

Sintering characteristics of CaO-B₂O₃-SiO₂ glass-ceramic powders prepared by spray pyrolysis

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CaO-B₂O₃-SiO₂ glass powders for low-temperature co-fired ceramic applications were directly prepared by high temperature spray pyrolysis. The glass powders with a spherical shape, dense structure, fine size and narrow size distribution were prepared at a temperature of 1400 °C by complete melting and quenching processes. The composition of the spray solution was well maintained in the glass powders prepared by spray pyrolysis. The glass transition temperature (T_g) and glass crystallization temperature (T_c) of the glass powders were 704 and 836 °C respectively. Melting of the glass powders prepared occurred at a temperature of 750 °C. A pellet sintered at a temperature of 900 °C had a fully-crystallized structure and dense structure. The main crystal structure of the sintered pellets was CaSiO₃.

Key words: Glass powder, Glass-ceramic, Spray pyrolysis, Gas phase reaction.

Introduction

The CaO-B₂O₃-SiO₂ system has been reported as the basis of promising materials for use in low-temperature co-fired ceramics (LTCC) because of a low firing temperature, low dielectric loss, low thermal expansion coefficient, and good compatibility with Au, Ag or Cu conductors [1-11]. The sintering characteristics of the CaO-B₂O₃-SiO₂ system with various compositions were studied in many investigations [8-11]. The densification and dielectric properties of the CaO-B₂O₃-SiO₂ system are important in low-temperature co-fired ceramics (LTCC). CaO-B₂O₃-SiO₂ glass powders have been prepared by conventional melting and quenching process. Reagent-grade materials of Ca, B, and Si components were mixed uniformly by a mixing apparatus. After mixing, the powders were put into Pt or Pt/Rh crucibles and melted in the temperature range of 1500-1600 °C for several hours, and then the molten glass was quenched into distilled water to form cullet. The cullet was dried and milled to course glass powders. Subsequently, the course glass powders were re-milled in an aqueous media using a powerful milling apparatus to prepare the fine-sized glass powders.

The sintering characteristics of the glass powders are affected by the properties of the glass powders such as mean size, morphology and composition. However, 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 a change of the composition of glass powders.

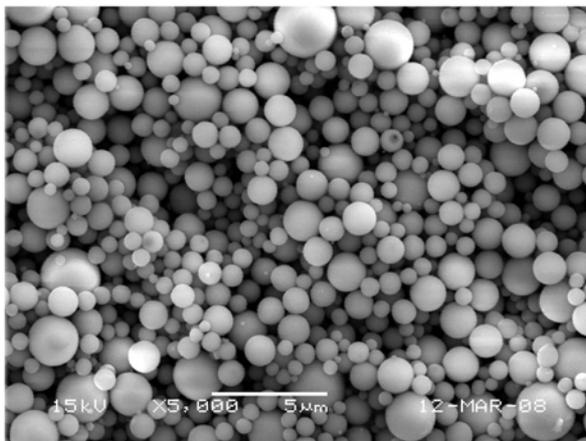
Spray pyrolysis is one of the more promising processes for the preparation of improved ceramic and metal powders [12-18]. The powders synthesized by spray pyrolysis are relatively uniform in size and composition, spherical in shape, fine-sized, and have non-aggregation characteristics because of their micro-scale reactions within a droplet and the lack of a milling process. Spray pyrolysis has also been applied to the preparation of glass powders [19-22]. Glass powders with amorphous phases were directly prepared by high temperature spray pyrolysis even with a short residence time of the glass powders inside the hot wall reactor of a few seconds. The glass powders prepared by spray powders had a submicrometre size, a spherical shape and non-aggregation characteristics. The glass powders prepared also had a narrow size distribution, even without a sieving process.

In this study, CaO-B₂O₃-SiO₂ glass-ceramic powders for LTCC application were directly prepared by high temperature spray pyrolysis. The effect of the preparation temperature on the morphologies and crystal structures of the powders were investigated. The sintering characteristics of the glass powders prepared were also investigated.

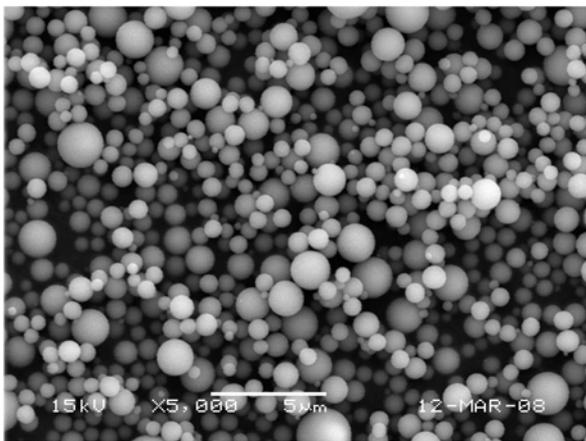
Experimental Procedure

Glass powders with a 47.8 wt% CaO-8.6 wt% B₂O₃-43.6 wt% SiO₂ 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 50-mm internal diameter, and a bag filter. The glass powders were prepared by spray pyrolysis at temperatures between 1250 °C and 1500 °C. The spray solutions were obtained by adding Ca(NO₃)₂·4H₂O, H₃BO₃, TEOS (tetraethyl ortho-silicate) and nitric acid to distilled water. The overall solution

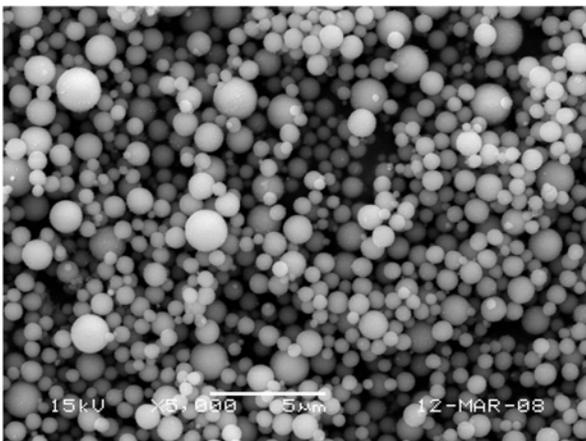
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(a) 1250°C



(b) 1400°C



(c) 1550°C

Fig. 1. SEM images of $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ glass powders prepared by spray pyrolysis at different temperatures.

concentration was 0.5 M. The spray solution was atomized with the ultrasonic spray generators and introduced into the hot reaction column, where the droplets were dried, decomposed, and melted. Rapid quenching of the melted glass outside the reactor formed the glass powder. The flow rate of air used as a carrier gas was 20 l/minute^{-1} . The glass

powders were added to a 5% polyvinyl alcohol (PVA) solution and pressed into disc-shaped compacts using a 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 700 and 900°C for 15 minutes and cooled naturally to room temperature while the furnace power was off. The thermal properties of the glass powders prepared were studied using a differential scanning calorimeter (DSC, Netzsch, STA409C, Germany). 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 $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The compositions of the glass powders were analyzed using energy dispersive X-ray spectroscopy (EDX).

Results and Discussions

The morphologies of the powders prepared by spray pyrolysis are shown in Fig. 1. The powders had spherical shapes and fine sizes irrespective of the preparation temperatures. On the other hand, the powders prepared at temperatures of 1400 and 1550°C had a narrower size distribution than those prepared at a temperature of 1250°C . The size distributions of the powders prepared by spray pyrolysis at different temperatures could be changed by the different morphologies of the powders. The concentration gradient of precursors inside the large-sized droplet in the drying stage is higher than that inside the small-sized droplet. Therefore, the powders prepared from the large-sized droplets had a more hollow and porous structures than those prepared from the small-sized droplets. The different morphologies of the powders obtained from the small and large-sized droplets at a preparation temperature of 1250°C increased the size distribution of the powders. However, the powders prepared at temperatures of 1400 and 1550°C had narrow size distributions because of the dense morphologies of the powders. Complete melting of the powders obtained from the small and large-sized droplets at preparation temperatures of 1400 and 1550°C decreased the size distributions of the powders. The submicrometre size of powders enabled the melting of the powders even when the short residence time of the powders inside the hot wall reactor was 0.58 s .

Fig. 2 shows the XRD patterns of the powders prepared at different temperatures. The powders prepared had broad peaks between 20 and 40° in the XRD patterns irrespective of the preparation temperature. Therefore, glass phases were formed by melting and quenching processes at preparation temperatures between 1250 and 1500°C .

Fig. 3 shows the EDX spectrum of the glass powders obtained at a preparation temperature of 1400°C . The composition ratio of Ca and Si components of the glass powders measured from the EDX spectrum was $1.05 : 1$. The composition ratio of Ca and Si components in the

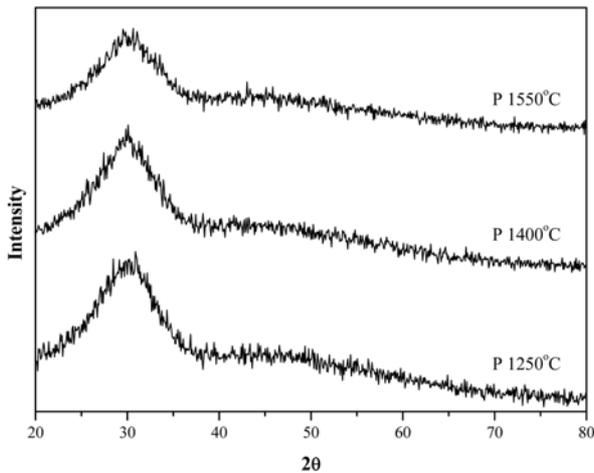


Fig. 2. XRD patterns of the CaO-B₂O₃-SiO₂ glass powders prepared by spray pyrolysis at different temperatures.

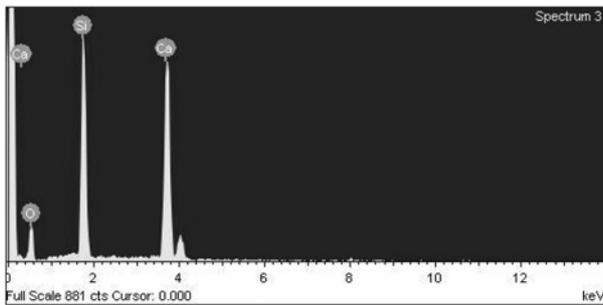


Fig. 3. EDS spectrum of the CaO-B₂O₃-SiO₂ glass powder prepared by spray pyrolysis at 1400°C.

spray solution was 1 : 1. Therefore, the composition of the spray solution was well maintained in the glass powders prepared by spray pyrolysis because of the short residence time of the powders inside the reactor maintained at 1400 °C.

Fig. 4 shows DSC and TG curves of CaO-B₂O₃-SiO₂ glass powders prepared by spray pyrolysis at a preparation temperature of 1400 °C. The glass transition temperature (T_g) and glass crystallization temperature (T_c) of the glass were 704 and 836 °C respectively. An exothermic peak at a temperature above 800 °C corresponded to the formation of CaSiO₃ crystal.

The sintering and crystal formation properties of the CaO-B₂O₃-SiO₂ glass powders prepared by spray pyrolysis at a preparation temperature of 1400 °C were investigated by SEM. Fig. 5 shows the SEM images of the pellets sintered at different temperatures. The glass powders sintered at a temperature of 700 °C maintained a spherical morphology. On the other hand, the pellet sintered at a temperature of 750 °C had a clean surface and a dense structure. One could assume that the softening temperature of the glass powders was above 700 °C which was similar to the results of previous studies [9, 11]. Precipitated crystals were observed in the SEM image from the sample with a sintering

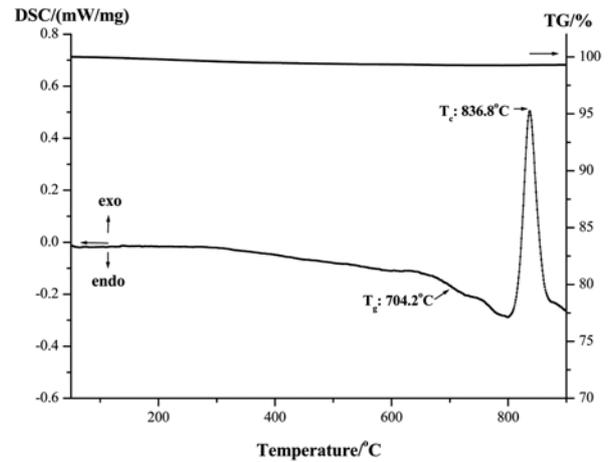


Fig. 4. TG/DSC curves of CaO-B₂O₃-SiO₂ glass powders prepared by spray pyrolysis at 1400 °C.

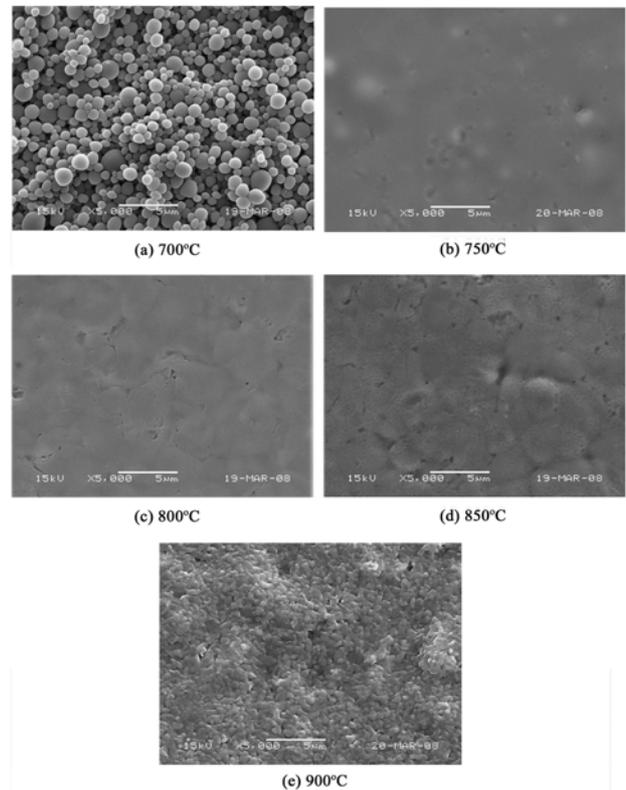


Fig. 5. SEM images of the surfaces of pellets sintered at different temperatures.

temperature of 800 °C. The pellet sintered at a temperature of 900 °C had a fully-crystallized structure and apparent crystal grains were observed. Fig. 6 shows the XRD patterns of the sintered pellets. Crystallization of the glass did not occur at a sintering temperature of 700 °C. The crystal peaks were observed at a sintering temperature of 750 °C, and the crystallinity of powders increased with an increase of the sintering temperature. The main crystal structure of the pellets was CaSiO₃.

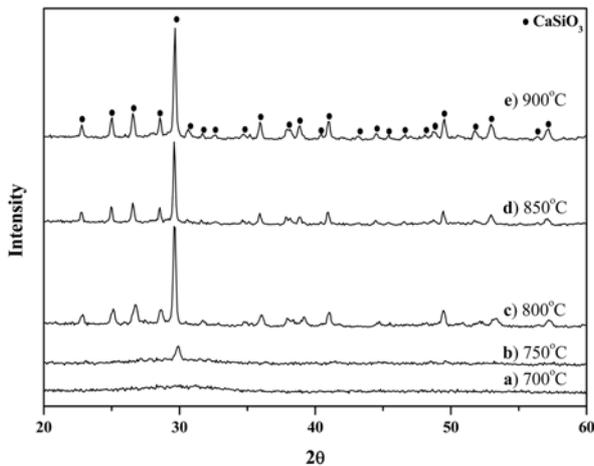


Fig. 6. XRD patterns of the pellets sintered at different temperatures.

Conclusions

In spray pyrolysis, the characteristics of CaO-B₂O₃-SiO₂ glass powders were optimized by controlling the preparation temperatures. Complete melting of the powders obtained from small and large-sized droplets at a preparation temperature of 1500 °C decreased the size distribution of the glass powders. Submicrometre size powders enabled the melting of the powders even with a short residence time of the powders inside the hot wall reactor of 0.58 s. The pellet sintered at a temperature of 900 °C had a dense structure and fully-crystallized structure of CaSiO₃.

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