1.2 μm because of the low glass content in the glass paste. The transmittances of the dielectric layers, shown in Fig. 6, increased with the firing temperature. The dielectric layers that were fired at 560 and 580 °C had transmittances of 70% in the visible range. However, the dielectric layers formed from the nanosized glass powders had lower transmittances and thicknesses than those formed from the submicron-sized glass powders prepared by spray pyrolysis [4,7]. The composition of the latter glass

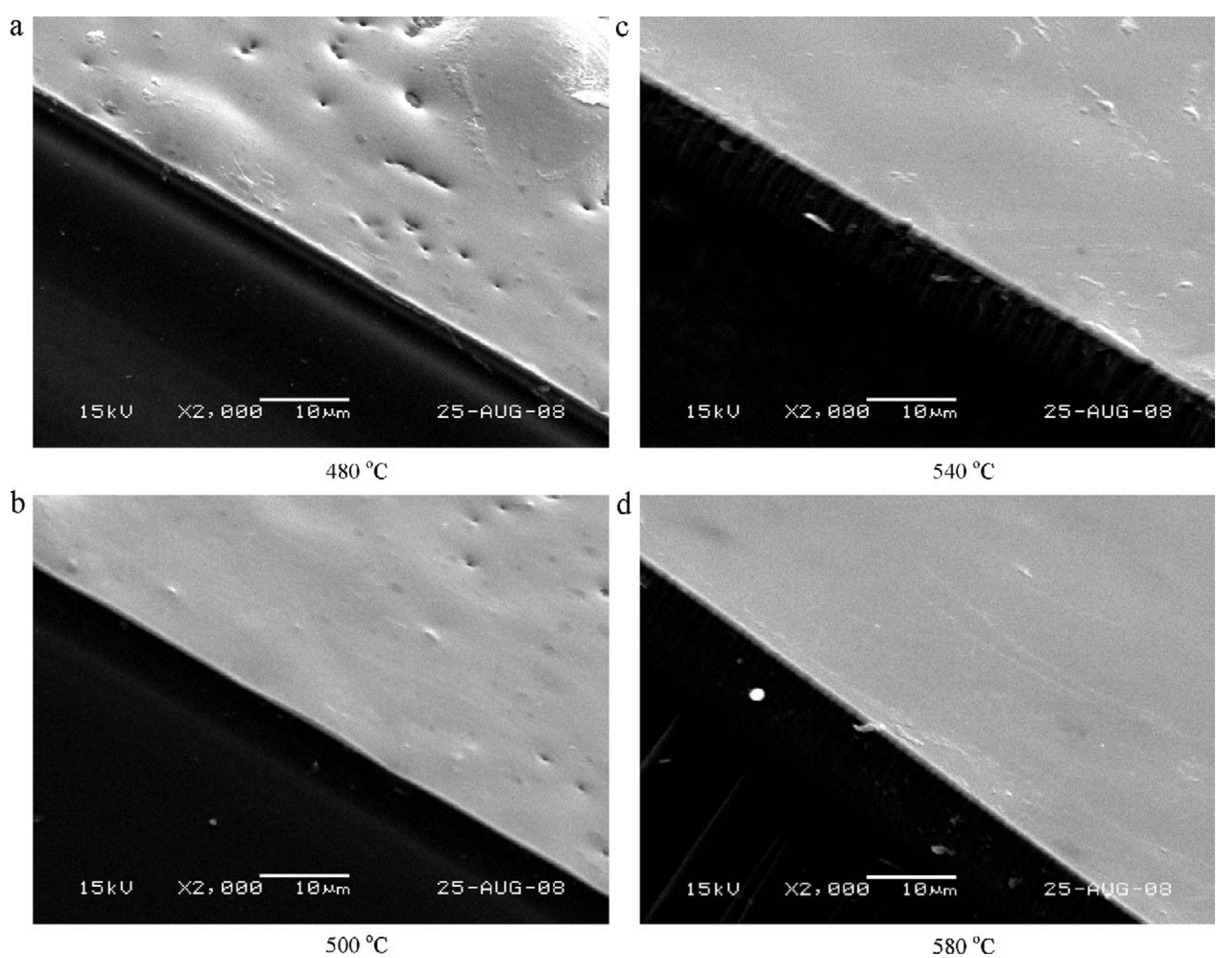

Fig. 5. Dielectric layers formed from the glass powders prepared by flame spray pyrolysis at various firing temperatures: (a) 480 °C; (b) 500 °C; (c) 540 °C; (d) 580 °C.

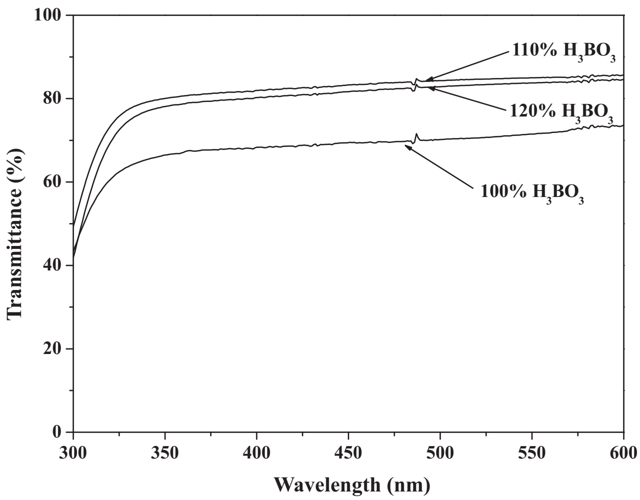

Fig. 7. Transmittances of dielectric layers obtained from the spray solutions with boron excess at a firing temperature of 580 °C.

powders was similar to that of the spray solution. On the other hand, the composition of the nanosized powders prepared by flame spray pyrolysis was slightly different from that of the spray solution. It was thus inferred that the change in the composition of the nanosized glass powders resulted in a decrease in the transmittances of the dielectric layers.

Boron is highly volatile at high temperatures. Therefore, the effects of excess boron in the spray solution on the transmittances of the dielectric layers were investigated. Fig. 7 shows the dielectric layers formed from the nanosized glass powders obtained from the spray solutions containing excess boron to have high transmittances.

4. Conclusions

Nanometer-size, spherical and narrow size distribution Bi-based glass powders were prepared by high temperature flame spray pyrolysis. The change in their composition resulted in a decrease in the transmittances of the dielectric layers. However, dielectric layers formed from nanosized glass powders obtained from the spray solutions containing excess boron had higher transmittances than those formed from the spray solution containing a stoichiometric amount of boron.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea Government (MEST) (No. 2009-0074023). This work was supported by a grant (M2009010025) from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy (MKE), Republic of Korea.

References

[1] J.Y. Song, S.Y. Choi, Fabrication and characterization of Pb-free transparent dielectric layer for plasma display panel, Displays 27 (2006) 112–116.

[2] J.Y. Song, T.J. Park, S.Y. Choi, Preparation and characterization of CuO doped Bi_2O_3–B_2O_3–BaO–ZnO glass system for transparent dielectric layer, J. Non-Cryst. Solids 352 (2006) 5403–5407.

[3] B.L. Choi, J.S. Lee, S.C. Choi, Thermal and mechanical properties of lead-free transparent dielectric materials for plasma display panels, J. Electroceram. 17 (2006) 331–334.

[4] S.K. Hong, H.Y. Koo, D.S. Jung, Y.C. Kang, Transparencies of dielectric layers formed from size-controlled Bi-based glass powders obtained by spray pyrolysis, Appl. Phys. A 85 (2006) 63–68.

[5] H.Y. Koo, S.K. Hong, S.H. Ju, I.S. Seo, Y.C. Kang, PbO–B_2O_3–SiO_2 glass powders with spherical shape prepared by spray pyrolysis, J. Non-Cryst. Solids 352 (2006) 3270–3274.

[6] H.Y. Koo, S.K. Hong, S.H. Ju, D.Y. Kim, Y.C. Kang, Effect of preparation temperature on the characteristics of PbO–B_2O_3–SiO_2 glass powders with spherical shape, J. Alloys Compd. 428 (2007) 344–349.

[7] S.K. Hong, H.Y. Koo, D.S. Jung, I.S. Suh, Y.C. Kang, Preparation of Bi_2O_3–B_2O_3–ZnO–BaO–SiO_2 glass powders with spherical shape by spray pyrolysis, J. Alloys Compd. 437 (2007) 215–219.

[8] J.S. Cho, S.K. Hong, D.S. Jung, Y.C. Kang, The effects of solvent on the properties of nano-sized glass powders prepared by flame spray pyrolysis, J. Ceram. Soc. Jpn. 116 (2) (2008) 334–340.

[9] J.S. Cho, D.S. Jung, S.K. Hong, Y.C. Kang, Thermal and mechanical properties of lead-free transparent dielectric materials for plasma display panels, J. Ceram. Soc. Jpn. 116 (5) (2008) 600–604.

[10] A. Gurav, T. Kodas, T. Pluym, Y. Xiong, Aerosol processing of materials, Aerosol Sci. Technol. 19 (1993) 411–452.