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Nano size $BaTiO_3$ powder coated with silica

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Abstract

Physical characteristics of silica-coated $BaTiO_3$ powders were studied. $BaTiO_3$ powders (~30 nm) were coated with TEOS and ethanol, and KOH solution was used as a catalyst. As the silica content was increased, silica coating changed the surface state of $BaTiO_3$ powders and improved dispersion of the powder. Effects of silica coating on the sintering behavior of $BaTiO_3$ were investigated using TMA. The specimen coated with 5.0 wt.% silica showed the maximum shrinkage of 25.5%, whereas the shrinkage of the uncoated $BaTiO_3$ was 20.4%. At the silica content greater than 1.0 wt.%, the characteristic X-ray peaks of fresnoite ($Ba_2TiSi_2O_8$) were observed. The specimen coated with silica less than 1.0 wt.% completed densification below 1250 °C, whereas the specimen with greater than 3.0 wt.% gave rise to swelling.

Keywords: D. $BaTiO_3$; TEOS; Silica; Nano; Fresnoite ($Ba_2TiSi_2O_8$); Coating

1. Introduction

Barium titanate ($BaTiO_3$) is a material of choice for dielectric components such as multilayer capacitors (MLCC), thermistors and transducers. Dielectric layers of MLCC are made thinner and the total number of layers has been increased to meet the miniaturization of electronic devices, downsizing passive components. As the thickness of ceramic layers decreases, uniformly distributed nano size $BaTiO_3$ particles are required. $BaTiO_3$ powders are normally synthesized by the solid-state reaction of $BaCO_3$ and TiO_2 at high temperatures around 1000 °C [1,2]. However, such a high calcination temperature leads to coarsening of $BaTiO_3$ particles (2–5 μm) with a wide distribution of grain sizes. Various synthetic methods such as hydrolysis of barium titanate alkoxides [3], sol–gel processing [4] and hydrothermal processing [5,6] have been developed to produce nano size $BaTiO_3$ powders with high purity, narrow particle size distribution and high homogeneity.

Temperature stability of dielectric constant is important for capacitor applications, which is associated with the core-shell structure having a different chemical composition between bulk grain and grain boundary [7,8]. These microstructures are usually obtained by admixing small amounts of several oxide additives to $BaTiO_3$ powders. Currently, oxide additives are mechanically mixed with the $BaTiO_3$ powder to achieve a uniform distribution of the additives. The distribution of additives in $BaTiO_3$ powders becomes critical since the additives are coarse and very small in amount. As the $BaTiO_3$ particle size is getting smaller, the uniform distribution of additives is more difficult. Thus, chemical mixing techniques are preferred to solid-state mixing. Chemical mixing techniques such as sol–gel coating [9], precipitation coating [10] and solution coating [11] could be effective in enhancing the uniform distribution of additives along the grain boundaries.

A homogeneous distribution of silica in the grain boundaries is very important because the inhomogeneous presence of small amounts of liquid phases gives rise to the exaggerated grain growth [12] and the segregation of SiO_2 into grain boundaries was found to deteriorate electrical properties [13].

Effects of silica coating on the physical properties of $BaTiO_3$ have been studied by numerous researchers [14–16]. Shih et al. reported that the stability of $BaTiO_3$ particles in

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acidic aqueous suspensions can be improved significantly by coating the particles with sol–gel silica materials [14] and Chen et al. pointed out that silica coating increases the shrinkage rate of $BaTiO_3$ [15]. Silica coating may also lead to an improved sintering behavior of $BaTiO_3$ particles since silica is known to be a good sintering aid [17,18]. In this paper, effects of silica coating on the powder characteristics, sintering behavior and micro structural properties of nano size $BaTiO_3$ powders have been studied.

2. Experimental procedure

Nano size $BaTiO_3$ powders were prepared using the liquid mix method developed by Pechini [19,20]. Approximately 10 g samples of $BaTiO_3$ were prepared by dissolving the weighed amounts of $BaCO_3$, dried by ignition in CO_2, in the weighed portions of Ti stock solutions. Dissolution of carbonates, by the reaction with citric acids, was achieved by heating over a period of several hours. Then the mixture was calcined in air at 600 °C for 60 min to yield a fine $BaTiO_3$ powder. The silica coating on barium titanate powders was achieved via sol–gel method. The barium titanate particles were suspended in ethanol and the pH of the suspension medium was adjusted to about 10 using KOH to stabilize the particles from dissolution and to catalyze the subsequent sol–gel reactions. Tetraethylorthosilicate(TEOS) was added to the suspension system with distilled water, and stirring at 50 °C for 2 h to allow the hydrolysis and condensation of TEOS to form silica coating on the surface of barium titanate particles. The amount of SiO_2 addition was 0.5, 1.0, 3.0 and 5.0 wt.%. The silica-coated $BaTiO_3$ particles were dried at 80 °C overnight and the powders were pressed into disks at 300 MPa followed by sintering in air at 1150, 1200 and 1250 °C for 2 h.

Particle sizes were determined from transmission electron microscopy (TEM, Jeol-300 kV) and X-ray diffraction analysis (Rigaku Rotaflex D/MAX System). Coated $BaTiO_3$ particles were characterized by field emission scanning electron microscope (FE-SEM, Jeol-JSM890) and Zeta potential analyzer (ELS-8000). The dilatometric behavior of specimens was measured over a temperature range from room temperature to 1300 °C using a dilatometer (TMA, Netzsch-STA409PC) and thermally etched surfaces of sintered specimens were investigated using a scanning electron microscope (SEM, Hitachi-S2150). The dielectric constants were measured over the temperature range from −55 to 145 °C using a capacitance measurement system (Saunders & Associates).

3. Results and discussion

Fig. 1 shows TEM photograph and XRD peaks of $BaTiO_3$ powders. This nano powder was synthesized from thermal decomposition of the polymerized metalorganics of titanium isoproxide and barium carbonate. The primary particles were heavily agglomerated with a uniform distribution of particle sizes about 30 nm. This observed particle size is in good agreement with the estimation from the half-width of (1 1 0) plane according to Scherrer's equation [21]. Fig. 2 shows microstructure developments of silica-coated $BaTiO_3$ powders at various levels. There was observed some discernible progress as the SiO_2 content increased. The powder agglomeration decreased with increasing silica content. At 5.0 wt.% SiO_2, the powder exhibits a uniform distribution without agglomeration. This disappearance of agglomeration could be due to the electrostatic repulsion between the coated silica layers on the surface of $BaTiO_3$ particles.

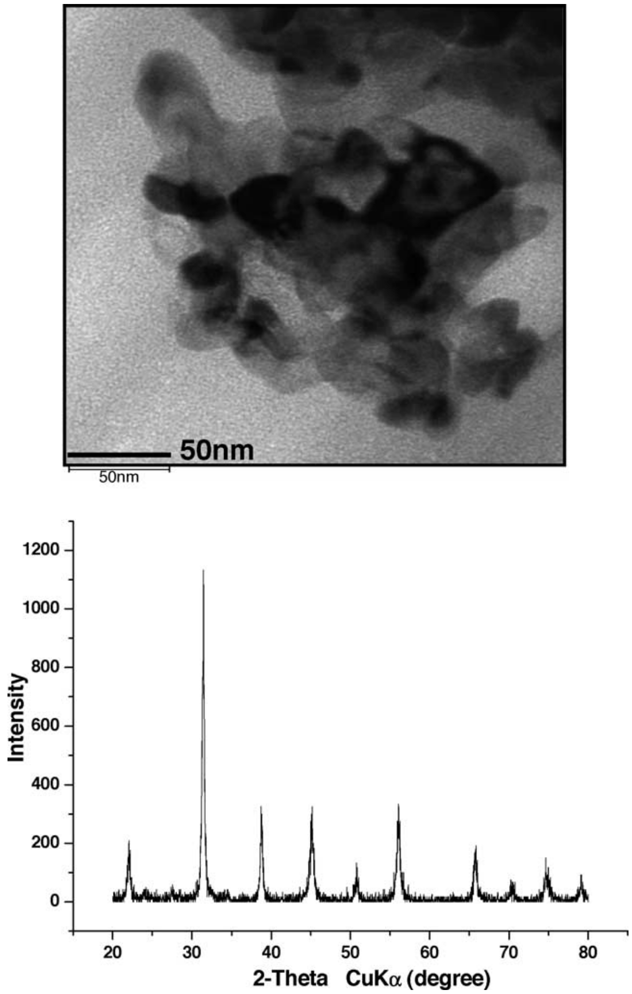

Fig. 1. TEM image and XRD patterns of $BaTiO_3$ powder.

Zeta potential of uncoated $BaTiO_3$ particles and 5 wt.% SiO_2-coated particles are plotted as a function of pH in Fig. 3. The electrophoretic mobility was measured as a function of pH values. Above pH 3.0, the zeta potential of the coated $BaTiO_3$ is more negative than that of the uncoated $BaTiO_3$, indicating that the coated specimen is more negatively charged than the uncoated one. This result is similar to the previous report that the zeta potential of silica-

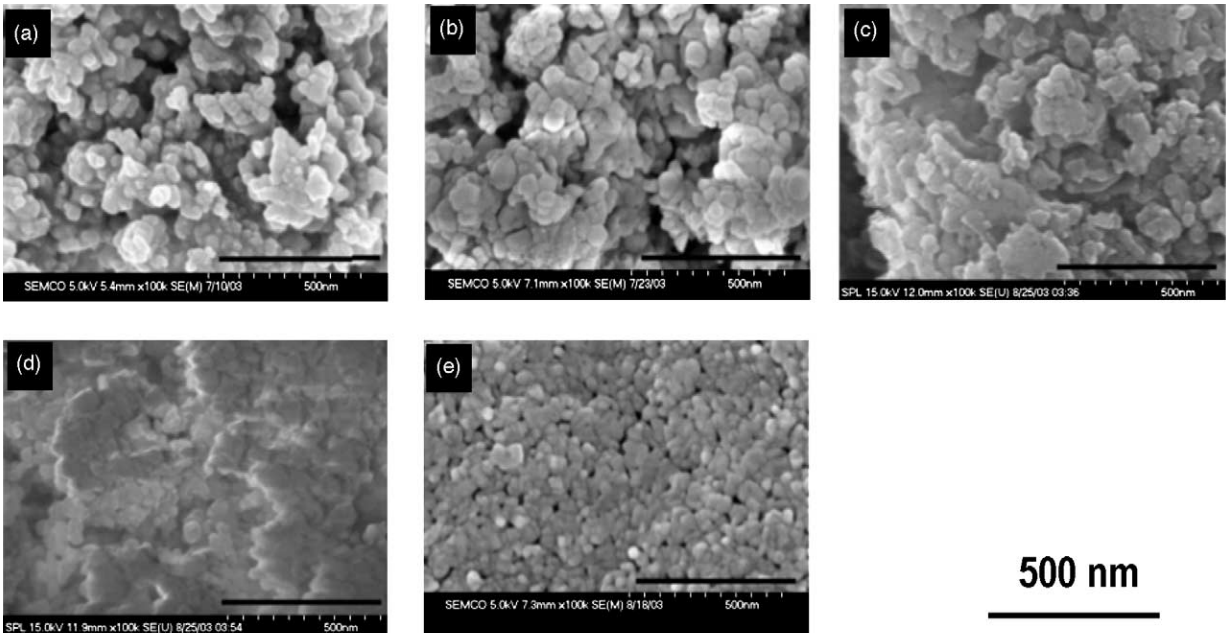

Fig. 2. Powder morphology of $BaTiO_3$ with various SiO_2 contents. (a) 0.0 wt.%, (b) 0.5 wt.%, (c) 1.0 wt.%, (d) 3.0 wt.%, (e) 5.0 wt.%.

coated $BaTiO_3$ is close to that of pure silica and more negative than that of the uncoated $BaTiO_3$ [14]. This is compatible with the morphology of 5 wt.% SiO_2-coated $BaTiO_3$ SEM images shown in Fig. 2(e), where the heavy agglomeration of primary particles disappeared. It is thus confirmed that silica coating could modify the surface characteristics of $BaTiO_3$ nano powders and improve the dispersion of $BaTiO_3$ primary particles.

Fig. 4 exhibits the shrinkage curves of $BaTiO_3$ as a function of temperature for various silica contents. The onset temperature of shrinkage curves is dependent on silica contents and shifts to higher temperatures with increasing SiO_2. Silica coating layer could retard densification at the initial stage of sintering. The specimen with 5.0 wt.% SiO_2 showed the maximum shrinkage 25.5%, whereas the shrinkage of the uncoated $BaTiO_3$ was 20.4%. The temperatures at which the maximum shrinkage occurred were 1265 and 1300 °C for 5.0 wt.% SiO_2-coated and the uncoated $BaTiO_3$, respectively. It should be noted that there is a slight shrinkage with 5.0 wt.% SiO_2 coating around 800 °C. The minor shrinkage at ~800 °C might be due to the reaction between SiO_2 and $BaTiO_3$ matrix, which is in accord with the previous study [15]. It was also reported that the secondary phase, fresnoite ($Ba_2TiSi_2O_8$) emerges in the SiO_2 containing $BaTiO_3$ powder mixture at temperature above 800 °C [22]. X-ray diffractograms for the silica-coated $BaTiO_3$ samples for various heating temperatures and silica contents are shown in Fig. 5. Below 700 °C, any second phase was not observed even with 5.0 wt.% SiO_2-coated $BaTiO_3$. However, fresnoite phase was detected at the temperature higher than 900 °C. This is in good agreement with the previous report that fresnoite phase is fully developed around 800 °C [22]. The sample sintered at 1300 °C with 1.0 wt.% SiO_2 shows the weak characteristic X-ray diffraction peaks of fresnoite phase, whereas there was no such peak observed on the specimen with less than 0.5 wt.% SiO_2. The minor shrinkage of the specimen with 5.0 wt.% SiO_2 at 800 °C implies the formation of the fresnoite second phase as shown in Fig. 4.

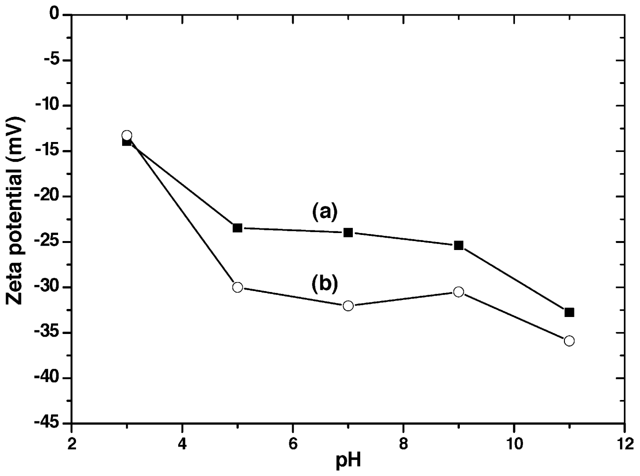

Fig. 3. Zeta potential as a function of the pH value of (a) uncoated $BaTiO_3$ and (b) 5.0 wt.% SiO_2-coated $BaTiO_3$.

Fig. 6 shows microstructures of $BaTiO_3$ sintered at 1150 and 1250 °C for various silica contents. The specimen coated with 0.5 wt.% SiO_2 made some densification with grain growth at 1150 °C comparing with the uncoated one, whereas the specimen with 5.0 wt.% SiO_2 exhibited poor densification with small grains. This result is compatible with the shrinkage behavior shown in Fig. 4. The specimen with 5.0 wt.% SiO_2 showed the smallest shrinkage compared with the 0.5 wt.% SiO_2-coated and the uncoated

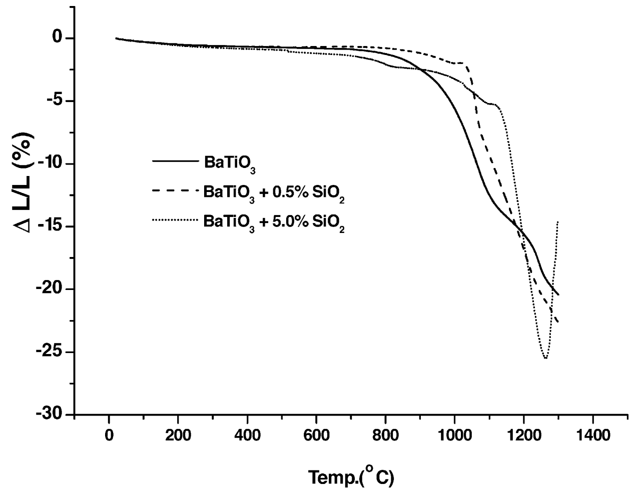

Fig. 4. Dilatometric curves of silica-coated and uncoated $BaTiO_3$.

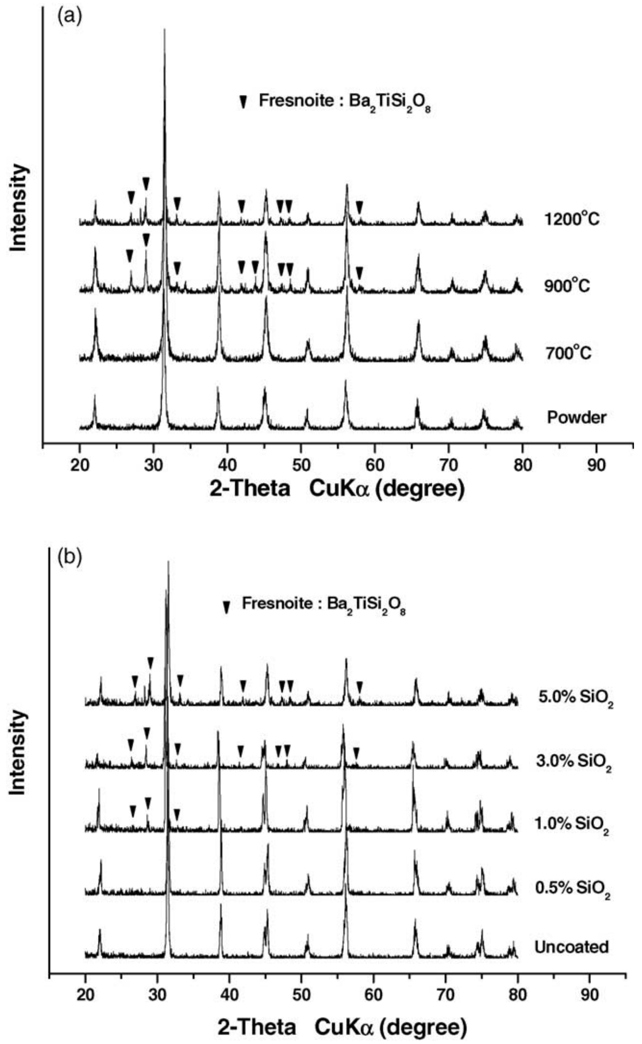

Fig. 5. XRD diffractograms of samples with (a) various heating temperature of 5.0 wt.% SiO_2-coated $BaTiO_3$ and (b) various SiO_2 contents at 1300 °C.

one at the same temperature. At 1250 °C, the specimen with 0.5 wt.% SiO_2 exhibited the microstructure similar to the uncoated one, and unlike the densification progress at 1150 °C the microstructure of the specimen with 5 wt.% SiO_2 showed exaggerated grain growths (~45 μm) and a large number of pores. This result implies that the microstructure development due to the silica addition is strongly dependent on the sintering temperature.

Fig. 7 shows apparent density and grain size as a function of SiO_2 content and sintering temperature, respectively. As SiO_2 content was increased, the density first increased up to 0.5 wt.% and then decreased at the sintering temperatures studied. When SiO_2 content was greater than 3.0 wt.%, exaggerated grain growth was observed at 1250 °C and the density decreased abruptly. It was reported that the dominant mechanism for the exaggerated grain growth in the $BaTiO_3$ ($BaO/TiO_2 = 0.997$) and SiO_2 system is the Ostwald ripening due to the formation of inter-granular SiO_2-rich liquid phases at temperatures between 1260 °C (eutectic temperature between $BaTiO_3$ and SiO_2) and 1320 °C (eutectic temperature between $BaTiO_3$ and TiO_2) [23]. A sudden decrease in density was reported above 1320 °C and such a densification behavior was explained due to the formation of a liquid phase in the specimen. However, in this study, density increased as the content of SiO_2 was raised up to 0.5 wt.%, and then density decreased rapidly. The density of the specimen sintered at 1250 °C decreased from 5.8 to 4.1 g/cm^3 as the SiO_2 content was changed from 0.5 to 5.0 wt.%. Such a significant change in density may be due to the swelling of the specimen as shown in Fig. 8. The specimen coated with SiO_2 less than 1.0 wt.% completed densification below 1250 °C, whereas the specimen with SiO_2 greater than 3.0 wt.% gave rise to swelling.

Swelling is a common difficulty in the liquid phase sintering when the specimen is heated. It was reported that abnormal grain growth in the undoped $BaTiO_3$ results from the presence of a liquid phase at grain boundaries due to the presence of background impurities [24]. As a consequence the plasticity of the material is enhanced, promoting swelling owing to internal CO_2 pressure, originating from the decomposition of $BaCO_3$. Also, German interpreted that the existence of a solid skeleton inhibits further rearrangement in the last stage of liquid phase sintering, and the residual pores will enlarge if gas is entrapped, therefore it makes compact swelling [25]. Besides previously mentioned factors, there are some parameters associated with swelling in liquid phase sintering, such as solubility between liquid and solid, particle size, green density and sintering temperature. It is assumed that swelling of $BaTiO_3$ with more than 3.0 wt.% SiO_2 is resulted from not only the liquid phase content but also solubility of the glass and sintering condition.

Fig. 9 shows the changes in dielectric constants of $BaTiO_3$ sintered at 1250 °C with various SiO_2 contents over the temperature range from −55 °C to 150 °C. Dielectric constants decrease with increasing SiO_2 contents, where a slight difference was observed between 0.5 and 1.0 wt.%

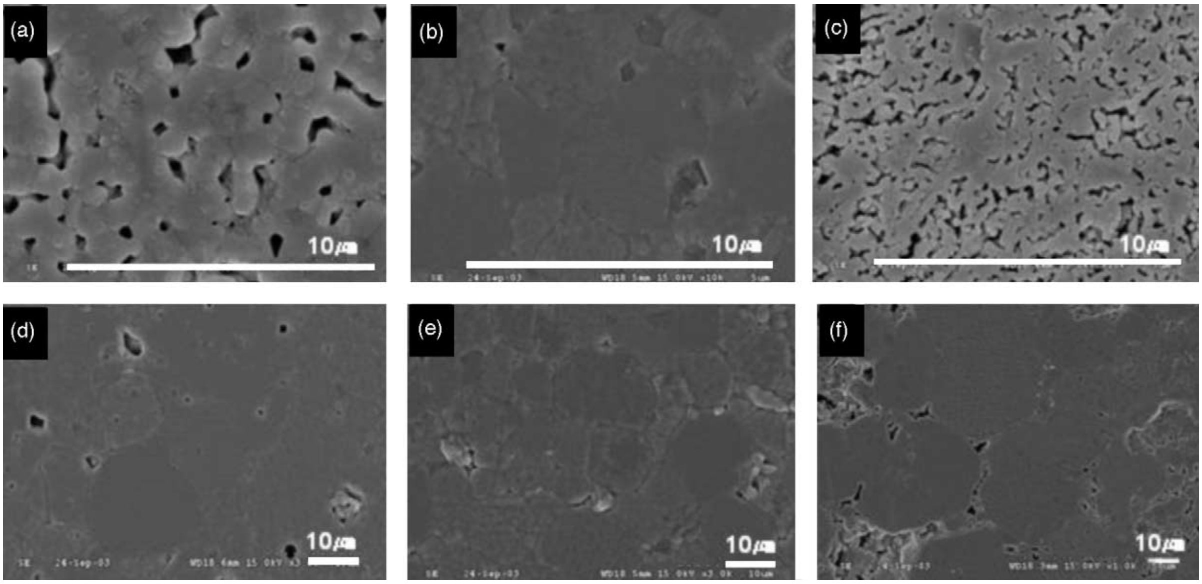

Fig. 6. Microstructure of $BaTiO_3$ samples with various SiO_2 contents: (a) 0.0 wt.%, (b) 0.5 wt.%, (c) 5.0 wt.% at 1150 °C, (d) 0.0 wt.%, (e) 0.5 wt.%, (f) 5.0 wt.% at 1250 °C.

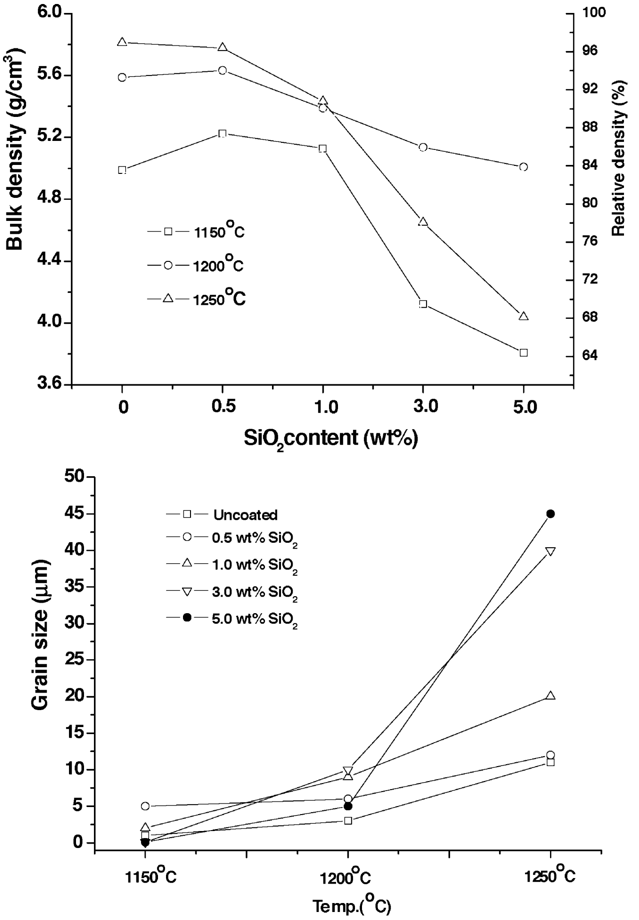

Fig. 7. Apparent density and grain size of $BaTiO_3$ as a function of SiO_2 content at various sintering temperatures.

SiO_2. The specimens with greater than 1.0 wt.% SiO_2 show lower dielectric values, which could be due to the second phase having the low dielectric permittivity such as fresnoite [26]. Moreover, exaggerated grain growth and large pores could cause lower dielectric constants. This result is in good

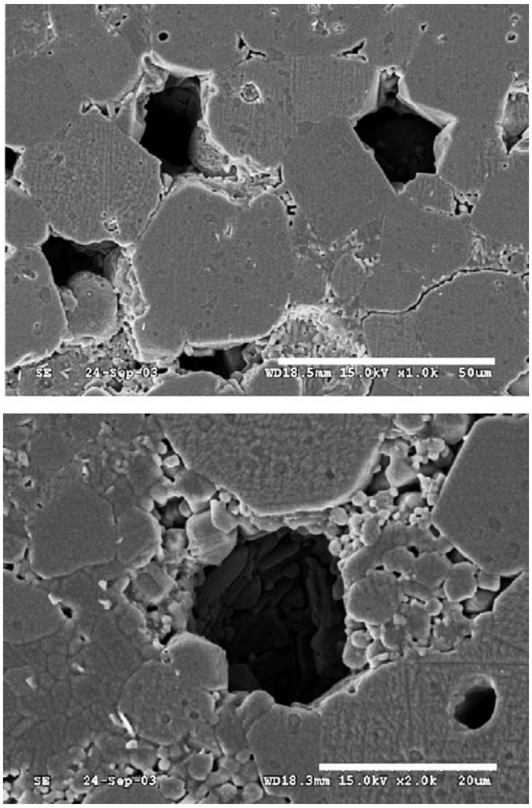

Fig. 8. SEM images of $BaTiO_3$ with 5.0 wt.% SiO_2 sintered at 1250 °C.

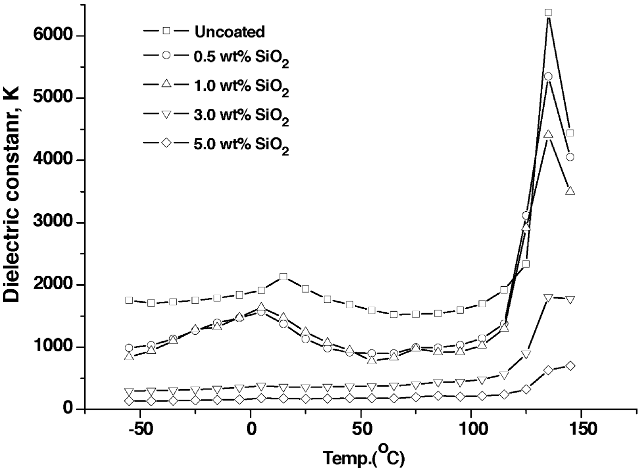

Fig. 9. Temperature dependence of dielectric constant of $BaTiO_3$ at various SiO_2 contents at 1250 °C.

agreement with the apparent density and grain size of $BaTiO_3$ shown in Fig. 7.

4. Conclusion

As the SiO_2 content was increased, powder dispersion was improved because the coated silica layer has an electrostatic repulsion effect on the surface of $BaTiO_3$ particles. $BaTiO_3$ specimens coated with greater than 1.0 wt.% SiO_2 showed a second phase, $Ba_2TiSi_2O_8$ at ~800 °C. The specimen coated with 5.0 wt.% silica exhibited a slight shrinkage around 800 °C due to the reaction between SiO_2 and $BaTiO_3$ matrix. At higher sintering temperatures, exaggerated grain growth was observed as SiO_2 content was increased. At 1250 °C, the density increased as the content of SiO_2 was raised up to 0.5 wt.%, and then the density decreased rapidly because of swelling at 5.0 wt.% SiO_2. Swelling of $BaTiO_3$ with greater than 3.0 wt.% SiO_2 is assumed due to the increase in liquid phase content, the different solubility of glass and sintering condition. The uncoated $BaTiO_3$ showed the highest dielectric constant over the temperature range studied, and the samples with greater than 1.0 wt.% SiO_2 exhibited lower dielectric values. This is due to the second phase, large pores and large grains.

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