Densification and Dielectric Properties of $Ba_{0.5}Sr_{0.5}TiO_3$-Glass Composites for LTCC Applications

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ABSTRACT

Barium zincoborate (BZB) glass was added to $Ba_{0.5}Sr_{0.5}TiO_3$, and sintered at 875°C for 2 h in air. When the BZB glass was added in quantities ranging from 15 to 20 wt%, the relative bulk density ranged from 93.1% to 94.2%, while the density decreased to roughly 81% thereafter up to 30 wt% glass addition. Quantitative XRD analysis showed that the $Ba_{0.5}Sr_{0.5}TiO_3$ filler was significantly dissolved into the BZB glass. However, no secondary phase was identified by XRD up to 30 wt% glass addition. The dielectric constant was about 130 to 140 at 1 MHz up to 20 wt% BZB glass addition, while it decreased to about 60 thereafter, which may be ascribed to decreased density, partial dissolution of the $Ba_{0.5}Sr_{0.5}TiO_3$, and associated changes in the glass composition. The dielectric loss of the 20 wt% glass added specimen was 0.008.

Key words : Dielectric materials/properties, Glass, Low temperature, Composites

1. Introduction

Barium strontium titanate (BST) *thin* films have received interest for application in electrically tunable materials in microwave devices for telecommunication applications.[1,2] Currently, BST *thick* films fabricated by low temperature co-firing ceramic (LTCC) technology are receiving a high interest for application in microwave tunable components, capacitors[3-5] and so on, due to their moderate cost and good dielectric properties. The LTCC technology involves slurry preparation and tape casting to obtain green tapes. The green tape is subsequently punched to form via holes. Then, metal electrode patterns are printed onto the green tape layers, which are then stacked, laminated, and co-fired to form mulit-layer structures.

The sintering temperature of pure BST is over 1350°C. To co-sinter BST with silver electrode requiring a sintering temperature of about 900°C, appropriate sintering aids need to be used. In general, the addition of sintering aids degrades the dielectric properties of BST; therefore,the selection of the appropriate sintering aid is important. In the literature,[6] the use of 0.5 wt% B_2O_3 alone as a sintering aid to $Ba_{0.7}Sr_{0.3}TiO_3$ could reduce the sintering temperature to 1150°C, but further addition of B_2O_3 yielded secondary phases with degraded dielectric properties. Thus far, the developed sintering aids yielding sintering temperature of about 900°C include B_2O_3-Li_2CO_3[7-9] and Li_2CO_3.[10-14] In this work, the feasibility of a barium zincoborate (BZB) glass as a sintering aid for $Ba_{0.5}Sr_{0.5}TiO_3$ was investigated by systematically varying the glass addition to the $Ba_{0.5}Sr_{0.5}TiO_3$-BZB glass composites. The resultant densification and dielectric properties are reported herein.

2. Experimental Procedure

A commercial BaO-ZnO-B_2O_3 (BZB) glass frit (TM05) was provided by Temen Technology, Inc. (Gangneung, Korea). Its manufacturer-provided properties are shown in Table 1. $Ba_{0.5}Sr_{0.5}TiO_3$ powder (Assay of 99.9%, dielectric constant of 2300 at 1 kHz, and average particle size of 1.5 μm) was provided by Gmics Co., Ltd. (Gangneung, Korea). Various compositions of BZB glass frit (10, 15, 20, 25, and 30 wt%) and $Ba_{0.5}Sr_{0.5}TiO_3$ powder were ball milled using zirconia balls in distilled water medium for 6 h. The dried composite powder was uniaxially pressed in a mold with diameter of 20 mm at 100 MPa, followed by a cold isostatic press at 300 MPa. The disk specimens were sintered at 875°C for 2 h in air.

The apparent density of the sintered specimens was measured by Archimedes principle. Bulk density was determined by measurement of specimen dimensions and dry weight. The microstructure of the specimens was observed by FE-SEM

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Table 1. Manufacturer-provided Properties of the Barium Zincoborate Glass

Property	Value
Dilatometric softening point (°C)	550~600
Coefficient of thermal expansion (K^{-1})	7.5×10^{-6}
Density (g/cm^3)	3.5
Dielectric constant (at 1 MHz)	12~14
Dielectric loss (at 1 MHz)	< 0.005

(Model S-4700, Hitachi, Tokyo, Japan). After application of the silver paste to both sides of the disk specimens, their dielectric properties were measured by using an impedance phase analyzer (Model 4192A, Hewlett Packard, Yokogama, Japan) at 1 MHz.

The residual amount of $Ba_{0.5}Sr_{0.5}TiO_3$ in each sintered specimen was quantified by X-ray diffraction (internal standard method[15]). Silicon powder (Assay 99.999%; Sigma-Aldrich, Inc., St. Louis, USA) was used as an internal standard. A 30 wt% silicon was added to artificial mixtures of varying $Ba_{0.5}Sr_{0.5}TiO_3$ and glass frits, and was subjected to XRD to construct the calibration curve of $I_{BST\,(110)}/I_{Si\,(111)}$ (I is the intensity of the diffraction peak) as a function of the initial amount of $Ba_{0.5}Sr_{0.5}TiO_3$. Then, an unknown sintered specimen was pulverized and mixed with 30 wt% silicon, which was subjected to XRD. The $I_{BST\,(110)}/I_{Si\,(111)}$ ratio was determined from the XRD pattern of the unknown sintered specimen-silicon mixture, and the amount of the residual $Ba_{0.5}Sr_{0.5}TiO_3$ in the unknown sintered specimen was quantified by comparison with the calibration curve. Application of the internal standard method to other ceramic-glass composites is available in the literature.[16,17]

3. Results and Discussion

The relative density of the sintered specimens is shown in Fig. 1. The theoretical density of the composites necessary for the determination of the relative density was calculated with the assumption that $Ba_{0.5}Sr_{0.5}TiO_3$ and glass are sintered together without any reaction. The Theoretical density of 5.52 g/cm^3 was used for $Ba_{0.5}Sr_{0.5}TiO_3$ based on the XRD lattice parameter analysis. As the BZB glass was added in quantities ranging from 15 to 20 wt%, relative bulk densities ranging from 93.1% to 94.2% were achieved, while the density decreased to roughly 81% thereafter up to 30 wt% glass addition. As will be discussed later, a significant change of glass composition by the reaction with BST may degrade the capability
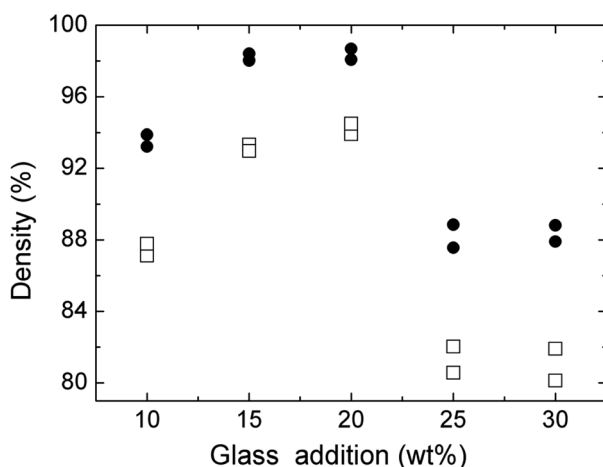
of the glass as a sintering aid when the initially added glass is overly high (25 to 30 wt %).

Fig. 2 shows the microstructures of the sintered $Ba_{0.5}Sr_{0.5}TiO_3$-glass composite specimens for polished surfaces. In the 10 wt% glass-added specimen, the pores seem to be interconnected due to insufficient sintering. From the glass addition of 15 wt%, pores are isolated, and the tendency of pore formation with glass addition matches the change in density (Fig. 1).

To understand the decrease of sinterability with the overly high glass addition (25~30 wt% glass), first, the possibility of forming secondary phases was checked by XRD, and the result (with 30 wt% silicon internal standard) is shown in Fig. 3. As seen in the figure, only the diffraction peaks of $Ba_{0.5}Sr_{0.5}TiO_3$ are observed up to the addition of 30 wt% BZB glass. This means that the possibility of the influence of any secondary phases on the poor sintering of the 25~30 wt% glass-added specimens is ruled out.

In next step, the residual amounts of $Ba_{0.5}Sr_{0.5}TiO_3$ in the sintered specimens were quantified by the internal standard method (XRD), and the result is shown in Fig. 4. Initial compositions of 10, 15, 20, 25, and 30 wt% of BZB glass yielded only 43.4, 22.6, 19.6, and 15.1, and 13.2 wt% of residual $Ba_{0.5}Sr_{0.5}TiO_3$, respectively, after sintering (Column C in Table 2).
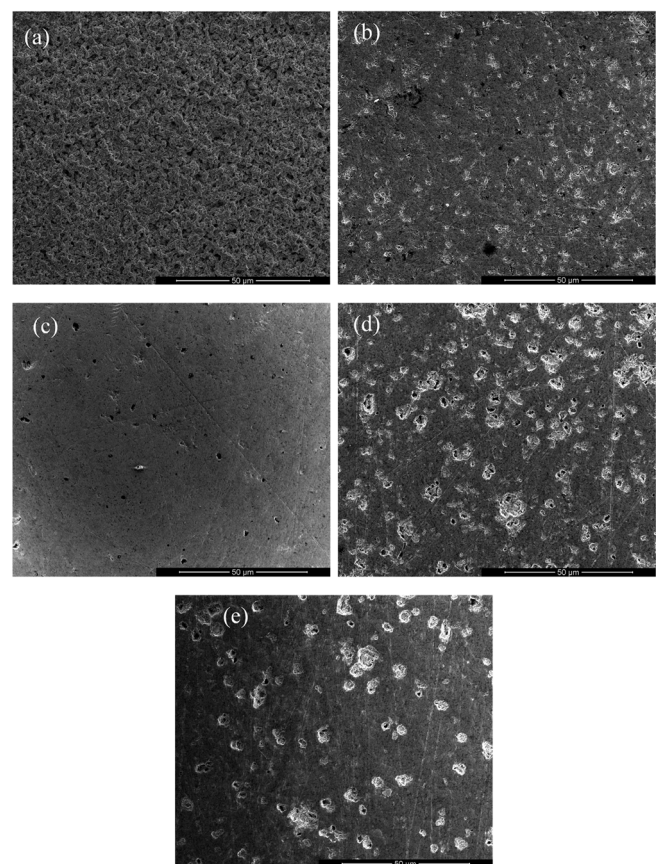

Fig. 2. FE-SEM images of the sintered specimens with BZB glass additions of (a) 10 wt%, (b) 15 wt%, (c) 20 wt%, (d) 25 wt%, and (e) 30 wt%.
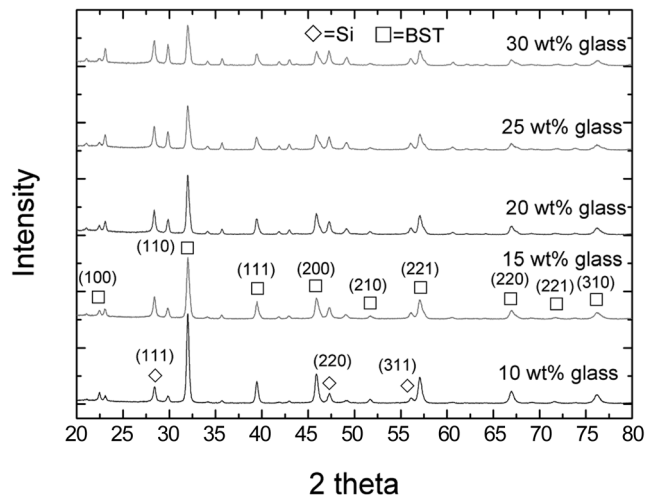

Fig. 1. Change in relative density of the sintered specimens as a function of glass addition (●: apparent density; □: bulk density).

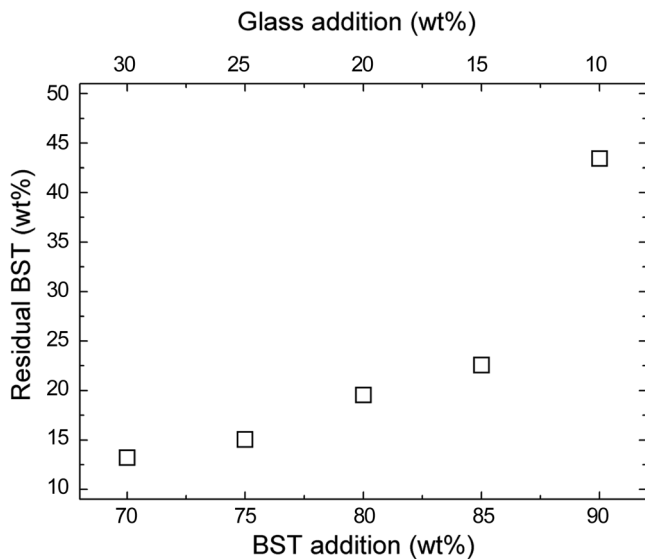**Fig. 3.** XRD patterns of sintered specimens with 30 wt% silicon as an internal standard.

Fig. 4. Amount of the residual $Ba_{0.5}Sr_{0.5}TiO_3$, quantified by the internal standard method, as a function of initial glass addition.

This observation clearly indicates that $Ba_{0.5}Sr_{0.5}TiO_3$ reacts with BZB glass and is significantly dissolved. The dissolution of $Ba_{0.5}Sr_{0.5}TiO_3$ increased with the BZB glass addition, so that, when the glass addition was high, e.g., 30 wt% (70 wt% of $Ba_{0.5}Sr_{0.5}TiO_3$), only 13.2 wt% of $Ba_{0.5}Sr_{0.5}TiO_3$ remained after sintering. The dissolved amount of $Ba_{0.5}Sr_{0.5}TiO_3$ turns out to be 45.6, 62.4, 60.4, 59.9, and 56.8 wt% for the initial $Ba_{0.5}Sr_{0.5}TiO_3$ compositions of 90, 85, 80, 75, and 70 wt%, respectively (Column D in Table 2).

Note that, interestingly, no secondary phase was identified by XRD up to 30 wt% glass addition despite of the significant dissolution of $Ba_{0.5}Sr_{0.5}TiO_3$ into the BZB glass. This indicates that the dissolved Ba-Sr-Ti-O component is well hosted by the original Ba-Zn-B-O glass network to avoid the formation of any secondary phases. A small addition of glass yields less dissolution of BST (subsequently a less dissolution percentage), and a larger amount of glass results in a larger dissolution quantity of BST (Columns D and E in Table 2). This means that, when the amount of glass is insufficient, there is a solubility limit in the barium zincoborate (BZB) glass network to host the dissolved Ba-Sr-Ti-O. Especially the increase of the BaO component in the $BaO-ZnO-B_2O_3$ (BZB) glass may limit the further dissolution of $Ba_{0.5}Sr_{0.5}TiO_3$ when the initial glass addition is small.

The interpretation of the phenomenon of poor densification with overly high glass addition (25~30 wt%) without any formation of secondary phases is not an easy task. There have been some reports that various crystalline oxide fillers are partially dissolved into glass during the sintering of ceramic-glass composites.[17] The fact that crystalline $Ba_{0.5}Sr_{0.5}TiO_3$ is significantly dissolved to BZB glass during sintering observed in the current work provides a clue to establish a scenario to interpret the phenomenon of poor densification at overly high glass addition. The change of glass composition by the significant dissolution of BST possibly degrades the wettability or fluidity of the glass, resulting in poor densification at overly high glass addition*. Further work is necessary to clarify the issue of poor densification of BZB glass-BST composites at overly high glass addition.

Fig. 5 shows change in the dielectric constant as a function

Table 2. Residual $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) Quantified by the Internal Standard Method (XRD analysis), Dissolution Amount, Resultant Percentages of Dissolution Amount, and Total Glass

Initial composition		Residual BST	Dissolution amount	Percentage of dissolved BST	Total glass
Glass (wt%; A)	BST (wt%; B)	(wt%; C)	(wt%; D=B-C)	(wt%; E=D/B × 100)	(wt%; A+D or 100-C)
10	90	43.4	46.6	51.8	56.6
15	85	22.6	62.4	73.4	77.4
20	80	19.6	60.4	75.5	80.4
25	75	15.1	59.9	79.9	84.9
30	70	13.2	56.8	81.1	86.8

*References reporting that the change of glass composition due to the dissolution of crystalline oxides results in poor densification could not be found by the current authors.

of glass addition. The dielectric constant is from 130 to 140 at 1 MHz up to 20 wt% BZB glass addition, while it decreases abruptly to about 60 thereafter. This is very similar to the change in density as a function of glass addition (Fig. 1). This fact indicates that the degree of densification is primarily responsible for the change in dielectric constant shown in Fig. 5. Since the dielectric constant of air in a pore is only 1, it is natural that the degree of densification (elimination of pores) will directly govern the dielectric constant. Other sources that account for the sudden change of dielectric constant with 25~30 wt% of glass include the change in the residual amount of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (Fig. 3) and the change in glass composition due to the significant dissolution of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$.

The dielectric loss (Fig. 6) of the specimen was in the range from 0.005 to 0.019, with no apparent dependency on the glass addition. When 20 wt% of BZB glass was added, the relative bulk density was 94.2% (Fig. 1), and its dielectric constant and dielectric loss were about 144 and 0.008, respectively (Figs. 5, 6).
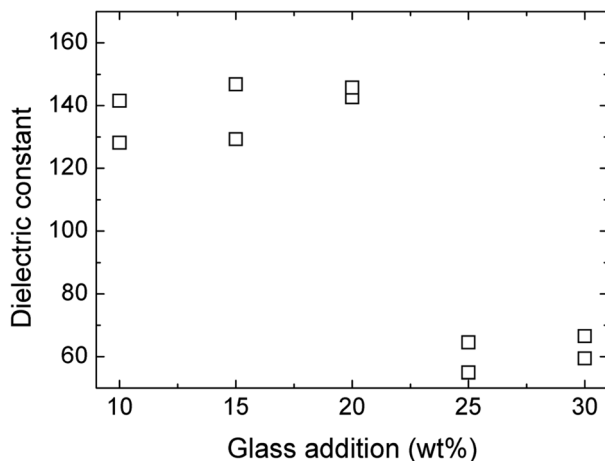

Fig. 5. Change in dielectric constant as a function of glass addition.
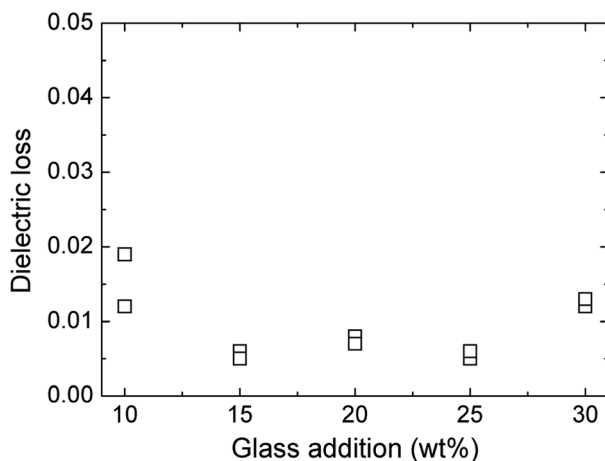

Fig. 6. Change in dielectric loss as a function of glass addition.

4. Conclusion

Various quantities of an LTCC glass, barium zincoborate (BZB), were added to Ba$_{0.5}$Sr$_{0.5}$TiO$_3$, and sintered at 875°C for 2 h for low temperature co-firing ceramic (LTCC) capacitor applications. As the BZB glass was added in quantities ranging from 10 to 20 wt%, the relative bulk density ranged from 93.1% to 94.2%, while the density decreased to roughly 81% thereafter up to 30 wt% glass addition. Quantitative XRD analysis showed that the Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ filler was significantly dissolved into the BZB glass. The dissolution of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ increased with the BZB glass addition, so that, when the glass addition was high, e.g., 30 wt% (70 wt% of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$), only 13.2 wt% of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ remained after sintering. However, interestingly, no secondary phase was identified by XRD up to 30 wt% glass addition. The dielectric constant was from 130 to 140 at 1 MHz up to 20 wt% BZB glass addition, while it decreased to about 60 thereafter, which may be ascribed to decreased density, partial dissolution of the Ba$_{0.5}$Sr$_{0.5}$TiO$_3$, and associated changes in glass composition. When 20 wt% of BZB glass was added, the relative bulk density was 94.2%, and its dielectric constant and dielectric loss were about 144 and 0.008, respectively.

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