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Sintering behavior of La_2O_3–B_2O_3–TiO_2 glass powders prepared by spray pyrolysis for low temperature co-fired ceramics

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Abstract

Fine-sized La_2O_3–B_2O_3–TiO_2 glass powders with spherical shape were directly prepared by spray pyrolysis at a temperature of 1500 °C. The optimum flow rate of the carrier gas to prepare the glass powders with dense inner structure and fine size by complete melting was 10 L/min. The ratio of La/Ti was identified to be 2.06:1, which was close to the original starting ratio of La/Ti in mixture of the spray solution. The T_g and T_c of the powders were 614 and 718 °C. The crystal structures within the powders were observed from the sintered disc at 630 °C. The mean sizes of the powders changed from 0.24 to 0.71 μm when the concentrations of the spray solution were changed from 0.025 to 0.5 M. The BET surface areas of the powders changed from 4.4 to 1.6 m^2/g. The grain sizes of the sintered discs increased with increasing the sintering temperatures. The main crystal structure of the sintered discs was $LaBO_3$.

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1. Introduction

Low-temperature-co-fired ceramics (LTCC) have been widely investigated due to the limited sintering temperature and the necessity for miniaturization of devices [1–3]. In the multilayer structure, the sintering temperature of the dielectric materials has to be reduced below 900 °C because the melting temperature of Ag or Cu electrodes in multilayer device limits the sintering temperature to 900 °C (the melting point of Ag is about 961 °C).

In LTCC technology, various methods to reduce the sintering temperature are developed [4–6]. The use of low-melting glass or glass–ceramic powders has been commonly applied in reducing the sintering temperature as an effective and cheap approach. However, network formers contained in the glass materials may absorb the microwave power profoundly in high frequency regime, degrading the quality factor of the materials [7]. Thus, several researchers have been studied to develop glass or glass–ceramic systems with desired properties. The La_2O_3–B_2O_3–TiO_2 glass–ceramic system has been reported as a promising material for use in LTCC due to low firing temperature, low dielectric loss, low thermal expansion coefficient, and good compatability with Au, Ag or Cu conductors. The characteristics of La_2O_3–B_2O_3–TiO_2 glass–ceramic powders prepared by conventional melting and quenching process were carefully studied [8–10]. The effects of powder sizes on the microwave properties of La_2O_3–B_2O_3–TiO_2 glass–ceramic were also investigated [8].

The properties of the glass–ceramic powders are affected not only by the composition but also the mean size, morphology of glass powder. In the conventional melting and quenching process, the mean sizes and morphologies of glass powders could not be well controlled. The high melting temperature and aqueous milling process would cause the change of the composition of glass–ceramic powders. Therefore, the characteristics of micron-sized glass–ceramic powders were mainly studied in the LTCC applications.

For this reason, new technologies to prepare the glass–ceramic powders with submicron size, homogeneous composition and regular morphology are under developing. Spray pyrolysis, which is one of the gas phase reaction methods, was applied to the preparation of glass powders [11–14]. The glass powders with amorphous phases were directly prepared by high-temperature spray pyrolysis even at short residence time

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of glass powders inside the hot wall reactor as several seconds. The glass powders prepared by spray pyrolysis had submicron size, spherical shape and non-aggregation characteristics. The prepared glass powers had also narrow size distribution even without sieving process. Moreover, the thermal properties of the glass powders could be controlled by changing the mean size of the powders. However, glass–ceramic systems were not well studied in the spray pyrolysis process.

In this study, La_2O_3–B_2O_3–TiO_2 glass–ceramic system was studied in the spray pyrolysis. La_2O_3–B_2O_3–TiO_2 glass powders with amorphous phase were directly prepared by high-temperature spray pyrolysis. The effect of preparation conditions on the morphologies and crystal structures of the glass powders were investigated. The crystallization characteristics of the prepared glass powders were also investigated.

2. Experimental

Glass powders with a 20 mol% La_2O_3–60 mol% B_2O_3–20 mol% TiO_2 composition were directly prepared by high-temperature spray pyrolysis. The spray pyrolysis equipment used consisted of six ultrasonic spray generator that operated at 1.7 MHz, a 1000-mm-long tubular alumina reactor of 50-mm ID, and a bag filter. The glass powders were prepared by spray pyrolysis at temperatures between 1200 and 1500 °C. The spray solutions were obtained by adding lanthanum nitrate, boric acid, titanium tetra-iso-propoxide (TTIP), and nitric acid to distilled water. The overall solution concentrations were changed from 0.025 to 0.5 M. The droplets generated by ultrasonic spray generator were dried, decomposed, and melted. Rapid quenching of the melted glass outside of the reactor formed the glass powder. The flow rates of air used as a carrier gas were 10 and 20 L/min. The glass powders were added with a 5% polyvinyl alcohol (PVA) solution and pressed into disc-shaped compacts using uniaxial press of 1000 kg force. The samples were then heat treated at 450 °C for 3 h to eliminate the PVA, followed by sintering at temperatures between 600 and 1000 °C for 1 h and cooled naturally to room temperature while furnace power was off.

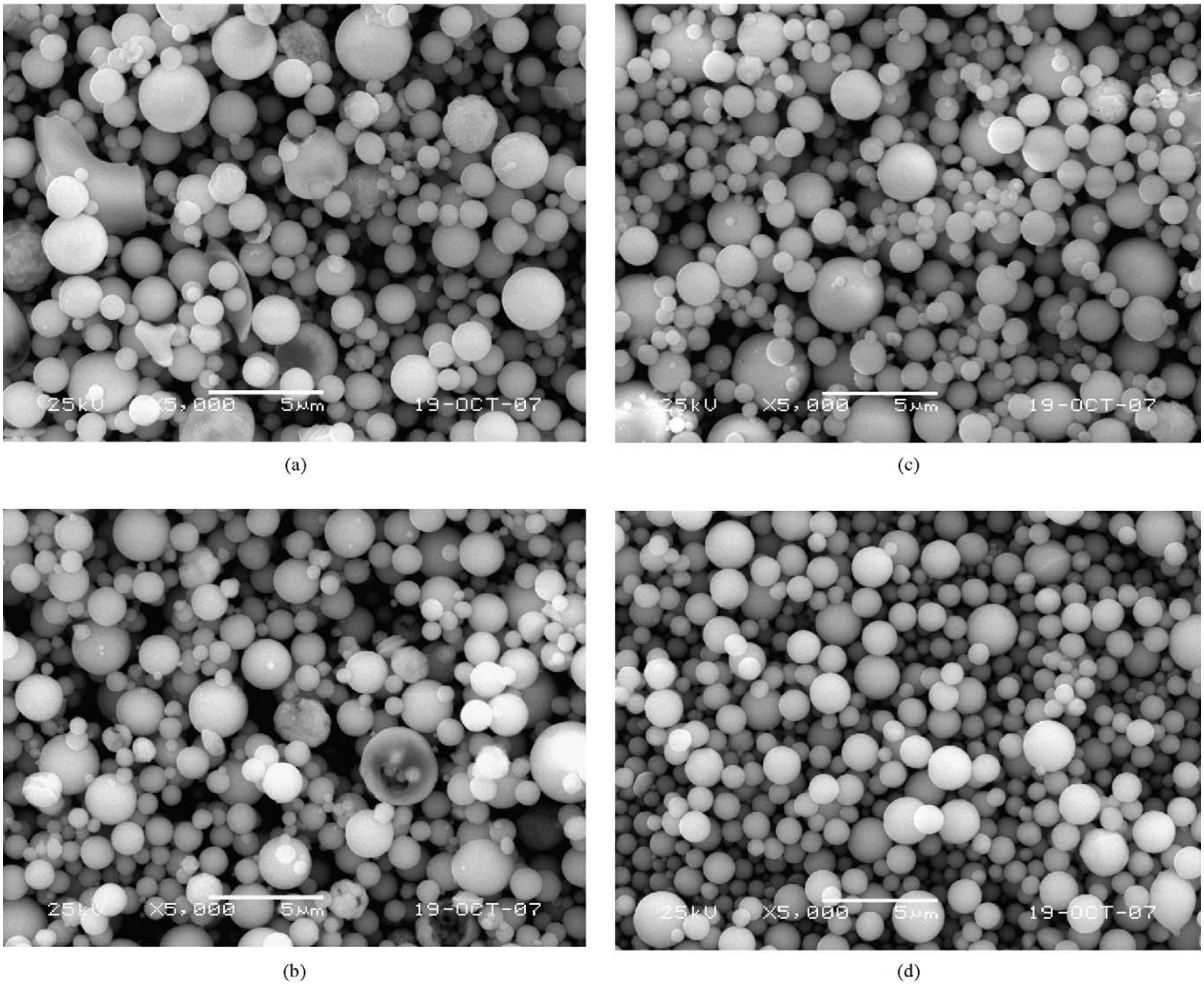


Fig. 1. SEM photographs of La_2O_3–B_2O_3–TiO_2 glass powders prepared at different preparation temperature when the flow rate of the carrier gas was 20 L/min. (a) 1200 °C, (b) 1300 °C, (c) 1400 °C, and (d) 1500 °C.

The thermal properties of the prepared glass powders were studied using differential scanning calorimeter (DSC, Netzsch, STA409C, Germany). The compositions of the glass powders were analyzed by using energy dispersive X-ray (EDX). Surface areas of the powders were measured by Brunauer–Emmett–Teller (BET) method using N_2 as adsorbate gas. The morphologies of the glass powders and sintered pellets were investigated using scanning electron microscopy (SEM, JEOL, JSM-6060, Japan). The crystal structures of the powders were studied using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation ($\lambda = 1.5418$ Å).

3. Results and discussion

The morphologies of the powders prepared by spray pyrolysis at different temperatures were shown in Fig. 1. The flow rate of the carrier gas was 20 L/min. The concentration of the spray solution was 0.5 M. The powders prepared at 1200 and 1300 °C had spherical shape and hollow morphology. On the other hand, the hollow morphologies of the powders prepared at high temperatures above 1400 °C were not observed in the SEM photographs. The mean size of the powders decreased with increasing the preparation temperatures. Fig. 2 shows the SEM photograph of the powders prepared at 1500 °C when the flow rate of the carrier gas was 10 L/min. The mean sizes of the powders as shown in Fig. 1(d)

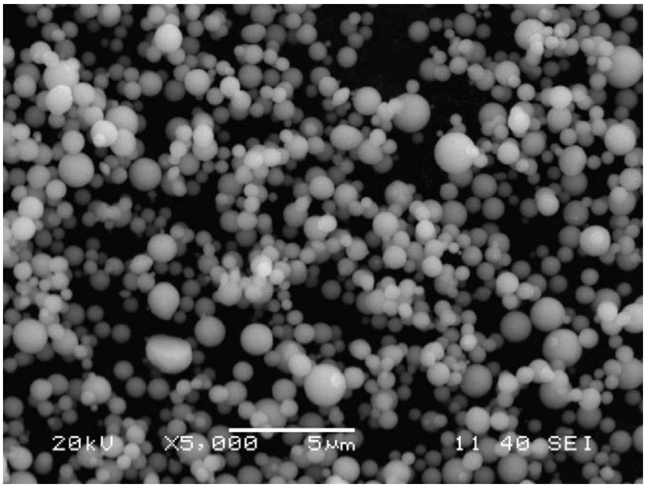


Fig. 2. SEM photograph of La_2O_3–B_2O_3–TiO_2 glass powders prepared at 1500 °C when the flow rate of the carrier gas was 10 L/min.

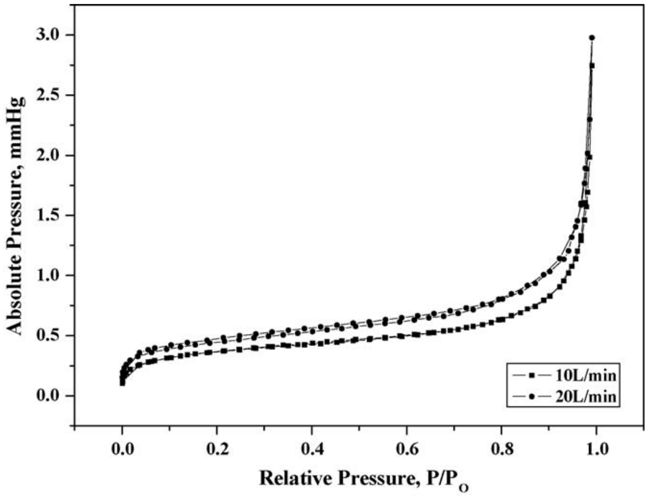


Fig. 3. Nitrogen adsorption isotherms for La_2O_3–B_2O_3–TiO_2 glass powders prepared at 1500 °C.

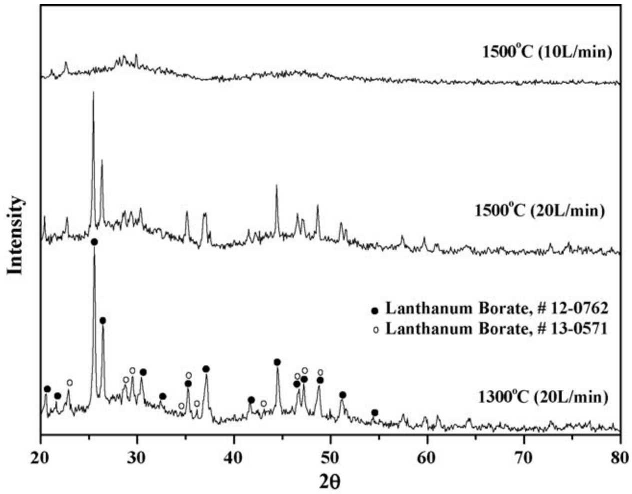


Fig. 4. XRD patterns of the La_2O_3–B_2O_3–TiO_2 glass powders prepared at different temperatures and flow rates of carrier gas.

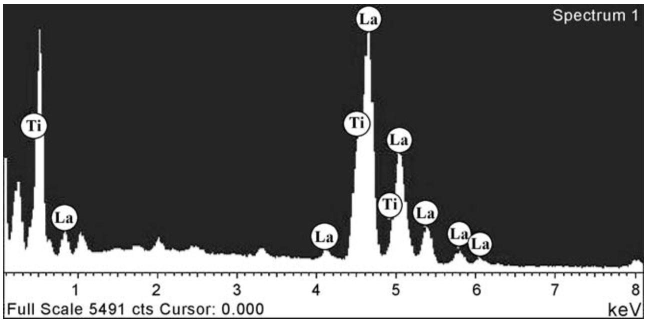


Fig. 5. EDX spectrum of the of La_2O_3–B_2O_3–TiO_2 glass powders prepared at 1500 °C.

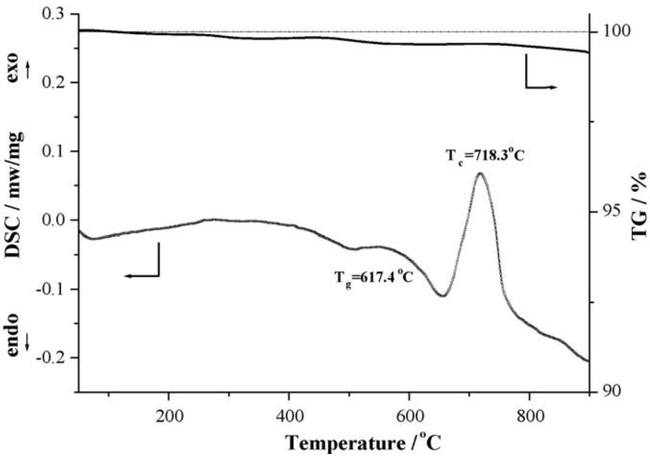


Fig. 6. TG/DSC curves of La_2O_3–B_2O_3–TiO_2 glass powders.

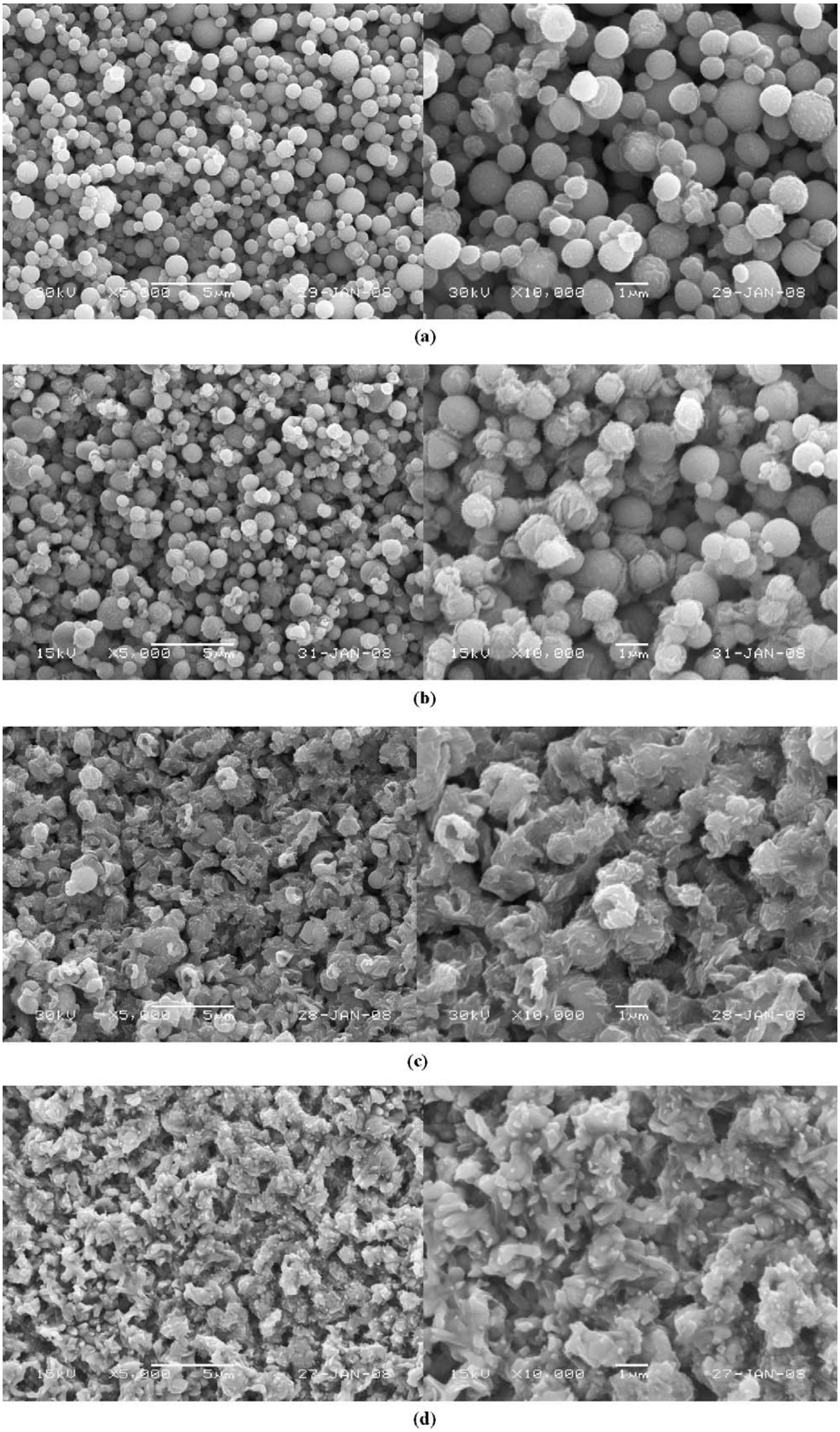
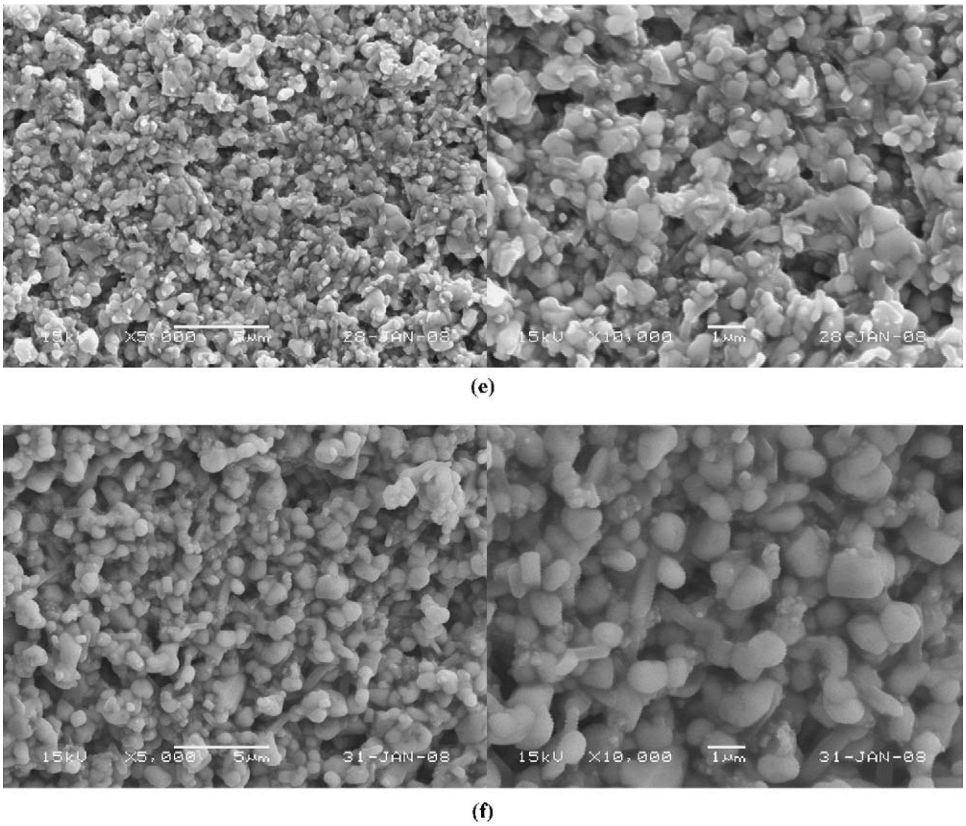


Fig. 7. SEM photographs of La_2O_3–B_2O_3–TiO_2 glass–ceramics sintered at different temperatures. (a) 600 °C, (b) 630 °C, (c) 650 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C.



(e)

(f)

Fig. 7. (*Continued*).

and Fig. 2 were 1.03 and 0.71 μm. The mean sizes of the powders were determined from SEM photographs by counting more than 500 powders in each sample in order to minimize errors. Fig. 3 shows the adsorption isotherms for glass powders prepared at 1500 °C. The pores of the powders were not observed in the adsorption isotherms irrespective of the flow rate of the carrier gas. However, according to the flow rate of the carrier gas, the mean sizes and surface areas had different values. The BET surface areas of the glass powders were 1.6 and 1.2 m^2/g when the flow rates of the carrier gas were 10 and 20 L/min. Therefore, the different inner structures of the powders prepared at different flow rates of the carrier gas affected the mean sizes of the glass powders. The glass powders prepared at flow rate of the carrier gas of 20 L/min had voids inside the powders. Incomplete melting of the powders occurred because of short residence time of the powders inside the hot wall reactor. On the other hand, the glass powders with dense inner structure were prepared by complete melting process in the spray pyrolysis at flow rate of the carrier gas of 10 L/min.

Fig. 4 shows the XRD patterns of the powders. The powders prepared at 1300 and 1500 °C had sharp crystalline peaks when the flow rate of the carrier gas was 20 L/min. The main crystal structure of the powders was $LaBO_3$ (JCPDS card #: 12-0762). On the other hand, the powders prepared at 1500 °C had broad peak at around 28° in the XRD pattern when the flow rate of the carrier gas was 10 L/min. The high temperature and long residence time of the powders inside the hot wall reactor were necessary to prepare the La_2O_3–B_2O_3–TiO_2 glass powders in the spray pyrolysis.

Figs. 5 and 6 show the EDX spectrum and TG/DSC curves of the powders prepared at 1500 °C when the flow rate of the carrier gas was 10 L/min. In the EDX analysis, a boron component could not be detected. Thus, the composition of the powders, except for boron, was compared with that of the spray solution. The ratio of La/Ti of the prepared glass powders was

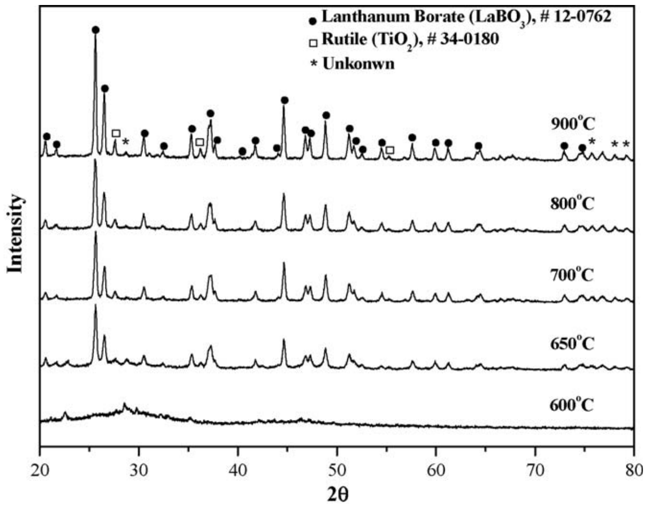


Fig. 8. XRD patterns of the La_2O_3–B_2O_3–TiO_2 glass–ceramics sintered at different temperatures.

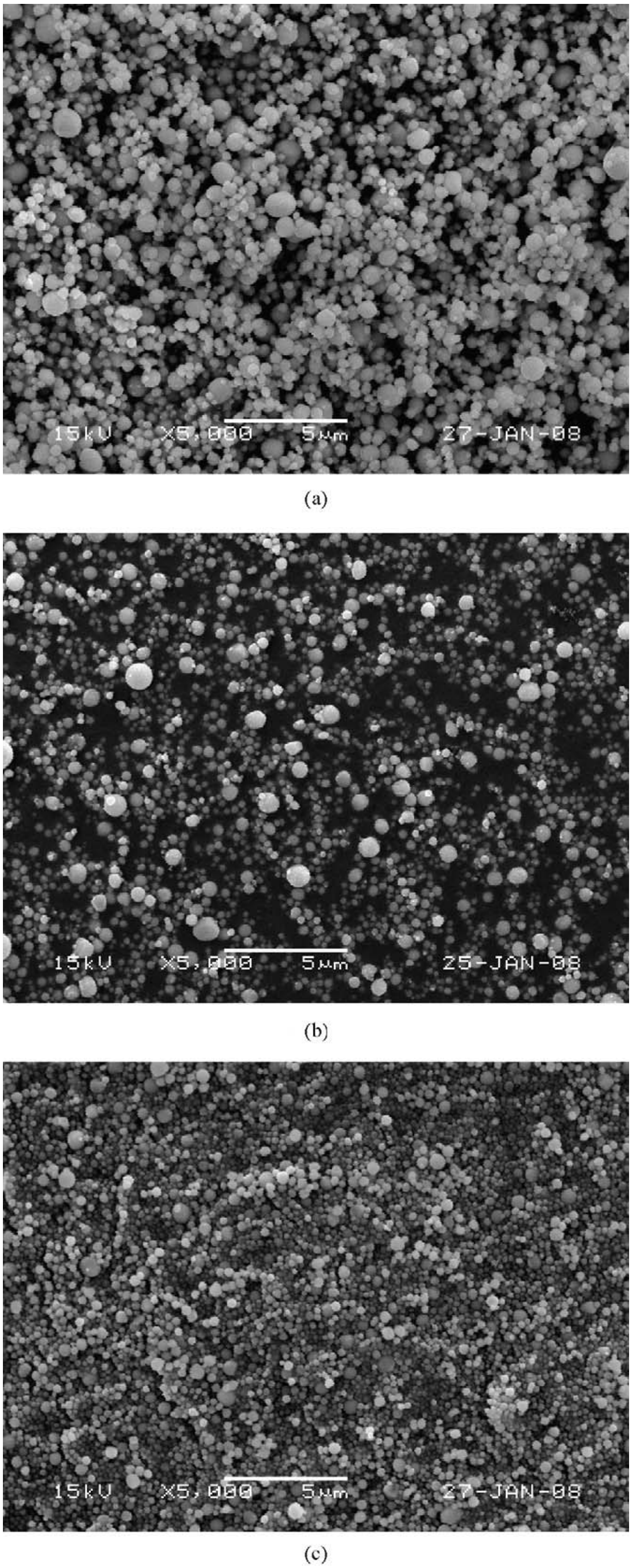


Fig. 9. SEM photographs of La_2O_3–B_2O_3–TiO_2 glass powders prepared from the spray solutions with different concentrations. (a) 0.1 M, (b) 0.05 M, and (c) 0.25 M.

Table 1
Surface areas and mean sizes of La_2O_3–B_2O_3–TiO_2 glass powders.

Mol concentration	Mean size (μm)	BET surface area (m^2/g)
0.025	0.24	4.4
0.05	0.37	3.1
0.1	0.61	2.6
0.5	0.71	1.6

2.06:1, which was close to the original starting ratio of La/Ti in the spray solution. In the TG curve as shown in Fig. 6, the weigh loss of the powder did not occur. The powders had a single peak of crystallization in the DSC curve. The glass transition temperature (T_g) and crystallization temperature (T_c) were 614 and 718 °C. The prepared glass powders had lower T_g and T_c than those of the glass powders prepared by conventional melting and quenching process [9].

Fig. 7 shows the SEM photographs of the surfaces of the sintered discs. The glass powders prepared at 1500 °C when the flow rate of the carrier gas was 10 L/min were added with a 5% polyvinyl alcohol solution and pressed into disc-shaped compacts. The spherical shape of the powers was maintained at a sintering temperature of 600 °C. Aggregation between the powders occurred at a sintering temperature of 630 °C. The crystal structures within the powders observed from the sintered disc at 630 °C. The spherical shape of the powders completely disappeared at a sintering temperature of 650 °C. The grain sizes of the sintered discs increased with increasing the sintering temperatures. Especially the grain size abruptly increased at a sintering temperature of 1000 °C.

Fig. 8 shows the XRD patterns of the discs sintered at various temperatures. The disc sintered at 600 °C had amorphous phase. On the other hand, the discs sintered at temperatures above 650 °C had crystal structures. The main crystal structure of the sintered discs was $LaBO_3$ (JCPDS card #: 12-0762). The mean crystallite sizes measured from the Scherrer's equation increased with increasing the sintering temperatures.

Fig. 9 shows the SEM photographs of the powders prepared from the spray solutions with various concentrations. The flow rate of the carrier gas and the reactor temperature were 10 L/min and 1500 °C. The glass powders had spherical shape and non-aggregation characteristics irrespective of the concentrations of the spray solutions. In the spray pyrolysis, one La–B–Ti–O glass particle was formed from one droplet by melting and quenching process. Therefore, the mean sizes and BET surface areas of the powders were affected by the concentrations of the spray solutions as shown in Table 1. The mean sizes of the powders changed from 0.24 to 0.71 μm when the concentrations of the spray solution were changed from 0.025 to 0.5 M. The BET surface areas of the powders changed from 4.4 to 1.6 m^2/g when the concentrations of the spray solution were changed from 0.025 to 0.5 M. Therefore, the particle size can be controlled by varying precursor solution concentration. This study was a preliminary investigation of the possibility to prepare the glass powders with nanometer size by spray pyrolysis. The effects of the mean sizes on the thermal properties and sintering behaviors of La–B–Ti–O glass powders prepared by spray pyrolysis will be performed.

4. Conclusions

The morphologies and mean sizes of La_2O_3–B_2O_3–TiO_2 glass powders prepared by spray pyrolysis were affected by the preparation temperatures and the flow rates of the carrier gas. The mean size and hollowness of the La_2O_3–B_2O_3–TiO_2 glass powders decreased with increasing the preparation temperatures. However, the glass powders prepared at 1500 °C had voids inside the powders when the flow rate of the carrier gas was 20 L/min. La_2O_3–B_2O_3–TiO_2 glass powders with fine size and dense inner structure were prepared by spray pyrolysis at 1500 °C when the flow rate of the carrier gas was 10 L/min. The mean sizes of the glass powders increased with increasing the concentrations of the spray solution. The disc sintered at 600 °C had amorphous phase. On the other hand, the discs sintered at temperatures above 650 °C had crystal structures. The grain sizes of the sintered discs increased with increasing the sintering temperatures.

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