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Sintering behavior and dielectric properties of $BaTiO_3$ ceramics with glass addition for internal capacitor of LTCC

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Abstract

The addition effects of $ZnO–B_2O_3–SiO_2$ (ZBS) glass on both the sintering behavior and dielectric properties of $BaTiO_3$ were investigated in developing low-temperature-fired $BaTiO_3$-based ceramics for LTCC devices. X-ray diffractometer (XRD), scanning electron microscopy (SEM), and a dilatometer were used to examine the effect of ZBS glass on $BaTiO_3$ densification and the chemical reaction between the glass and $BaTiO_3$. The results indicate that ZBS glass can be used as a sintering aid to reduce the sintering temperature of $BaTiO_3$ from 1300 to 900 °C without secondary phase formation. The dielectric properties of $BaTiO_3$ with ZBS glass sintered at 900 °C show a relative density of 95%, a high dielectric constant of 994, and a dielectric loss of 1.6%.

Keywords: $BaTiO_3$; LTCC; Sintering; Internal capacitor

1. Introduction

Recently, the microwave telecommunication and satellite broadcasting industries have progressed greatly through portable telephones. The dielectric components must also be miniaturized to reduce the size of devices. In recent years, low-temperature cofired ceramics (LTCC) have been developed to increase the volume efficiency by integrating passive components such as capacitors, resistor, and inductors [1,2]. Barium titanate is a well-known ferroelectric materials that is widely used as a dielectric for multilayer ceramic capacitors because of its high dielectric constant. However, the sintering temperatures of barium titanate-based ceramics must densify above 1300 °C which is too high for LTCC processing. Therefore, the development of low-temperature-sintered barium titanate-based ceramics is urgently desired to fabricate LTCC devices for microwave applications.

Improved ceramic densification at low-temperatures can be achieved by chemical processing, adding glass flux, and smaller particle sizes of the starting materials [3,4]. Of the above methods, lowering the sintering temperature through glass addition is the most effective and least expensive technique. However, glass addition often results in dielectric properties degradation in $BaTiO_3$ due to the low-dielectric-constant additives dilution effect or the chemical reaction between glasses and $BaTiO_3$ to form a low-dielectric-constant phase. Therefore, choosing a suitable glass flux that can reduce the sintering temperature below 900 °C and improve dielectric properties of $BaTiO_3$-based ceramics simultaneously is important for the fabrication of LTCC modules.

One of the most important processes in manufacturing defect-free internal capacitor of LTCC devices involves the cofiring of capacitor and LTCC materials at a low-temperature. Mismatched densification kinetics and severe chemical reaction between the different materials could generate undesirable defects such as delamination, cracks and camber in the final products. However, the reaction and diffusion between the $BaTiO_3$ added with sintering aids and LTCC substrates during cofiring has seldom been reported [5,6].

The main objective of this study was to develop a $BaTiO_3$-based ceramics sinterable at temperatures below 900 °C and thus compatible with high-conductivity silver. The sintering behavior and dielectric properties of $BaTiO_3$ with the addi-

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tion of $ZnO–B_2O_3–SiO_2$ (ZBS) glass were investigated. The relationships between the sintering temperature, microstructure evolution and dielectric properties of $BaTiO_3$ with various amounts of glasses are presented.

2. Experimental procedures

$BaTiO_3$ powder with Ba/Ti = 1, supplied by Nippon chemical Co. Ltd. (Palceram BT-4), was used as the raw material. For ZBS glass, high purity powders of ZnO, B_2O_3, and SiO_2 were weighed according to the composition of 60.7%ZnO–24.9%B_2O_3–14.4%SiO_2 (in mol%). The powders were mixed, dried, and melted at 1200 °C. The melt was then quenched in water to form glass. The glass was powdered homogeneously and then mixed with $BaTiO_3$ powder in 2, 5, and 12 wt% proportion. $BaTiO_3$ powder and glass were milled for 12 h in acetone using YTZ balls. The powders were dried in an oven and then added to PVA for granulation. The powders were dry-pressed at 150 MPa into pellets of 10 mm diameter and 2 mm height. These specimens were then debindered at 500 °C and sintered at various temperatures ranging from 850 to 900 °C for 2 h. In the following, the samples are denoted as ZBS-x-y, where x refers to the amount of glass addition and y refers to the sintering temperature (1 indicates 800 °C, 2 indicates 850 °C, and 3 indicates 900 °C). For example, the ZBS-2-1 sample indicates $BaTiO_3$ with the addition of 2 wt% ZBS glass sintered at 800 °C.

Thermal shrinkage was measured using a dilatometer (Netzsch DIL 420C). The densities of the sintered samples were determined using the Archimedean method. The true density of 3.706 gm/cm^3 for ZBS glass and 6.0 gm/cm^3 for the $BaTiO_3$ powder measured using pycnometer (Micromeritics, AccuPyc 1340) were used to calculate the theoretical densities of the sintered samples using the mixture rule. The crystalline phase identification was determined using X-ray diffractometry (Siemens, D5000) with Cu Kα radiation. The microstructure was observed by scanning electron microscopy (Hitachi, S-2700). Dielectric properties (dielectric constant (K), dielectric loss ($\tan\delta$)) were measured using an LCR meter (YHP 4291A, YHP Co. Ltd.) at 1 MHz.

Wetting behaviors between $BaTiO_3$ and glasses were studied by placing a piece of a glass compact on top of a dense $BaTiO_3$ substrate and firing at 900 °C with a heating rate of 10 °C/min. Contact angle was measured using a digital camera. The interfacial reaction between $BaTiO_3$ and glass was then investigated using SEM and EDX.

3. Results and discussion

Fig. 1 shows the result of dilatometric analysis of ZBS glasses. The softening temperature where ZBS glass starts to melt is about 559 °C. Fig. 2 shows the wetting behavior between ZBS glass and $BaTiO_3$ at 900 °C. As the temperature becomes higher than the melting point of ZBS glass, the glass starts to melt and spreads over the $BaTiO_3$ substrate. A small contact angle of less than 10° and an intimate contact between ZBS glass and $BaTiO_3$ substrate is obtained at 900 °C.

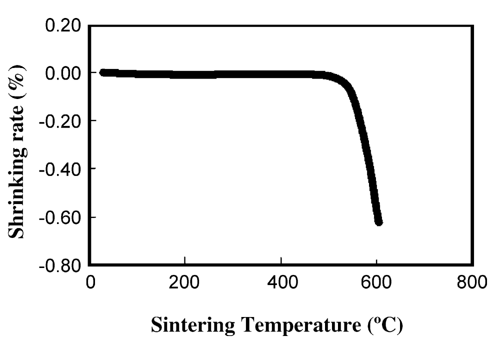

Fig. 1. Result of dilatometric analysis of ZBS glasses.

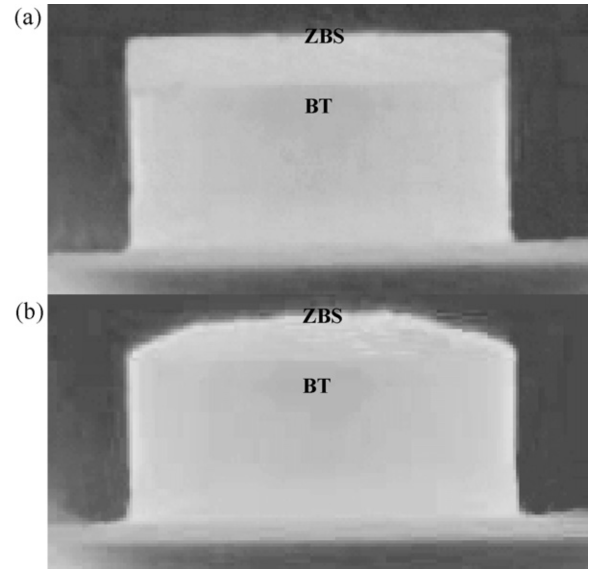

Fig. 2. Wetting behavior between ZBS glass and $BaTiO_3$ at 900 °C.

Fig. 3 shows XRD patterns of the samples with various amounts of added ZBS glass sintered in the 850–900 °C temperature regions. No secondary phase was detected for the samples added with 2 and 5 wt% ZBS glass. However, for the samples with the addition of 12 wt% ZBS glasses, a secondary phase, $Ba_2TiSi_2O_8$ (BTS), was observed and the amount of the secondary phase formed increased with increasing the sintering temperature.

Fig. 4 shows the variation of the relative densities of the $BaTiO_3$ ceramics with the amount of glass addition and sintering temperature. For the sample added with 2 wt% ZBS glass, the fully densification was not obtained, which may be the result of insufficient liquid phase. However, as the amount of added ZBS glass increased above 5 wt%, the high densification was achieved at less than 850 °C and the relative density reached above 95% at 900 °C. The results indicate that ZBS which possesses superior wetting characteristic on the surface of $BaTiO_3$ ceramic and does not react with $BaTiO_3$ to form the secondary phase may act as a liquid-phase sintering aid to enhance the densification.

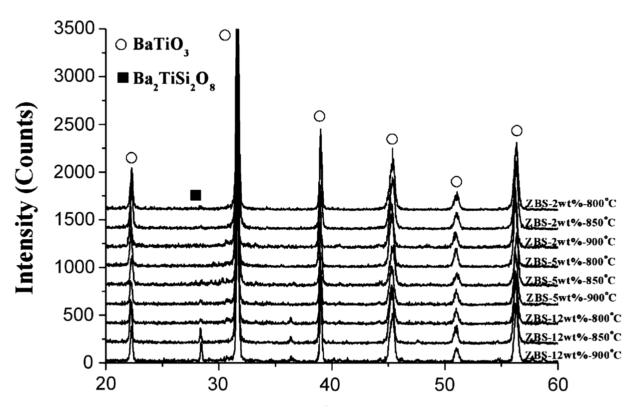

Fig. 3. XRD patterns of the samples with various amounts of added ZBS glass sintered in the 850–900 °C temperature regions.

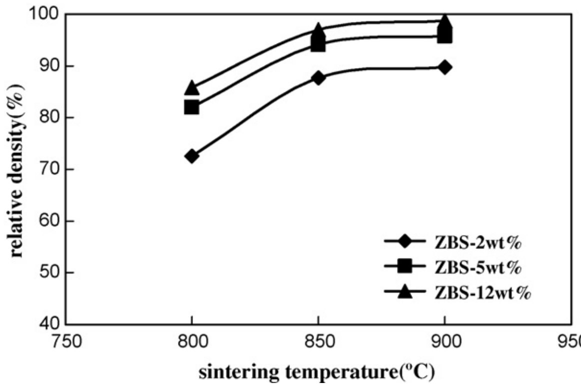

Fig. 4. Variation of the relative densities of the $BaTiO_3$ ceramics with the amount of glass addition and sintering temperature.

Typical microstructures of sintered ceramics are shown in Fig. 5. It can be seen that at 850 °C, the amount of pores appeared to decrease with increasing glass content (Fig. 5). The samples added with 2 wt% glass showed a fine grained, highly porous microstructure. However, the addition of glass above 5 wt% resulted in a sudden increase in the density (Fig. 4) and a decrease in the number of pores. At 900 °C, the microstructures of the samples added with 5 and 12 wt% glass were dense and consisted of uniform grain size of 0.8 and 1.2 μm, respectively.

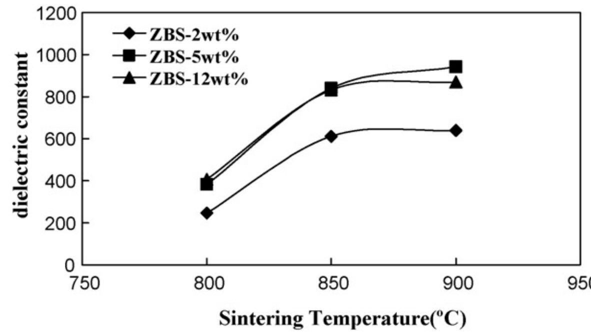

Fig. 6. Effects of the various amounts of added glass on the dielectric constant of $BaTiO_3$ ceramics.

The effects of the various amounts of added glass on the dielectric constant of $BaTiO_3$ ceramics are shown in Fig. 6. For the samples added with 2 and 5 wt% ZBS glass, the dielectric constant increased as the sintering temperature increased from 800 to 900 °C due to the increase of the relative density as shown in Fig. 4. However, for the sample with added 12 wt% ZBS glass, as the sintering temperature increased from 850 to 900 °C, the dielectric constant decreased, which is suggested to be originated from the formation of secondary phases (BTS) with low dielectric constant. The maximum dielectric constant of 994 was obtained from the sample added with 5 wt% ZBS glass sintered

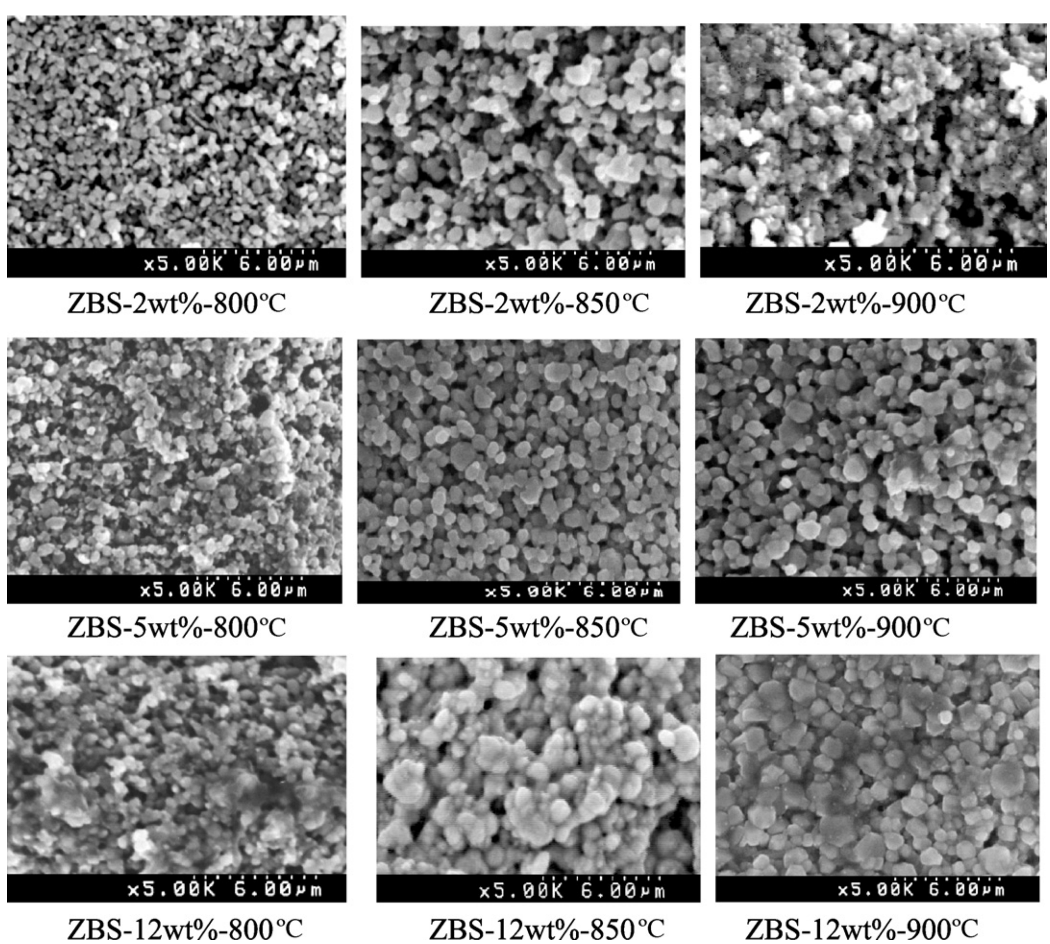

Fig. 5. Microstructure development of the samples with various amounts of added ZBS glass sintered in the 850–900 °C temperature regions.

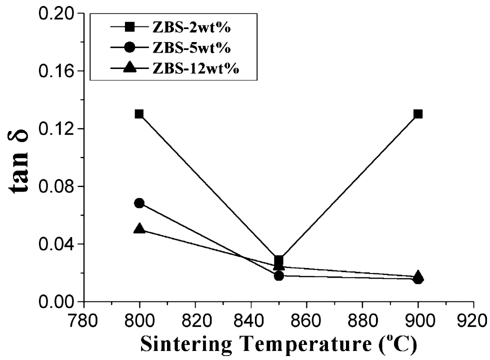

Fig. 7. Dielectric loss of the sample added with 5 wt% ZBS glass as a function of sintering temperature.

at 900 °C, which might be the result of the absence of secondary phase and pores. The dielectric loss of the sample added with 5 wt% ZBS glass as a function of sintering temperature is shown in Fig. 7. The dielectric loss decreased with increasing sintering temperature and the lowest dielectric loss value of 1.6% was obtained from the sample added with 5 wt% ZBS glass sintered at 900 °C.

4. Conclusions

ZBS glass can be used as a sintering aid to reduce the sintering temperature of $BaTiO_3$ from 1300 to 900 °C without secondary phase formation. The dielectric properties of $BaTiO_3$ with ZBS glass sintered at 900 °C show a relative density of 95%, a high dielectric constant of 994, and a dielectric loss of 1.6%.

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