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Effect of glass composition on the densification and dielectric properties of $BaTiO_3$ ceramics

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Abstract

An ongoing research goal of thick film capacitors and multilayer capacitors is to lower the firing temperature of the dielectrics. This paper presents the results of using three simple glass systems including $PbO–B_2O_3$, $PbO–SiO_2$, and $Bi_2O_3–B_2O_3$ as sintering aids for hydrothermal synthesized $BaTiO_3$. Glasses with different ratios of the modifier/glass former were employed. Effects of adding these glass systems on the $BaTiO_3$ ceramics sintered at 850°C were investigated through measuring and analyzing the density, grain size and dielectric property. It was found that $BaTiO_3$ sintered with glasses composed of 90 mol% PbO–10 mol% SiO_2 or 90 mol% PbO–10 mol% B_2O_3 to 60 mol% PbO–40% B_2O_3 are helpful to reduce the firing temperature for typical thick film and MLCC applications. They possess high dielectric constant (≈1650) due to their high densification characteristics with the grain size of ≈0.7 μm. In addition, glasses composed of 90 mol% Bi_2O_3–10 mol% B_2O_3 to 40 mol% Bi_2O_3–60 mol% B_2O_3 are beneficial for thin dielectric layer applications, on account of the high sintering density and a small grain size of ≈0.1 μm with an acceptable K value.

Keywords: C. Dielectric properties; D. $BaTiO_3$ ceramics; Densification

1. Introduction

Barium titanate ($BaTiO_3$) is a well-known material for multilayer ceramic and thick film capacitors because of its high dielectric constant. The trends of electronic packaging are toward miniaturization and cost saving. Lowering the sintering temperature of $BaTiO_3$ is required in multilayer ceramic capacitor (MLCC) technology in order to use relatively inexpensive internal electrodes such as Ag/Pd (silver/palladium), and also in thick film capacitor technology for achieving compatibility with other thick film components [1–5]. The addition of a fluxing agent such as glass with $BaTiO_3$ is an effective method which promotes densification by liquid phase sintering at low temperatures. Therefore, numerous kinds of glasses have been developed as sintering aids for $BaTiO_3$ [6–13].

Glass-sintered $BaTiO_3$, however, may not always result in the desired dielectric properties. This is especially true if the dielectric constant, K, is lowered by the presence of a continuous low-K grain boundary phase. In order to obtain materials with a high K, key steps are to tailor the glass composition to produce densification with limited grain growth and to reduce the volume fraction of low-K second phases and porosity [7]. Another important factor is to control the substitutions in the $BaTiO_3$ lattice. The glass may act as a fluxing agent for liquid-phase sintering as well as a modifier of the dielectric properties if the glass component is incorporated into the $BaTiO_3$ lattice [7,12,14–16]. The extent of incorporation and the distribution of the incorporated atoms may alter the Curie point temperature, the sharpness of the transition, and the volume fraction of the low-K second phase. Therefore, glass compositions and chemical interactions between $BaTiO_3$ and glasses are very important parameters in characterizing, understanding, and controlling their dielectric properties.

Burn [7] studied the grain growth behavior of flux-sintered $BaTiO_3$, focusing on both binary and ternary glass systems. He showed that the grain growth of the

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$BaTiO_3$ occurred only for specific ratios of glass formers and modifiers in the glass, which could be correlated to charge neutrality in the titanate lattice. A careful control of the cation stoichiometry is necessary for grain growth to occur. Grain growth is a factor which controls the extent of the modifier incorporated into the $BaTiO_3$ lattice and the volume of the liquid phase after sintering. Generally, commercially available glasses for low-fired $BaTiO_3$ are very complex and their formulations are primarily based on the empirical knowledge. Therefore, only limited information on the glass nature and its interaction with $BaTiO_3$ is available in the literature. In the previous study [17], the interactions between $BaTiO_3$ and simple glasses including PbO–B_2O_3, PbO–SiO_2, and Bi_2O_3–B_2O_3 systems were studied through the reaction of $BaTiO_3$ powder with glass powder. For PbO–B_2O_3 and PbO–SiO_2 glasses, the reaction led to a stable compound formation, the substitution of Pb in the $BaTiO_3$ structure, and a noticeable grain growth of $BaTiO_3$. The substitution of Pb into $BaTiO_3$ is assisted by chemical reactions in which BaB_2O_4 or Ba_2SiO_4 is formed. The substitution in $BaTiO_3$ also seems to be closely related to the grain growth of $BaTiO_3$. On the other hand, compound formation was observed only during the processing of $BaTiO_3$ with the Bi_2O_3–B_2O_3 glass system.

In order to investigate the influence of the glass additives on the densification, the microstructural evolution and the dielectric properties of $BaTiO_3$ ceramics, different modifier/glass former ratios of PbO–B_2O_3, PbO–SiO_2, and Bi_2O_3–B_2O_3 glass systems were used as sintering aids for a commercial hydrothermal synthesized $BaTiO_3$ powders. Effects of the glass systems on $BaTiO_3$ sintered at 850°C were investigated by measuring and analyzing the sintered density, grain size and dielectric properties.

2. Experimental procedure

2.1. Material

Hydrothermally derived $BaTiO_3$ powder (Sakai Chemical: BT-01) was used throughout this study. As shown in Fig. 1, the $BaTiO_3$ particle size was approximately 0.1 μm with a narrow particle size distribution. An XRD analysis of this raw material indicated a cubic structure at room temperature. Chemical analysis of this hydrothermally derived $BaTiO_3$ indicated only a very minor amount of impurities.

2.2. Glass preparation

Three binary glass systems with various ratios of glass modifier to glass former — 10 mol% PbO–90 mol% B_2O_3 to 90 mol% PbO–10 mol% B_2O_3, 50 mol% PbO–50 mol% SiO_2 to 90 mol% PbO–0 mol% SiO_2, and 10 mol% Bi_2O_3–90 mol% B_2O_3 to 90 mol% Bi_2O_3–10 mol% B_2O_3 (Fisher Scientific, reagent grade)—were chosen for the glass compositions. These glasses are commonly used as fluxing agents in thick film materials and MLCCs. In the PbO–SiO_2 system, glasses with SiO_2 content greater than 50 mol% were not used because of their high melting temperatures.

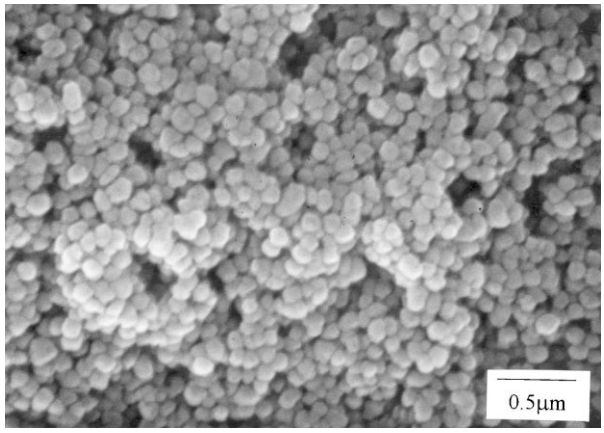

Fig. 1. SEM micrograph of as-received hydrothermal $BaTiO_3$.

Calculated amounts of reagent-grade chemicals (PbO, Bi_2O_3, SiO_2, and H_3BO_3) for the various glass compositions were weighed, mixed, and melted in platinum crucible in an air atmosphere at 1000°C for 5 h. The molten glasses were quenched on a platinum plate cooled by water and were then crushed in an agate bowl. Each crushed glass sample was sieved to pass through a 325 mesh screen. Although some compositions of glasses, particularly those containing a high amount of B_2O_3, PbO, or Bi_2O_3, did not produce a glassy phase, every sample was designated as a glass sample throughout this study. Chemical analyses carried out for each glass system indicated that impurities (0.1 wt.% or greater) were not introduced into the glass during the preparation procedure.

2.3. Sample preparation

90 mol% of hydrothermal derived $BaTiO_3$ and 10 mol% of glass powders were mixed thoroughly in an agate bowl. To prepare the powder for pressing, they were mixed with 3 wt.% of 15% PVA solution, dried, pulverized using a mortar and pestle, and then sieved through a 120 mesh screen. Disks with 10 mm in diameter and 1.5 mm in thickness were prepared by uniaxial pressing at 100 MPa. The green densities of the pressed samples, determined from their dimension, was 48–52% of theoretical density. For binder burnout, the disks were fired at 500°C for 2 h before they were sintered in a closed crucible at temperature of 850°C for periods of 30 min to 12 h. A soaking temperature of 850°C was used throughout this study because it is a

common firing temperature for thick film circuitry. A 10°C/min heating rate and 10°C/min cooling rate was used for all cases.

2.4. Characterization

Bulk density measurements were made using the Archimedes technique. Xylene was used as the liquid medium for specimens of 90% T.D. or higher, and distilled water was used for more porous specimens. For each type of samples, density measurements were carried out by averaging the data for at least three specimens. Microstructures of the ceramics were studied on the as-fired surfaces of the sintered ceramics using SEM with an accelerating voltage of 25 kV. Average grain size were determined using a linear intercept method.

Dielectric measurements were performed on plane parallel disks approximately 1 mm thick. Pt electrodes were sputtered onto the surface in a vacuum through a mask. Dielectric properties were measured as a function of temperature and frequency using a Hewlett-Packard 4274 LCR bridge and a low temperature Delta Design box furnace. An alternating voltage of 1 V was applied. Measurements were taken at a frequency of 1000 Hz.

3. Results and discussion

Three simple glass systems including $PbO–B_2O_3$, $PbO–SiO_2$, and $Bi_2O_3–B_2O_3$ commonly have been used as sintering aids for low-fired dielectrics, thick film components and low-fired multilayer monolithic substrates. The effects of glass constituents on the sintered $BaTiO_3$ ceramics are correlated with their densification, grain growth behavior and dielectric properties. Fig. 2 shows the densification of hydrothermal $BaTiO_3$ sintered with 70 mol% PbO–30 mol% B_2O_3 and 30 mol% PbO–70 mol% B_2O_3 glasses at 850°C for 2 h. It indicates that the densification of $BaTiO_3$ depends not only on the amount of glass addition but also on the glass former content. It is apparent that, with the same amount of glass addition, $BaTiO_3$ sintered with 70 mol% PbO–30 mol% B_2O_3 shows a better densification compared with that sintered with 30 mol% PbO–70 mol% B_2O_3. This is probably due to the better fluidity and the higher reactivity (better wettability) of the glass with the higher PbO content. They enhance the particle rearrangement and solution-reprecipitation during liquid phase sintering, causing a rapid densification [18,19]. For both glasses, the densification of $BaTiO_3$ increased as the addition of the glass raised up to 10 mol%. A further increase in the glass content does not improve the densification. Therefore, formulations of $BaTiO_3$ with the addition of 10 mol% glass were used throughout the rest of this study.

In order to clarify the effects of the glass modifier to the glass former ratio on densification, hydrothermal $BaTiO_3$ with 10 mol% of various glass additions were sintered at 850°C for 30 min. The densification and the grain size of the sintered ceramics with respect to the glass former (B_2O_3 or SiO_2) content in the $PbO–B_2O_3$, $PbO–SiO_2$, and $Bi_2O_3–B_2O_3$ glass systems are plotted in Figs. 3 and 4. It is evident that the glass former content influences significantly the densification and the grain size of the sintered ceramics. For the hydrothermal $BaTiO_3$ sintered with $PbO–B_2O_3$ glass, the sintered densities and the grain size of the $BaTO_3$ increased slightly with the B_2O_3 content up to 40 mol%, then dropped rapidly as the B_2O_3 content continues to rise. In the PbO-rich region, the sintered ceramics have a density of ≈5.35 g/cm^3 accompanied with an extensive grain growth (G.S. ≈ 0.7 μm). At a B_2O_3 content higher than 60 mol%, the grain sizes of the sintered ceramics reduced to ≈0.18 μm. This is probably due to the

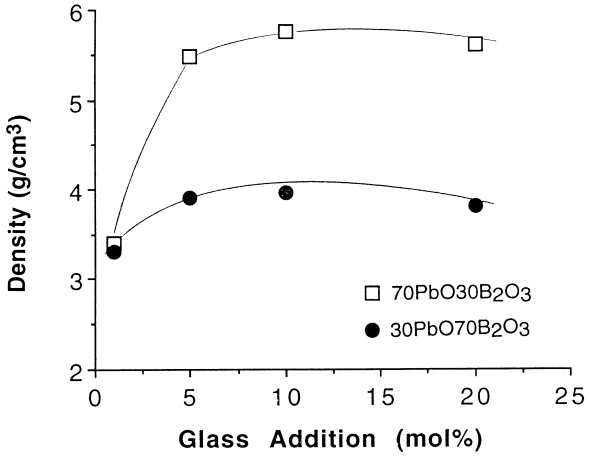

Fig. 2. Densification of hydrothermal $BaTiO_3$ sintered with 70 mol% PbO–30 mol% B_2O_3 and 30 mol% PbO–70 mol% B_2O_3 glasses at 850°C for 2 h.

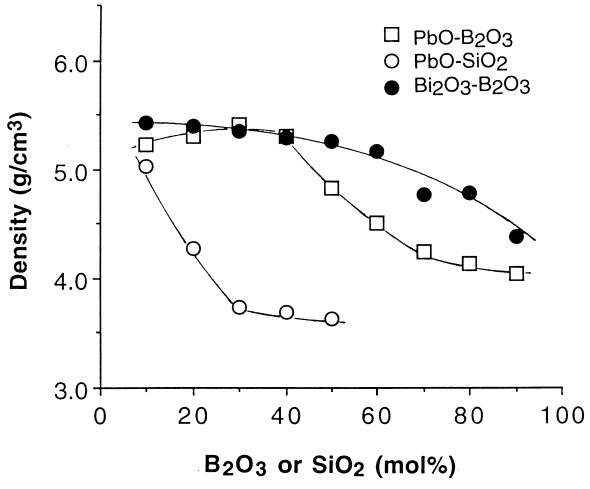

Fig. 3. Densification for hydrothermal $BaTiO_3$ sintered with 10 mol% glasses composed of various B_2O_3 or SiO_2 contents at 850°C for 30 min.

formation of $BaTi(BO_3)_2$ and BaB_2O_4 compounds, as reported by Kuromitsu et al. [17]. These newly formed compounds retard the densification process and inhibit the grain growth during the final stage of liquid phase sintering [18].

For the hydrothermal $BaTiO_3$ sintered with the PbO–SiO_2 glass system, the impact of the glass-modifier to the glass-former ratio on the densification and grain growth behavior are even more stronger than for those sintered with PbO–B_2O_3 glass, as shown in Figs. 3 and 4. The $BaTiO_3$ has a density of ≈5.05 g/cm^3 and a grain size of ≈0.5 μm when sintered with 90 mol% PbO–10 mol% SiO_2. Both values declined considerably as the SiO_2 content increased. This is due to the increasing melting temperature of the glasses and the formation of Ba_2SiO_4 and $Ba_2TiSi_2O_8$ compounds during sintering [7,17]. Liquid phase sintering becomes less efficient while using the glasses with high melting temperatures as sintering aids. Therefore, glasses with SiO_2 contents more than 50 mol% were not used in this study because of their high melting temperatures.

The impact of the glass-former content on the densification and the grain growth behavior for hydrothermal $BaTiO_3$ sintered with Bi_2O_3–B_2O_3 glasses are different from those sintered with PbO–B_2O_3 and PbO–SiO_2 glass systems. The densities of the ceramics were reduced gradually from ≈5.4 to 4.4 g/cm^3 as the B_2O_3 content was raised from 10 to 90 mol%. The microstructural study indicated that very little grain growth had occurred over the entire range of glass composition, even with an increased soaking time up to 120 min. It has been reported that interactions of $BaTiO_3$ with Bi_2O_3–B_2O_3 glasses lead to the formation of $BaBi_4Ti_4O_{15}$ and $BaTi(BO_3)_2$ compounds. These compounds plus the high viscosity of the Bi_2O_3–B_2O_3 glass may degrade the densification as well as retard the grain growth.

Fig. 5 shows the dielectric constants at room temperature, measured at 1 kHz, for the hydrothermal $BaTiO_3$ sintered with various glasses. Comparing the results with those shown in Figs. 3 and 4, it occurs that densification, grain size, as well as the nature of the glass may influence to the dielectric constant values of sintered $BaTiO_3$ ceramics. For the hydrothermal $BaTiO_3$ sintered with PbO–B_2O_3 glass, the dielectric constant increased slightly from 1350 to 1500 as the B_2O_3 content was raised from 10 to 40 mol%, then dropped rapidly to 500 as B_2O_3 reached 60 mol%. With glasses in the PbO-rich region, the sintered $BaTiO_3$ is characterized by a higher dielectric constant value, which is due to the fact that a better densification has been achieved and a grain size of ≈0.7 μm has been obtained. It is known that porosity existed in the ceramics can deteriorate the dielectric properties according to the mixing rule [16,20]. In addition, researchers [20–24] have also shown that the dielectric constant is a function of grain size. It reaches a maximum value while grain sizes are in the range of 0.6 to 0.8 μm, which can be explained by internal stress and domain wall models. As the B_2O_3 content in the glass increases, the resulting low sintering density and small grain size of $BaTiO_3$ led to a low dielectric constant.

For the hydrothermal $BaTiO_3$ sintered with PbO–SiO_2 glasses, the tendency of the dielectric constant versus the SiO_2 content coincides very well with the results of density and grain size (Figs. 3 and 4). Except in the case of 90 mol% PbO–10 mol% SiO_2, $BaTiO_3$ ceramics sintered with this glass system show a low density and little grain growth, resulting in a low dielectric constant.

For the $BaTiO_3$ ceramics sintered with Bi_2O_3–B_2O_3 glasses, no grain growth for all B_2O_3 contents was observed. The dependence of the dielectric constant and the sintered density on the B_2O_3 content seems to follows

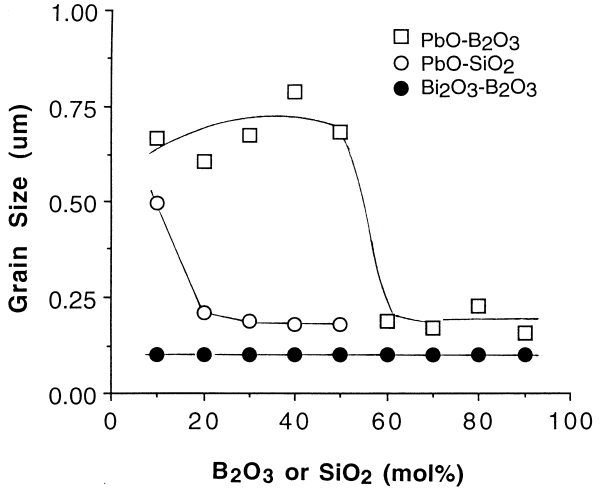

Fig. 4. Grain sizes for hydrothermal $BaTiO_3$ sintered with 10 mol% glasses composed of various B_2O_3 or SiO_2 contents at 850°C for 30 min.

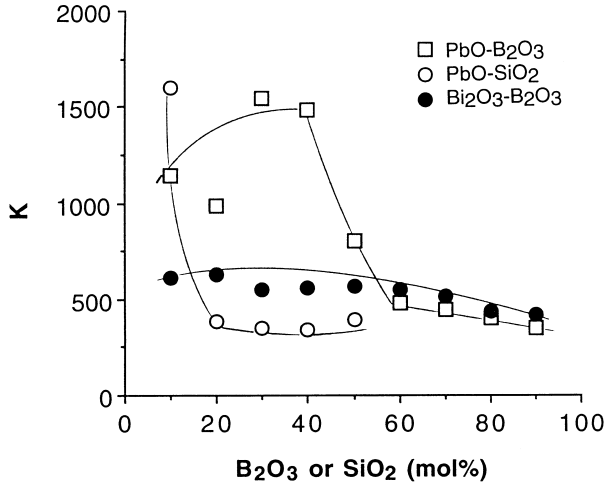

Fig. 5. Room dielectric constants, measured at 1 kHz, for hydrothermal $BaTiO_3$ sintered with various glasses at 850°C for 30 min.

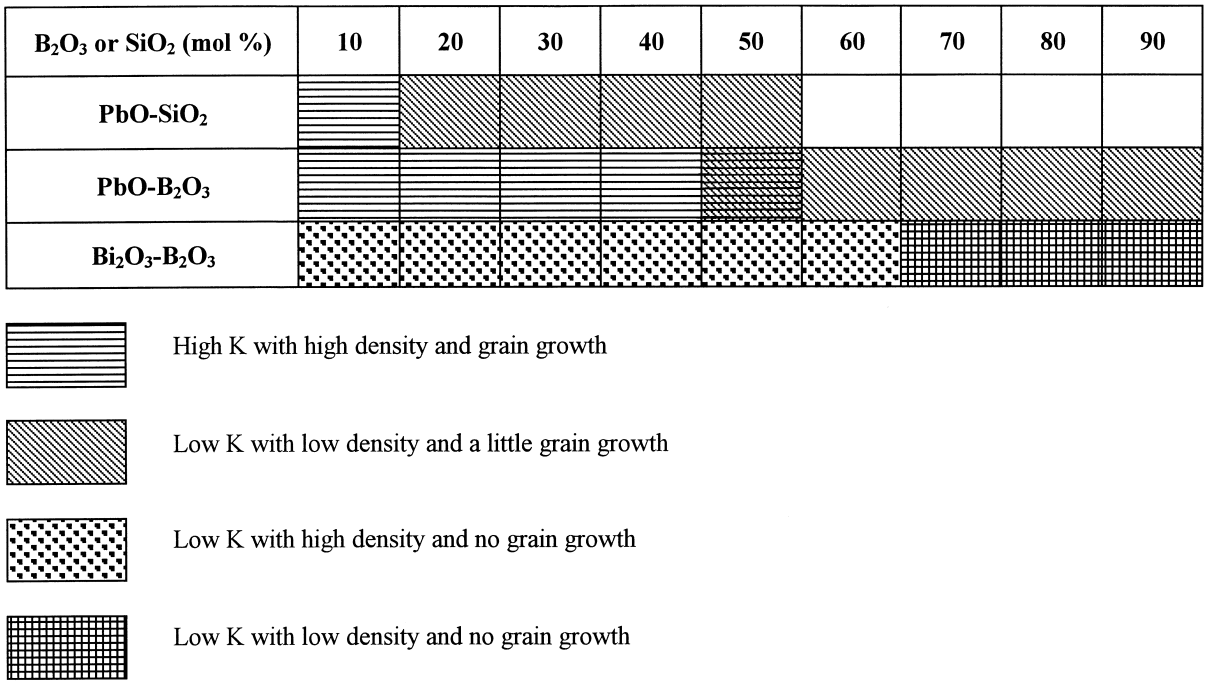

Fig. 6. Schematic diagram of the sintered density, grain size as well as dielectric constant as a function of glass former (B_2O_3 or SiO_2) content.

a similar path. These $BaTiO_3$ ceramics have a higher density than those sintered with PbO–B_2O_3 and PbO–SiO_2 glass systems. Therefore, the room dielectric constants for this system (≈650) are expected to be higher than those sintered with other glass systems having a similar grain size.

Fig. 6 shows a schematic diagram considering the sintered density, the grain size as well as the dielectric constant. $BaTiO_3$ sintered with glasses composed of 90 mol% PbO-10 mol% SiO_2 or 90 mol% PbO–10 mol% B_2O_3 to 60 mol% PbO–40% B_2O_3, possess a high dielectric constant and a high density associated with significant grain growth. They are useful for typical thick film and MLCC applications, which require a high K as well as a low firing temperature [5]. As the market drives the electronic components towards miniaturization, dielectric ceramics with a small grain size are essential for thin dielectric layer applications in order to retain good reliability. Based on the current study, $BaTiO_3$ sintered with glasses composed of 90 mol% Bi_2O_3–10 mol% B_2O_3 to 40 mol% Bi_2O_3–60 mol% B_2O_3 have a high densification at 850°C with an acceptable K of 630 and a grain size of ≈0.1 μm, which are favorable for uses in thin dielectric layer applications [3].

4. Summary

Three simple glass systems including PbO–B_2O_3, PbO–SiO_2, and Bi_2O_3–B_2O_3 were used as sintering aids for hydrothermal $BaTiO_3$. The effects of glass constituents on the $BaTiO_3$ ceramics are discussed with regard to densification, grain growth behavior and dielectric constant. For the hydrothermal $BaTiO_3$ sintered with PbO–B_2O_3 glass, densities of ≈5.35 g/cm^3 were achieved with an extensive grain growth (G.S.≈ 0.7 μm) and room dielectric constants of ≈1500 in the PbO-rich range. The dielectric constants dropped rapidly when the B_2O_3 content was greater than 60 mol%, due to low density and a small grain size. For the PbO-SiO_2 glass system, the sintered $BaTiO_3$ has a density of ≈5.05 g/cm^3 and a grain size of ≈0.5 μm when sintered with 90 mol% PbO–10 mol% SiO_2. Both the density and the grain size declined considerably as the SiO_2 content increased because of the increase in the glass melting temperatures. For the $BaTiO_3$ ceramics sintered with Bi_2O_3–B_2O_3 glasses, good densification and no grain growth were observed. Altogether, it was found that $BaTiO_3$ sintered with glass compositions of 90 mol% PbO–10 mol% SiO_2 or 90 mol% PbO–10 mol% B_2O_3 to 60 mol% PbO–40% B_2O_3 are useful for typical thick film and MLCC applications. In addition, glasses composed of 90 mol% Bi_2O_3–10 mol% B_2O_3 to 40 mol% Bi_2O_3–60 mol% B_2O_3 are beneficial for use in thin dielectric layer applications.

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