

Effect of glass powders with spherical shape and fine size on the sintering behavior and dielectric properties of BaTiO₃ ceramics

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In this study, it was found that BaO–B₂O₃–SiO₂ glass powders with fine particle sizes and spherical shapes improved the sintering characteristics of nanosized BaTiO₃ powders. The mean sizes of the prepared glass powders and BaTiO₃ powders were 940 nm and 110 nm, respectively. The densities of BaTiO₃ pellets containing 0, 1, 3, and 5 mass% of a glass additive were 4.2, 5.2, 5.5 and 5.7 gcm⁻³, respectively, at a sintering temperature of 900°C. The densities of BaTiO₃ pellets sintered at 900°C and containing 5 mass% of the glass additive were similar to that of the pellet sintered at 1280°C and containing no glass additive. Dielectric constants of pellets containing 5 mass% of the glass additive and of pellets containing no glass additive were 1599 and 469, respectively, at a sintering temperature of 900°C. Dielectric constants of pellets containing 1 mass% of the glass additive increased from 602 to 4109 when the sintering temperature was increased from 800 to 1200°C.

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1. Introduction

Barium titanate (BaTiO₃)-based ceramics are widely used in multilayer ceramic capacitors (MLCCs) owing to their good dielectric properties at temperatures less than 120°C.¹⁾ In particular, tetragonal BaTiO₃ has excellent dielectric properties, due to which it can be potentially used in MLCCs.^{2)–4)} However, in order to prepare BaTiO₃ with a high density and high dielectric constant, sintering temperatures higher than 1300°C and long soaking times are required; further, the use of expensive electrodes in the production process of multilayer ceramics is inevitable. All these factors would increase the production cost of such multilayer ceramics. Therefore, two main approaches have been adopted to decrease the sintering temperature of multilayer ceramics.^{5)–7)} One approach involves the addition of glass-phase materials that act as densification promoters by enhancing the formation of a liquid phase, thereby improving the diffusion of various species. The other approach involves reduction in particle sizes of starting materials.

To fabricate miniature MLCCs with high performance and low electric power consumption, the number of active dielectric layers is increased and their thicknesses are decreased. Thus, the mean sizes of dielectric and glass powders are decreased.⁸⁾ Nanosized BaTiO₃ powders with controlled morphology have been widely studied in many ceramic processing processes. However, the effects of characteristics of glass powders on characteristics of dielectric layers have not been studied extensively. Micron size glass powders with irregular morphology prepared by conventional melting process were mainly used to decrease the sintering temperature of BaTiO₃ ceramic.

Spray pyrolysis is one of the promising processes for the preparation of improved ceramic and glass powders.^{9)–13)} Powders prepared by spray pyrolysis are relatively uniform in size and

composition, spherical, fine-sized, and have nonaggregation characteristics because of the microscale reaction within a droplet and the absence of a milling process. In this study, nanosized BaTiO₃ and submicrometer-sized glass powders were prepared by spray pyrolysis. Further, the effects of fine-sized, spherical BaO–B₂O₃–SiO₂ glass powders prepared by spray pyrolysis on the sintering characteristics of nanosized BaTiO₃ powders were investigated.

2. 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. Glass powders with a 30 mass% BaO–60 mass% B₂O₃–10 mass% SiO₂ composition were directly prepared by high-temperature spray pyrolysis. The preparation temperature of glass powders was 1300°C. The flow rate of the carrier gas was 20 Lmin⁻¹, in which the residence time of the powders inside the hot wall reactor was 0.67 sec. The concentration of Ba, B and Si components was 0.5 M.

Barium carbonate and titanium tetra-iso-propoxide (TTIP) were used as starting materials to prepare BaTiO₃ powders. The starting materials were added into a mixed solution of water and nitric acid to form a clear solution. The concentration of Ba and Ti was fixed at 0.1 M. The concentration of citric acid used as an organic additive was 0.4 M. The preparation temperature of BaTiO₃ powders was 900°C. The flow rate of the carrier gas was 40 Lmin⁻¹, in which the residence time of the powders inside the hot wall reactor was 0.45 sec. The as-prepared powders obtained by spray pyrolysis were post-treated at 900°C for 2 h in air atmosphere.

The BaTiO₃ and glass powders prepared by spray pyrolysis were thoroughly wet-mixed with the addition of ethanol in an agate bowl and then small amount of PVA solution was added for granulation. The amount of glass powders were changed from 1 mass% to 10 mass% of BaTiO₃ powders. The mixed powders

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were pelletized at 24500 kPacm^{-2} pressure into a 15 mm diameter. The pellets were then sintered from 850 to 1200°C for 3 h and cooled naturally to room temperature while furnace power was off.

The crystal structures of the BaTiO₃ and glass powders and sintered pellets were investigated by using X-ray diffraction (XRD; RIGAKU Co., D/MAX-RB) with Cu K α radiation ($\lambda = 1.5418 \times 10^{-10} \text{ m}$). The morphological characteristics of the powders and pellets were investigated by using scanning electron microscopy (SEM; JEOL Ltd., JSM-6060) and transmission electron microscopy (TEM; FEI, TECHNAI 300K). The specific surface area was measured by Brunauer–Emmet–Teller (BET, PROTECH, TRISTAR 3000) method using N₂ adsorption. Sample densities were measured by Archimedes' method. Dielectric measurements of the samples were performed by using a LCR meter at 1 kHz.

3. Results and discussion

Characteristics of the glass powders and BaTiO₃ powders are shown in Figs. 1, 2, and 3. The glass powders prepared by spray pyrolysis were spherical and had narrow size distributions, as shown in Figs. 1 and 2. Their mean size measured from their

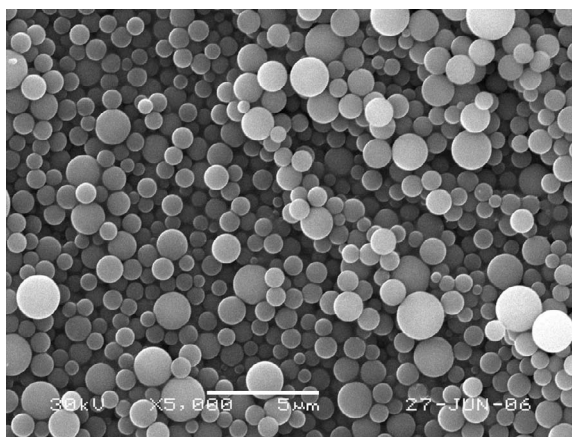


Fig. 1. SEM photograph of BaO–B₂O₃–SiO₂ glass powders prepared by spray pyrolysis.

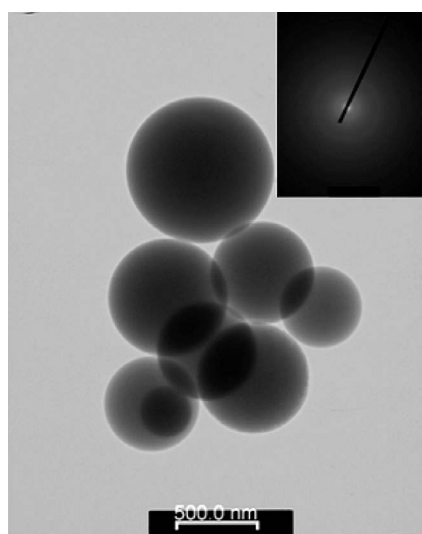


Fig. 2. TEM micrograph of BaO–B₂O₃–SiO₂ glass powders prepared by spray pyrolysis.

SEM images was 940 nm. The geometric standard deviation of the glass powders was 1.2. The electron beam diffraction pattern and XRD pattern of the powders shown in Figs. 2 and 3, respectively, reveal the amorphous nature of these prepared glass powders. The crystal structures of these powders were not investigated by TEM.

The BaTiO₃ powders used in this study were prepared by

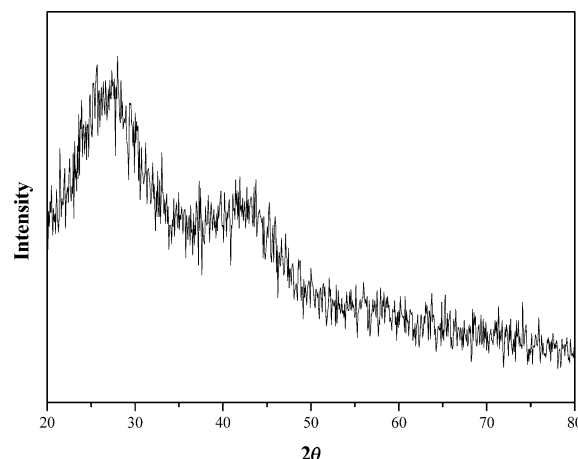
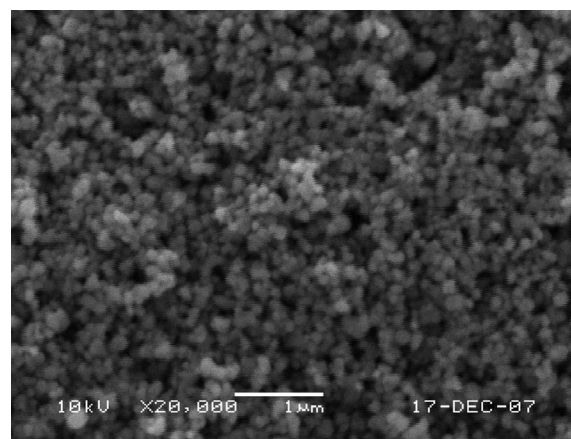
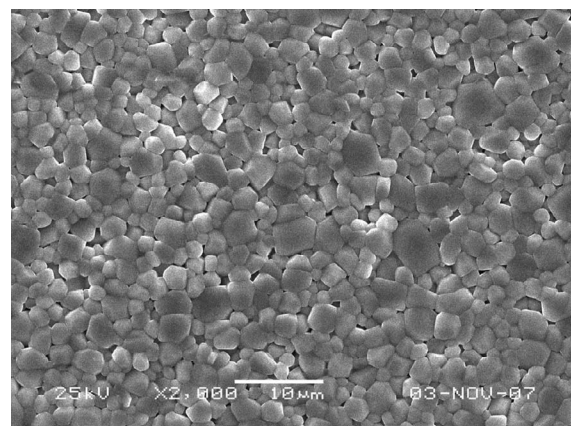


Fig. 3. XRD pattern of BaO–B₂O₃–SiO₂ glass powders prepared by spray pyrolysis.



(a)

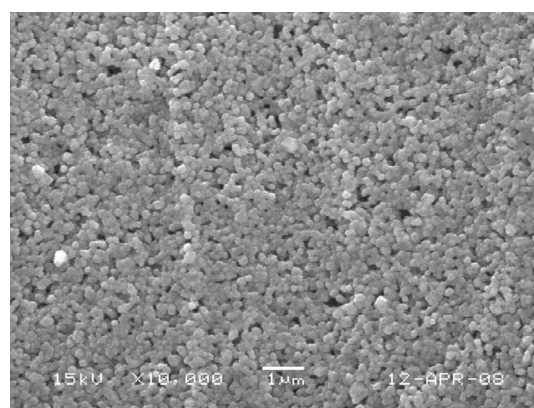


(b)

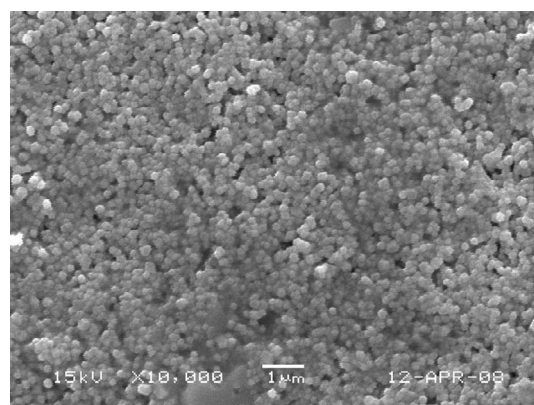
Fig. 4. SEM photographs of (a) raw BaTiO₃ powders prepared by spray pyrolysis and (b) BaTiO₃ ceramic sintered at 1280°C for 5 h.

citric-acid-assisted spray pyrolysis.¹¹⁾ Precursor powders prepared by spray pyrolysis from a spray solution containing citric acid had a hollow and porous structure. These precursor powders converted into nanosized BaTiO_3 powders after being post-treated at 900°C . As shown in Fig. 4(a), the mean size and geometric standard deviation of the BaTiO_3 powders were 110 nm and 1.1, respectively. The BET surface area of the BaTiO_3 powders was $9.1 \text{ m}^2/\text{g}$. Fig. 4(b) shows the sintering characteristics of the prepared BaTiO_3 powders at a sintering temperature of 1280°C . BaTiO_3 pellets sintered in the absence of a glass additive had dense structures and uniform grain sizes.

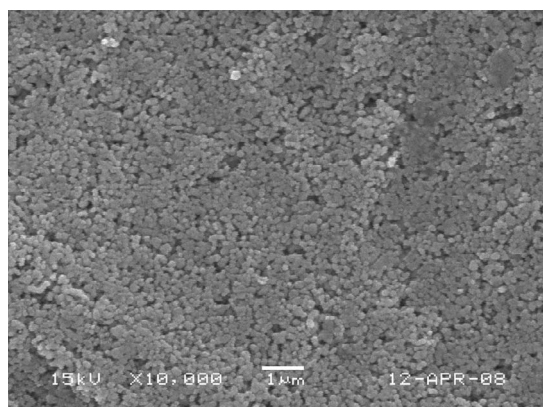
Surface morphologies of BaTiO_3 pellets containing and not containing glass powders are shown in Figs. 5 and 6, respectively. Figure 5 shows the surface morphology of a pellet to which glass powders were added before sintering. The added amount of glass powders was 5 mass% with respect to BaTiO_3 . The spherical shape of the glass powders was lost after pressing. The glass phase that dispersed in the BaTiO_3 matrix is represented by arrow. Figure 6 shows surface morphologies of sintered pellets containing various amounts of glass, ranging from 1 to 10 mass% with respect to BaTiO_3 . The pellets were sintered at a temperature of 900°C . Although sintering between the BaTiO_3 powders was possible even in the absence of the glass additive, the addition of the glass additive improved the sintering characteristics of the powders. Pellets containing the glass additive, shown in Fig. 6(b), had a fine grain size and homogeneous phase. However, secondary phases, shown by the arrows in Figs. 6(c) and (d), were observed in pellets containing a high



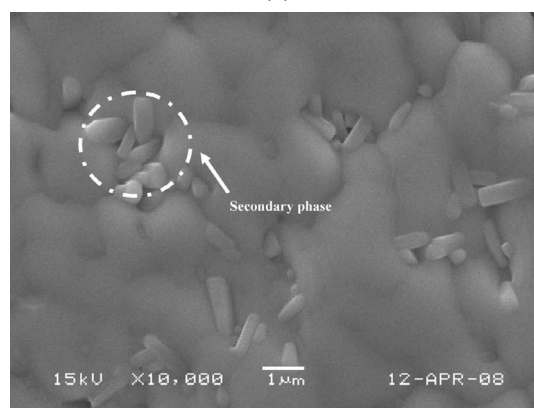
(a)



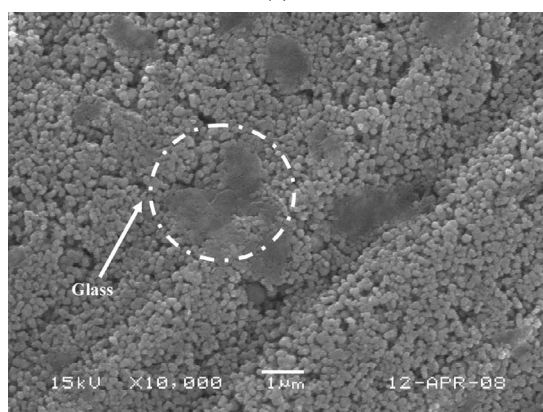
(b)



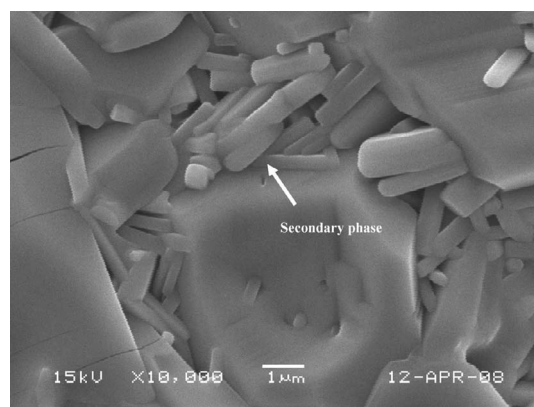
(a)



(c)



(b)



(d)

Fig. 5. SEM photographs of (a) pelletized BaTiO_3 and (b) pelletized BaTiO_3 with glass powders.

Fig. 6. SEM photographs of BaTiO_3 ceramics sintered at 900°C with various amount of glass. (a) 1 mass% glass; (b) 3 mass% glass; (c) 5 mass% glass; (d) 10 mass% powder.

amount of the glass additive. **Figure 7** shows a comparison of the densities of the sintered pellets. The densities of the pellets were measured by Archimedes' method. The density of the BaTiO₃ pellet containing no glass additive was 4.2 gcm⁻³. The addition of the glass additive caused an increase in the densities of the sintered pellets. The densities of the sintered pellets containing 1, 3, and 5 mass% of the glass additive were 5.2, 5.5, and 5.7 gcm⁻³, respectively. On the other hand, the density of the sintered pellet containing 10 mass% of the glass additive was 5.1 gcm⁻³. The porous structure of the sintered pellet, shown in Fig. 6(d) and formed as a result of the formation of the secondary phase, caused a decrease in the density. The density of the pellet sintered at 1280°C and containing no glass additive was 5.9 gcm⁻³. Further, the density of the BaTiO₃ pellet sintered at 900°C and containing 5 mass% of the glass additive was similar to that of the pellet sintered at 1280°C and containing no glass additive. The relative densities of the sintered pellets could also be estimated from their shrinkages. **Figure 8** shows the change in the diameters of the pellets sintered at various temperatures. The diameters of the BaTiO₃ pellets containing no glass additive did not change even after sintering at 850°C. On the other hand, the diameters of the pellets containing the glass additive decreased at a sintering temperature of 850°C; i.e., the pellets shrank. The addition of the glass additive caused a decrease in the sintering

temperature of the BaTiO₃ pellets. At sintering temperatures below 1000°C, the diameters of the pellets containing the glass additive were smaller than those of the pellets containing no glass additive. On the other hand, at a sintering temperature of 1100°C, the diameters of the pellets containing and not containing the glass additive were the same. At 1100°C, the nanosized BaTiO₃ powders prepared by spray pyrolysis could be sintered satisfactorily, even in the absence of the glass additive.

Figure 9 shows XRD patterns of pellets sintered at 900°C. Pellets containing 0 and 1 mass% of the glass additive showed a pure BaTiO₃ phase. On the other hand, in the XRD patterns of pellets containing 5 and 10 mass% of the glass additive, several impurity peaks attributed to barium borate phases were observed. However, the tetragonality of the BaTiO₃ pellets estimated from peak splitting at $2\theta = 45.5^\circ$ improved with an increase in the amount of the glass additive.

Figure 10 shows dielectric constants of the BaTiO₃ pellets containing various amounts of the glass additive. The sintering temperature was increased from 850 to 1200°C. Irrespective of the amount of the glass additive, the pellets sintered at 850°C had low dielectric constants because of their low densities. The dielectric constants of the pellets sintered at 900°C were affected by the amount of the glass additive. The dielectric constants of the pellets containing 5 mass% of the glass additive and of pel-

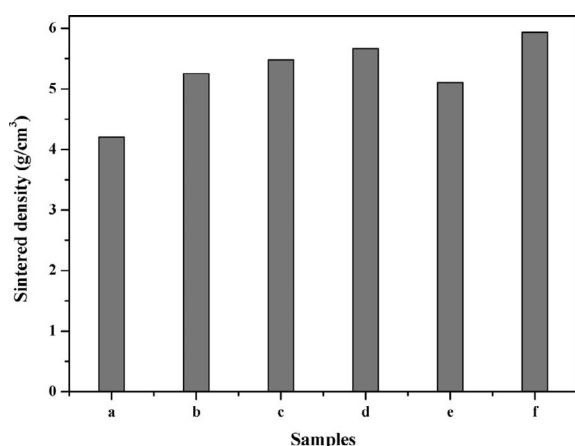


Fig. 7. Densities of BaTiO₃ ceramics sintered at 900°C with various amount of glass. (a) 0 mass%; (b) 1 mass%; (c) 3 mass%; (d) 5 mass%; (e) 10 mass%; (f) pure BaTiO₃ ceramic sintered at 1280°C.

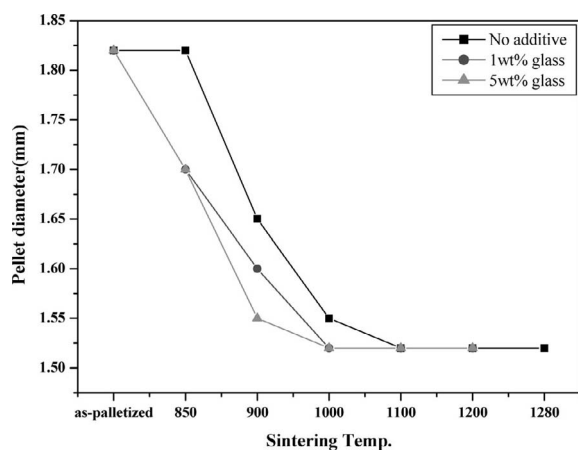


Fig. 8. Diameters of the pellets sintered at various temperatures.

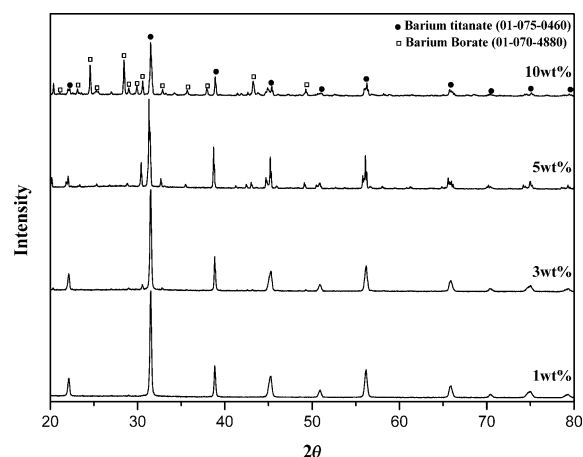


Fig. 9. XRD patterns of BaTiO₃ ceramics sintered at 900°C with various amount of glass.

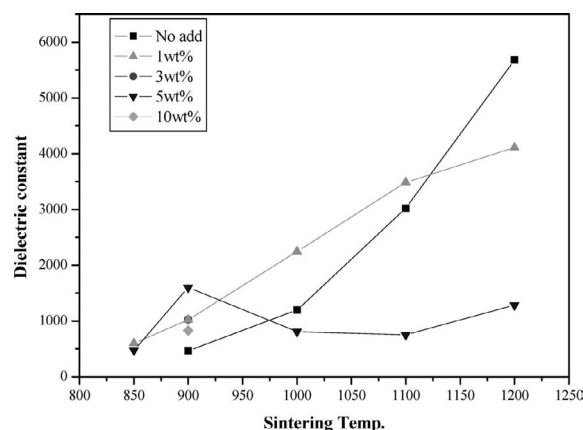


Fig. 10. Dielectric constants of BaTiO₃ ceramics sintered at different temperatures with various amount of glass.

lets containing no glass additive were 1599 and 469, respectively. The high densities and improved tetragonality of the BaTiO₃ pellets containing 5 mass% of the glass additive resulted in an increase in their dielectric constants. Further, the dielectric constants of the pellets containing 1 mass% of the glass additive and of pellets containing no glass additive increased with sintering temperatures because of the improved densities and tetragonality of the BaTiO₃ pellets. On the other hand, the dielectric constant of the pellet containing 5 mass% of the glass additive reached its maximum value at a sintering temperature of 900°C. The formation of secondary phases due to the reaction between glass and BaTiO₃ at high sintering temperatures (above 1000°C) caused a decrease in the dielectric constants of the pellets.

4. Conclusion

Sintering characteristics of nanosized BaTiO₃ powders prepared by spray pyrolysis were investigated. The amount of added glass powders and sintering temperatures affected the morphologies, crystal structures, densities, and dielectric constants of BaTiO₃ pellets. The addition of a small amount of glass additive resulted in an increase in the densities of the sintered pellets. Pellets containing 0 and 1 mass% of the glass additive showed a pure BaTiO₃ phase. On the other hand, in the XRD patterns of pellets containing 5 and 10 mass% of the glass additive, several impurity peaks attributed to barium borate phases were observed. The high densities and improved tetragonality of BaTiO₃ pellets containing small amounts of the glass additive resulted in an increase in their

dielectric constants at low sintering temperatures.

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