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Characteristics of $ZnO-B_2O_3-SiO_2$ glass powders prepared by spray pyrolysis as densification promoter for $BaTiO_3$ ceramics

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Spherical shape $ZnO-B_2O_3-SiO_2$ glass powders were prepared by spray pyrolysis. The optimum preparation temperature is 1500 °C when the flow rate of the carrier gas is 5 $Lminute^{-1}$. The mean size and geometric standard deviation of the glass powders is 0.78 μm and 1.38. The glass transition temperature of the glass powders is 489.1 °C. Melting of the $ZnO-B_2O_3-SiO_2$ glass powders occurs at 500 °C. On the other hand, some of the glass powders maintain a spherical morphology after firing at 500 °C. Complete melting of the glass powders occurs at firing temperatures of 600 and 700 °C, in which crystalline structures are observed. The dielectric constant of the $BaTiO_3$ pellet with 3 wt.% $ZnO-B_2O_3-SiO_2$ glass is 2682 at a firing temperature of 1000 °C.

Key words: barium titanate, glass powder, spray pyrolysis, dielectric material.

Introduction

Barium titanate ($BaTiO_3$) powders are widely used in multilayer ceramic capacitors (MLCCs) owing to their good dielectric properties [1-4]. However, the sintering temperature of barium titanate is too high above 1300 °C. Lowering the sintering temperature by the addition of glass is the most effective and least expensive technique. The composition of the glass material affects the reduction of the sintering temperature and improves the dielectric properties of $BaTiO_3$ ceramics. Therefore, various types of glass compositions have been used to decrease the sintering temperature of $BaTiO_3$ [5-8]. $ZnO-B_2O_3-SiO_2$ (ZBS) glass materials prepared by a conventional melting process have also been studied as a sintering agent [8, 9]. Hsiang *et al.* showed that ZBS glass can be used as a sintering aid to reduce the sintering temperature of $BaTiO_3$ from 1300 °C to 900 °C without the formation of a secondary phase. The $BaTiO_3$ with ZBS glass sintered at 900 °C showed a relative density of 95 % and a high dielectric constant [8, 9].

The mean size and morphology as well as the composition of the glass powders affect the characteristics as the sintering agent [10]. In this study, $ZnO-B_2O_3-SiO_2$ (ZBS) glass powders with a spherical shape and fine size were prepared by spray pyrolysis. The effects of ZBS glass powders prepared by spray pyrolysis on the sintering characteristics of nano-sized $BaTiO_3$ powders were investigated.

Experimental Procedure

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. $ZnO-B_2O_3-SiO_2$ glass powders were directly prepared by high-temperature spray pyrolysis. The preparation temperature was changed from 1000 to 1500 °C. The concentration of Zn, B and Si components was 0.5 M. Zinc oxide, boric acid and tetraethyl orthosilicate (TEOS) were used as starting materials to prepare ZBS glass powders.

The ZBS glass powders and nano-sized $BaTiO_3$ powders were thoroughly wet-mixed with the addition of ethanol in an agate bowl and then a small amount of polyvinyl alcohol solution was added for granulation. The amount of glass powders was fixed at 3 wt.% of the $BaTiO_3$ powders. The mixed powders were pelletized at 3000 $kgfcm^{-2}$ (294 MPa) pressure into 18 mm diameter cylinder. The pellets were then sintered at temperatures between 700 and 1000 °C for 2 h and cooled naturally to room temperature while the furnace power was off.

The crystal structures of the glass powders and sintered pellets were investigated by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation ($\lambda = 1.5418 \times 10^{-10}$ m). The thermal properties of the prepared glass powders were measured using a thermo-analyzer (TG-DSC, Netzsch, STA409C, and Germany). The morphological characteristics of the powders and pellets were investigated by scanning electron microscopy (SEM, JEOL, JSM-6060). Dielectric measurements of the samples were performed using a LCR meter at 1 kHz.

Results and Discussions

In spray pyrolysis, the morphologies and crystal structures of glass powders are strongly affected by the preparation temperature and residence time of the powders inside the hot wall reactor because one particle is formed from one

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droplet. Figs. 1 and 2 show the SEM images and XRD patterns of the ZBS powders prepared by spray pyrolysis at various temperatures. The flow rate of the carrier gas was 10 Lminute^{-1} and the residence times of the powders inside the hot wall reactor were 1.7 and 1.2 s at 1000 and 1500 °C. The powders prepared at 1000 °C have a large size, and hollow with a porous morphology. The hollowness of the powders decreases with an increase of the preparation temperature by melting of the powders. Therefore, the mean size of the powders decreases with an increase of the preparation temperature. The mean size of the powders prepared at 1200 and 1500 °C are 1.1 and 0.80 μm. The powders have broad XRD peaks around 30° irrespective of the preparation temperature. On the other hand, peaks from crystals are observed in the XRD patterns of the powders. ZBS glass powder was prepared by a conventional process at a melting temperature of 1200 °C [10]. However, ZBS glass powder with an amorphous structure were not prepared by spray pyrolysis at 1500 °C because of short residence time of the powders inside the hot wall reactor.

The flow rate of the carrier gas was reduced from 10 to 5 Lminute^{-1} to increase the residence time of the powders inside the hot wall reactor which was maintained at 1500 °C.

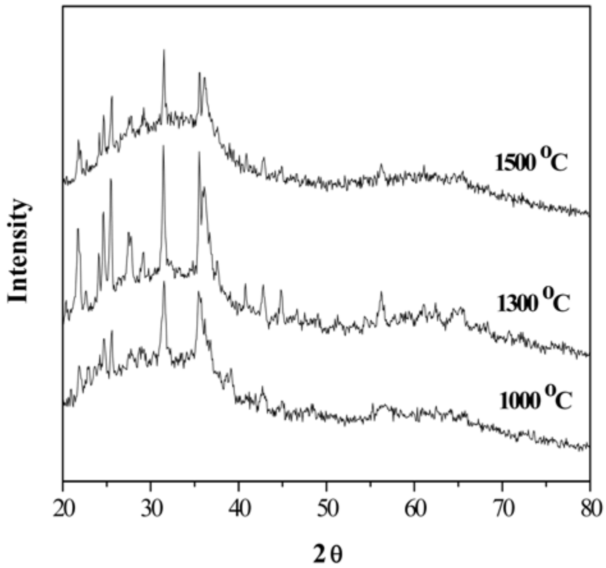


Fig. 2. XRD patterns of the glass powders prepared by spray pyrolysis at various temperatures.

The morphology and crystal structure of the powders are shown in Figs. 3 and 4. The powders had a fine size,

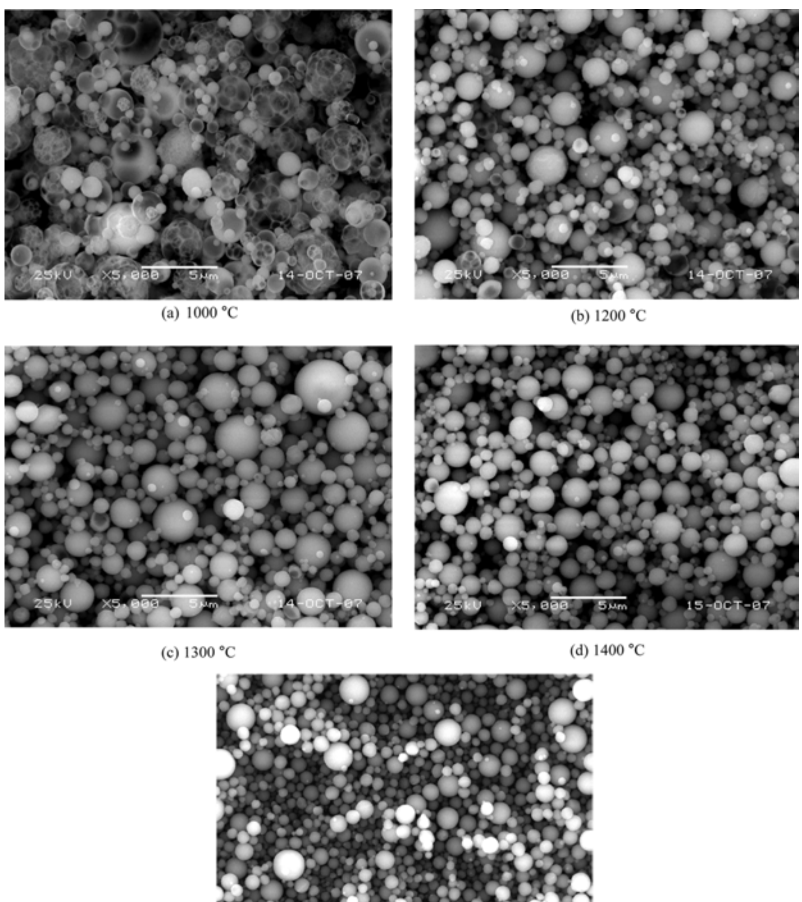


Fig. 1. SEM images of the glass powders prepared by spray pyrolysis at various temperatures.

dense morphology and amorphous structure. ZBS glass powders were prepared by a complete melting and quenching process. Fig. 5 shows the TG/DSC curves of the ZBS glass powders. In the TG curve, the weight loss is 1% in the temperature range from 40 to 800 °C. The glass transition temperature (T_g) of the glass powders is 489.1 °C. A small exothermic peak for crystallization of the glass powders is observed at 664.1 °C.

The sintering characteristics of the ZBS powders were investigated. The pellets formed from the ZBS glass powders with an amorphous structure were fired at temperatures of 500, 600 and 700 °C. Fig. 6 shows the SEM images

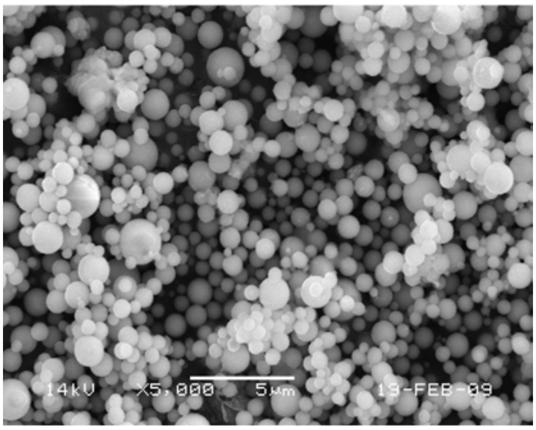


Fig. 3. SEM image of the glass powders prepared by spray pyrolysis at a low flow rate of the carrier gas.

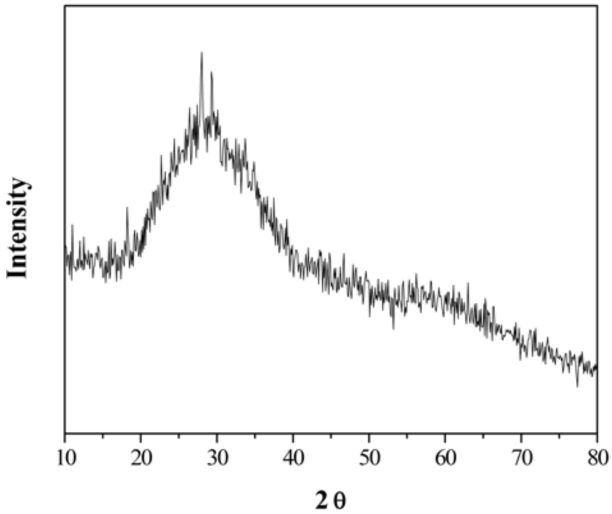


Fig. 4. XRD pattern of the glass powders prepared by spray pyrolysis at a low flow rate of the carrier gas.

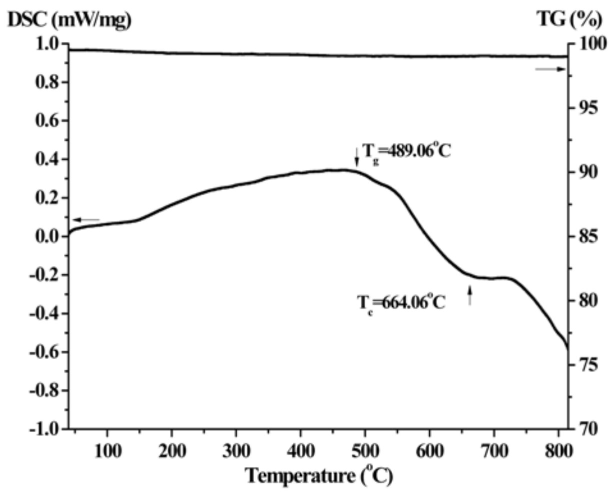


Fig. 5. TG/DSC curves of the glass powders prepared by spray pyrolysis at a low flow rate of the carrier gas.

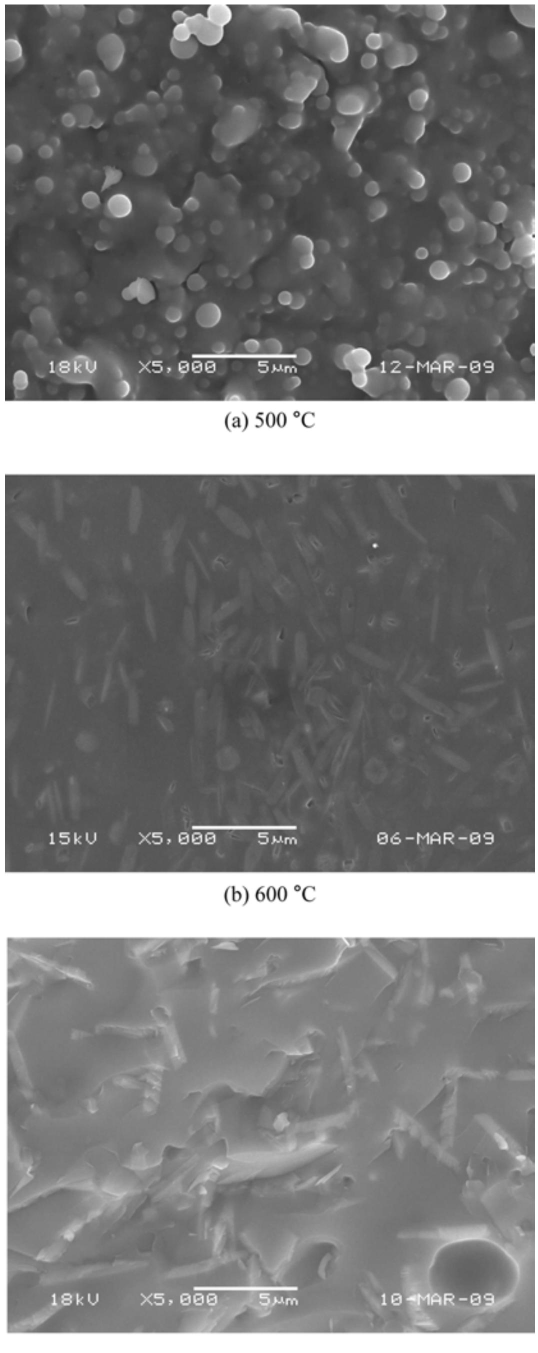
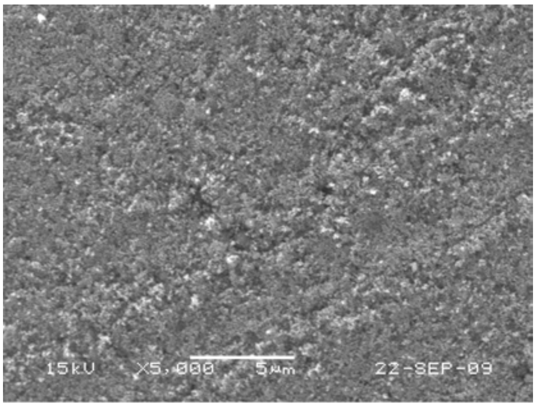


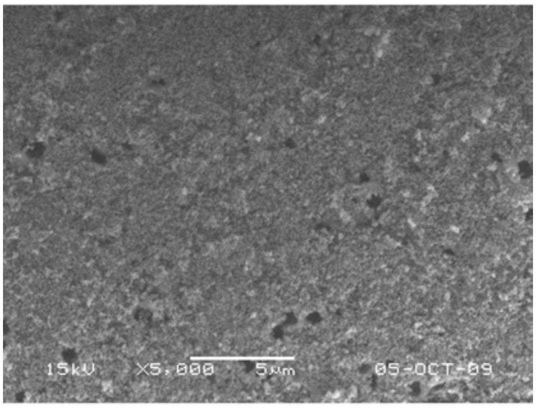
Fig. 6. SEM images of the surfaces of the glass pellets sintered at various temperatures.

of the surfaces of the sintered ZBS pellets. Melting of the glass powders occurred at 500 °C. On the other hand, some of the glass powders maintained a spherical morphology after firing at 500 °C. Complete melting of the glass powders occurred at firing temperatures of 600 and 700 °C, in which crystalline structures were observed from the SEM images.

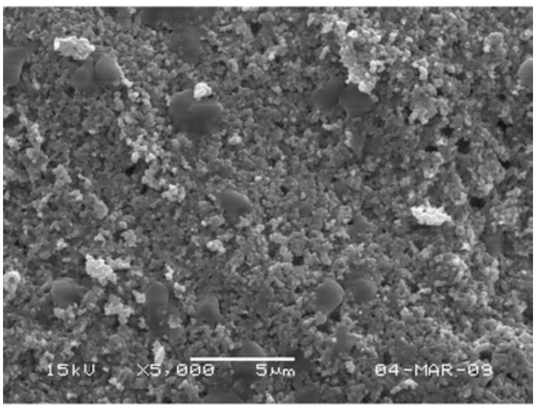
The effects of ZBS glass powders on the sintering characteristics of $BaTiO_3$ pellets were investigated. Nano-sized $BaTiO_3$ powders prepared by spray pyrolysis were applied [11]. The surface morphologies of $BaTiO_3$ pellets containing ZBS glass powders before and after firing are shown in Fig. 7. Holes with a submicrometre size are observed inside the pellet formed by melting of the glass powders at a firing temperature of 700 °C. Glass materials are heterogeneously distributed inside the $BaTiO_3$ pellets. Therefore, abnormal grain growth of the $BaTiO_3$ pellet fired at 1000 °C is caused by the heterogeneous distribution of the glass material [6]. The dielectric constant of the pellet fired at 1000 °C was 2682.



(a) Before firing



(b) 700 °C



(c) 1000 °C

Fig. 7. SEM image of the surface of $BaTiO_3$ pellets sintered at various temperatures.

Conclusions

The characteristics of $ZnO-B_2O_3-SiO_2$ (ZBS) glass powders prepared by spray pyrolysis as the sintering agent of $BaTiO_3$ pellets were investigated. The ZBS glass powders prepared by spray pyrolysis at the optimum preparation conditions have a spherical shape and submicrometre size. The ZBS glass powders have good sintering characteristics at low temperatures. The $BaTiO_3$ pellet with 3 wt.% ZBS glass has a high dielectric constant at a firing temperature of 1000 °C.

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