

# Spherical shape Ba-based glass powders prepared by spray pyrolysis for MLCCs

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**Abstract** Spherical shape BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders were directly prepared by high temperature spray pyrolysis at >1000 °C. The thermal and morphological characteristics of the prepared glass powders were investigated. The glass powders prepared at temperature of 1000 °C had spherical shape and hollow inner structure. On the other hand, the powders prepared at high temperature of 1300 °C had complete spherical shape and dense inner structure by complete melting. The mean size of the glass powders was 0.9 μm. The glass transition temperatures ( $T_g$ ) of the glass powders obtained by spray pyrolysis at preparation temperatures between 1000 and 1300 °C were 601.1 °C regardless of the preparation temperatures. The specimen of the glass powders obtained by spray pyrolysis at the preparation temperature of 1300 °C had small number of voids even at low sintering temperature of 700 °C. In addition, the specimen sintered at temperature of 800 °C had dense microstructure without voids.

**Keywords** Glass power · Spray pyrolysis · MLCC · Fluxing agent

## 1 Introduction

Multi-layer ceramic capacitors (MLCCs) are essential passive components in the circuitry of electronic products because of their properties of high capacitance with small size,

high reliability, and excellent high-frequency characteristics [1, 2]. MLCCs has the multilayer structure of alternate dielectric ceramic and metal electrode layers formed by screen printing process. The dielectric ceramic layer is formed from the paste containing dielectric powder, glass powder, and organic vehicle. The metal electrode layer is formed from the conductive paste containing metal powder, glass powder, and organic vehicle. Because of its excellent dielectric properties, barium titanate is the most widely used as the dielectric material for MLCCs. High sintering temperature and long soaking time are necessary to achieve a high-density barium titanate [3]. However, the metal powders used as electrode material had low sintering temperature. The difference in sintering behavior between electrode material and dielectric material cause the problems of the layers locally detaching from each other (delamination), porosity and crack-formation. Therefore, glass powders are used as the fluxing agent in the dielectric paste to decrease the sintering temperature of dielectric layer. The addition of a fluxing agent promotes densification by liquid phase sintering at low temperatures [4–6]. Recently, it was reported that adding BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass lead BaTiO<sub>3</sub> to high density, high dielectric constant at low sintering temperature without formation of secondary phases [7].

In the MLCC, to meet the growing requirements for miniaturization, higher performance, and lower electric power consumption, the number of the dielectric active layers is increased, and thickness of the dielectric active layers is decreased. Thus, the mean sizes of the dielectric powders become smaller [8]. However, the glass powder formed by the conventional melting process had a large size, an irregular morphology, and a rough surface, which is insufficient for the fluxing agent.

Spray pyrolysis is one of the more promising processes for the preparation of improved ceramic and metal powders

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[9–15]. The powders synthesized by spray pyrolysis are relatively uniform in size and composition, spherical in shape, fine-sized, and have non-aggregation characteristics because of their micro-scale reaction within a droplet and the lack of a milling process. However, spray pyrolysis process did not well applied to the preparation of glass powders. In this study, BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders for MLCC applications were directly prepared by high temperature spray pyrolysis. The thermal and morphological characteristics of the prepared glass powders were investigated.

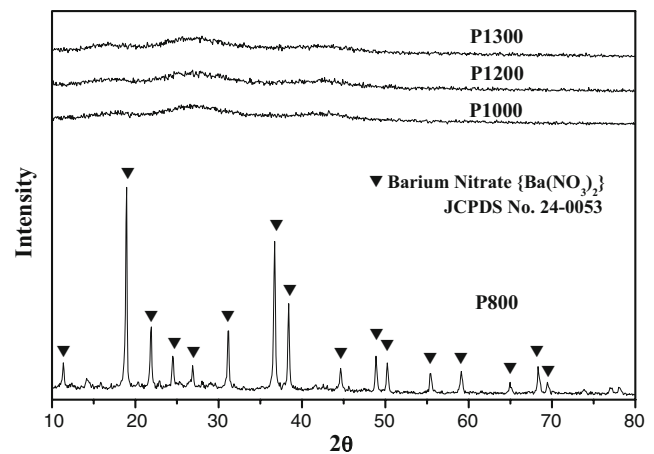
## 2 Experimental

Glass powders with a 30 wt% BaO–60 wt% B<sub>2</sub>O<sub>3</sub>–10 wt% SiO<sub>2</sub> composition were directly prepared by high-temperature spray pyrolysis. The spray pyrolysis equipment used consisted of six ultrasonic spray generators that operated at 1.7 MHz, a 1,000-mm-long tubular alumina reactor of 50-mm ID, and a bag filter. The glass powders were prepared by spray pyrolysis at temperatures between 800 and 1300 °C. The spray solutions were obtained by adding BaCO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, TEOS (tetraethyl orthosilicate) as a source of SiO<sub>2</sub> and nitric acid to distilled water. The overall solution concentration was 0.5 M. The spray solution was atomized with ultrasonic spray generators and introduced into a hot reaction column, where the droplets were dried, decomposed, and melted. The flow rate of air used as a carrier gas was 20 l/min.

The glass transition temperature ( $T_g$ ) of the prepared glass powders was studied using differential scanning calorimeter (DSC, Netzsch, STA409C, Germany). The morphologies of the glass powders and dielectric layers 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–K $\alpha$  radiation ( $\lambda=1.5418$  Å).

## 3 Results and discussion

Glass powders could be formed by melting and quenching processes in the spray pyrolysis. The steps of glass formation mechanism in reactor were drying of solution droplet, decomposition of precursor, melting of raw materials, and quenching of molten glasses with forming glass networks. Therefore, reactor temperature of the spray pyrolysis system is a critical variable to the preparation of glass powders. Figure 1 shows the XRD spectra of the BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> powders prepared by spray pyrolysis at various preparation temperatures. The BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>

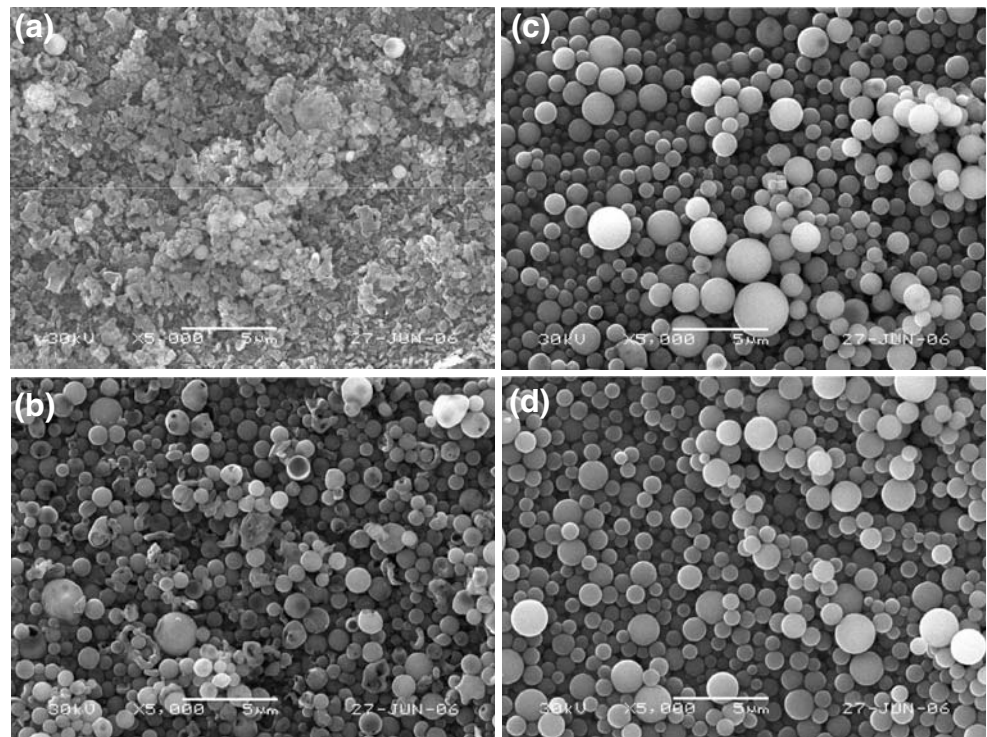


**Fig. 1** XRD spectra of powders prepared by spray pyrolysis at different temperatures

powders prepared at temperature of 800 °C had crystalline structure. The crystalline structure of the powders was defined as barium nitrate by JCPDS Card (no. 24-0053). The peaks of boron and silicon components were not found in the XRD spectra. On the other hand, the BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> powders prepared by spray pyrolysis at temperatures above 1000 °C had broad peaks at around 28° in the XRD spectra. The BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders were prepared by spray pyrolysis even within a short residence time of the powders inside the hot wall reactor maintained at temperatures above 1000 °C. The residence time of the powders inside the hot wall reactor maintained at 1000 °C was 1.4 s.

Figure 2 shows the SEM photographs of the BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> powders prepared by spray pyrolysis at various preparation temperatures. The powders prepared at low temperature of 800 °C had irregular shape and aggregated morphology. As shown in the XRD spectrum, incomplete decomposition of barium nitrate precursor destroyed the spherical shape of the powders obtained by spray pyrolysis at low temperature of 800 °C. The powders with spherical shapes were prepared at preparation temperatures above 1000 °C. On the other hand, the powders prepared at temperature of 1000 °C had hollow inner structure. In the case of relatively low reaction temperature, molten glasses dose not have low viscosity to exclude gas come up the outer molten glass. Thus, these powders had spherical shape and hollow inner structure. The powders prepared at temperature of 1200 °C had spherical shape and filled inner structure except some of the large size powders. On the other hand, the powders prepared at high temperature of 1300 °C had complete spherical shape and dense inner structure. In the spray pyrolysis, complete melting of the BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders occurred at high preparation temperatures even at the short residence time of the powders inside the hot wall reactor. Figure 3 shows the size distribution of the BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders measured

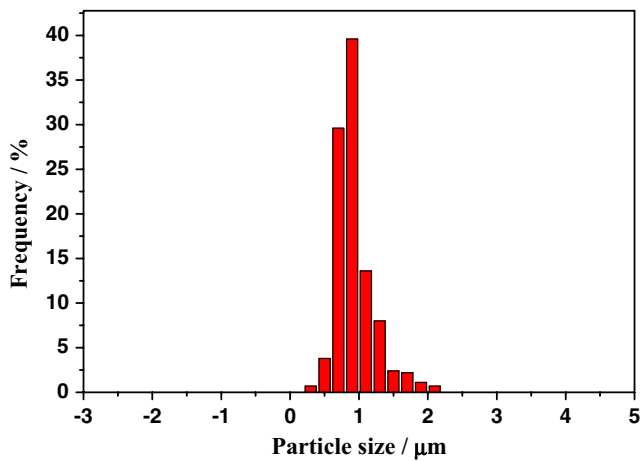
**Fig. 2** SEM photographs of powders prepared by spray pyrolysis at different temperatures of (a) 800 °C, (b) 1000 °C, (c) 1200 °C and (d) 1300 °C



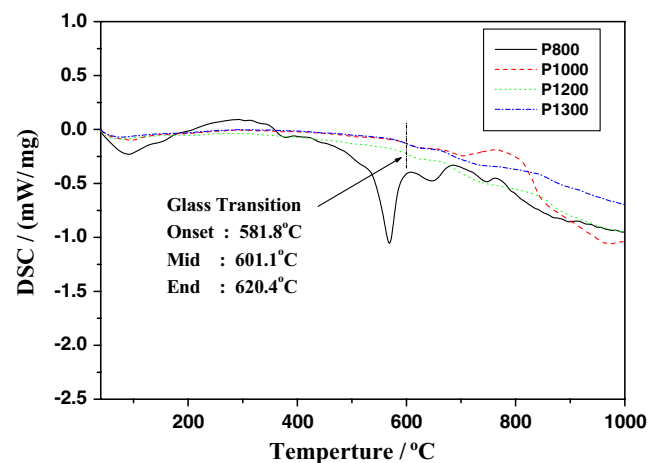
from the SEM photograph [Fig. 2(d)]. The BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders prepared by spray pyrolysis had narrow size distribution and fine size. The mean size of the powders was 0.9 μm. One glass powder was formed from one droplet by drying, decomposition, melting and quenching processes. Evaporation of some components consisting of glass powders did not occur even at high reactor temperature of 1300 °C.

Figures 4 and 5 show DSC and TG curves of BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders prepared by spray pyrolysis. As shown in Fig. 4, the glass transition temperatures (*T<sub>g</sub>*) of the glass powders obtained by spray pyrolysis at preparation

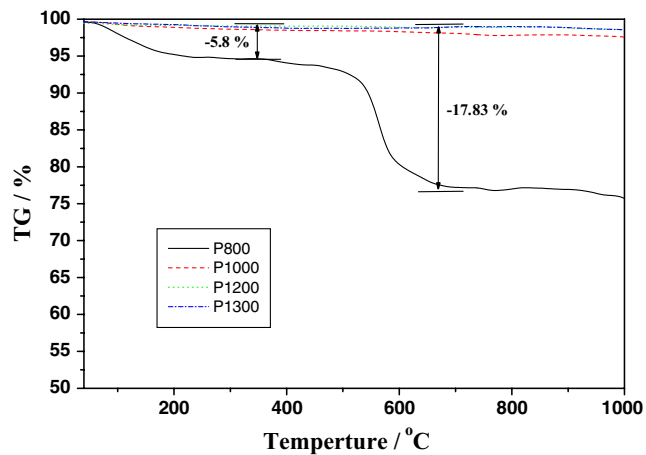
temperatures between 1000 and 1300 °C were 601.1 °C regardless of the preparation temperatures. However, the glass powders obtained at 1000 °C had exothermic peak at temperatures near 750 °C. It indicates that the crystallization can be occurred at the glass powders obtained at 1000 °C. The glass powders prepared by spray pyrolysis at preparation temperatures above 1200 °C showed amorphous stability without crystallization. The powders obtained at low temperature of 800 °C had a large endothermic peak at 570 °C by decomposition of barium nitrate precursor. As shown in Fig. 5, the powders obtained at temperature of 800 °C showed large weight loss. The initial weight loss of



**Fig. 3** Size distribution of glass powders prepared by spray pyrolysis



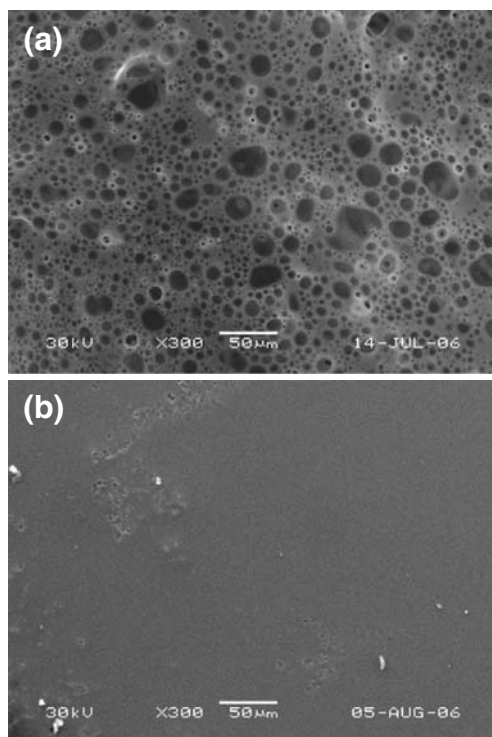
**Fig. 4** DSC curves of glass powders prepared by spray pyrolysis at different temperatures



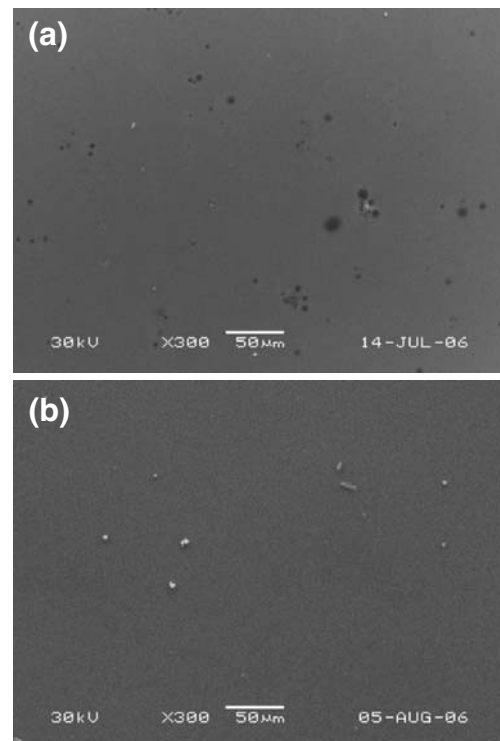
**Fig. 5** TG curves of glass powders prepared by spray pyrolysis at different temperatures

about 5.8% that took place in the range of 50–150 °C was observed due to the evaporation of adsorbed water molecules. Another weight loss of about 17.8% at temperatures 500–600 °C, was attributed to the decomposition of barium nitrate precursor.

The sinterability of the glass powders prepared by spray pyrolysis at the preparation temperatures of 1000 and 1300 °C were investigated. The specimens of glass powders were made by press of 1000 kg force and sintered at 700 and 800 °C for 30 min. Figures 6 and 7 show the SEM



**Fig. 6** SEM photographs of sintered specimens at temperatures of (a) 700 °C and (b) 800 °C of glass powders obtained by spray pyrolysis at preparation temperature of 1000 °C



**Fig. 7** SEM photographs of sintered specimens at temperatures of (a) 700 °C and (b) 800 °C of glass powders obtained by spray pyrolysis at preparation temperature of 1300 °C

photographs of sintered specimen of BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders. The specimens of the glass powders prepared by spray pyrolysis at the preparation temperature of 1000 °C had a number of voids with large size. On the other hand, the number of voids of the specimen decreased after sintering at temperature of 800 °C. The morphologies of the specimens were affected by the preparation temperatures of the glass powders. The specimen of the glass powders obtained by spray pyrolysis at the preparation temperature of 1300 °C had small number of voids even at low sintering temperature of 700 °C. In addition, the specimen sintered at temperature of 800 °C had dense inner structure without voids.

#### 4 Conclusion

Spray pyrolysis is applied to the preparation of BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders. The prepared BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders are uniform in size and composition, spherical in shape, fine-sized, and have non-aggregation characteristics because of their micro-scale reaction within a droplet and the lack of a milling process. The prepared BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders had a stable thermal properties and good sintering properties. Thus, the BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass powders prepared by spray pyrolysis can be used as fluxing agent of BaTiO<sub>3</sub> in high capacities MLCC.

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