Dense and fine-grained barium titanate prepared by spark plasma sintering

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Abstract. Dense and fine-grained barium titanate were successfully sintered by spark plasma sintering at 900 – 1100 °C for 10 minutes under an applied pressure of 30 MPa. The effect of temperature on the densification and microstructure were examined. The relative density of 96.8% was achieved at sintering temperature 1000 °C, and almost fully dense barium titanate was obtained at 1100 °C. In contrast, the relative density of barium titanate prepared by conventional sintering at 1200 °C for 2 h was only 80.1%. These results indicated the effectiveness of spark plasma sintering for fabrication of dense barium titanate. Another characteristic of barium titanate sintered by spark plasma sintering was fine-grained microstructure, as observed at sintering temperature 900 and 1000 °C. In addition, there was crystal structural transformation from cubic to tetragonal after sintering. XRD analysis revealed the cubic structure of as-received powder was changed to tetragonal structure after sintering at 1100 °C. The tetragonality (c/a) of sintered barium titanate was 1.0068, 1.0072 and 1.0088 for sintering temperature of 900, 1000 and 1100 °C, respectively.

1. Introduction
Barium titanate (BaTiO3) is a well-known dielectric material that has high permittivity and widely used as multi-layer ceramic capacitor (MLCC) [1, 2]. Dielectric property of BaTiO3 is influenced by temperature, whereby ferroelectric BaTiO3 changed to paraelectric at above 130 °C. This temperature is known as Curie temperature [3] i.e. the temperature that crystal structure of BaTiO3 changes from tetragonal to cubic. The crystal structure of BaTiO3 is also affected by grain size, wherein small grain size has tendency to be the cubic structure instead of tetragonal [4]. In addition, the additive also alters the crystal structure of BaTiO3 from tetragonal to cubic [5].

Conventional sintering of BaTiO3 generates coarse microstructure and abnormal grain growth due to high temperature application to achieve high density of BaTiO3 [6]. The typical sintering temperature of BaTiO3 is 1200 – 1450 °C with 2 – 5 h holding time [7–11]. Therefore, there are many
efforts to obtain dense BaTiO$_3$ with fine-grained microstructure. Two-step sintering is another option to obtain the dense BaTiO$_3$ and fine-grained microstructure [12, 13]. Initially, sintering temperature is raised from room temperature to 1230 °C, then in second step, temperature is decreased immediately to 1160 °C and is hold for 10 hours [13]. The results of this two-step sintering are dense BaTiO$_3$ with 30 nm in grain size. However, the long holding time in the second step is not preferred for industrial application. The use of pressure-assisted sintering technique is an alternative to obtain dense and fine grained BaTiO$_3$ in relatively short holding time. For instance, dense SiC was obtained by hot-pressing vacuum furnace at 1750 °C [14] compared to pressureless sintering technique at 2100 °C [15].

![Figure 1. Schematic of (a) spark plasma sintering and (b) hot pressing furnace](image)

One of the pressure-assisted sintering techniques is spark plasma sintering (SPS). SPS is a relatively new technique with ability to sinter materials less than conventional sintering time. The different between hot pressing conventional furnace with spark plasma sintering furnace is the heating source, as shown in figure 1. The mold is surrounded by heating elements in hot pressing conventional furnace, while in spark plasma sintering the mold itself act as heating element because DC source through the punch and mold. Therefore, the heating rate is very fast, and the densification is faster due to joule heating compare to conventional method. Recently, SPS is able to sinter high covalent bonding ceramics, i.e. SiC, without the addition of sintering aids [16]. The present objectives of this study are to obtain dense and fine-grained BaTiO$_3$ utilizing spark plasma sintering. The data on densities, microstructure, phase and tetragonality of BaTiO$_3$ were examined.

2. **Experimental Methods**

A commercial powder of BaTiO$_3$ with purity 99.5% (Wako, Japan) was used as starting materials. Two grams of BaTiO$_3$ powder was poured into graphite die with diameter 10 mm and was sintered by using spark plasma sintering (Dr. Sinter, Fuji Tech Industry, Japan) in vacuum condition under an applied pressure of 30 MPa. Initially, the temperature was raised from room temperature to 600 °C for two minutes, then the heating rate kept at 100 °C /min to designated temperature (900, 1000 and 1100 °C) and was hold for 10 minutes. After cooling, the samples were polished by using sand paper to remove the graphite sheet. Although the graphite sheet was completely removed from the samples, the color of samples was black due to carbon contamination from the furnace. In order to remove the carbon contamination, the samples were heat-treated at 800 °C for 5 h in air atmosphere. The color of samples was changed into white after heat treatment, which confirmed the nature of BaTiO$_3$’s color. The pressureless sintering of BaTiO$_3$ at 1200 °C for 2 h was also prepared for comparative purpose.
The density of samples was measured by using the Archimedes principle, where distilled water was used as immerse media. The powder and sintered pellets morphology was observed with scanning electron microscope (SEM: S-4800, Hitachi, Japan). The average particle and grain size were estimated from the SEM images and were analyzed statistically. The phases of starting powder and sintered pellets were examined by room temperature X-ray diffraction (XRD: D8 Advance, Bruker, Germany).

3. Results and Discussion

Figure 2 shows the SEM image and XRD pattern of BaTiO$_3$ powder. It is very clear that the shape of powder was round shape with average particle size 96.3±24.8 nm, as shown in figure 2 (a). Moreover, figure 2 (b) shows the single phase cubic BaTiO$_3$ instead of tetragonal.

\[\text{Figure 2. (a) SEM image and (b) XRD pattern of BaTiO}_3\text{ powder.}\]

\[\text{Table 1. Sintered density and relative density of BaTiO}_3\text{ prepared by SPS except for 1200 }\text{°C}\]

| Temp. (ºC) | Density (g cm$^{-3}$) | Relative density (%) |
|-----------|-----------------------|----------------------|
| 900       | 5.10 ± 0.03           | 84.7                 |
| 1000      | 5.83 ± 0.07           | 96.8                 |
| 1100      | 5.92 ± 0.05           | 98.3                 |
| 1200$^*$  | 4.82 ± 0.02           | 80.1                 |

$^*$conventional sintering

Table 1 shows the density and relative density of BaTiO$_3$ after sintering with SPS and conventional sintering furnace. Relative density higher than 95% was obtained by SPS at temperature higher than 900 ºC. The density of spark plasma sintered BaTiO$_3$ at 900, 1000 and 1100 ºC were 5.10, 5.83 and 5.92 g cm$^{-3}$, respectively. Although higher temperature was used in conventional sintering, i.e. 1200 ºC, the density is only 4.82 g cm$^{-3}$, which is corresponding to 80.1% of theoretical density. Moreover, it only took 10 min for SPS to achieve relative density higher than 95% at 1000 ºC, showing the effectiveness of SPS to obtain high density BaTiO$_3$.

Figure 3 shows the morphology of the sintered BaTiO$_3$ powders in different temperature. The enhanced densities and remained fine grain size might result from special sintering way of SPS because its fast heating and cooling rate can alter some mechanism of sintering [17]. At 900 ºC, the microstructure of the sample was dense and consisted of uniform grain size of <100 nm. Interestingly, the grain size of BaTiO$_3$ sintered at 1000 ºC was maintained fine, however, the density increased significantly compared to 900 ºC. Furthermore, the density of sintered BaTiO$_3$ at 1000 ºC showed coarse grain compared to 900 ºC, which is similar to pressureless sintered BaTiO$_3$, as shown in figure 3 (d). It seems that the critical temperature between grain growth and density for this study was 1000 ºC, since the density did not improve drastically at temperature higher than 1000 ºC. On the contrary,
the density of BaTiO₃ sintered by pressureless sintering technique revealed coarse grain and open pore structure with relative density of only 80.1%. According to solid state sintering theory [18], the present pressureless BaTiO₃ was stop after the second stage without further proceeding to the next stage, which is a pore elimination. Therefore, the pore of BaTiO₃ with pressureless sintering technique, was observed clearly, as shown in figure 3. Thus, it can be concluded that the SPS is able to enhance the density and refrain the grain growth of BaTiO₃.

**Figure 3.** SEM images of spark plasma sintered BaTiO₃ at (a) 900, (b) 1000, (c) 1100 °C and (d) pressureless sintered BaTiO₃ at 1200 °C for 2 h
XRD patterns of SPS products obtained at different processing time periods are presented in figure 4. It showed that single phase of BaTiO₃ observed without secondary phase detected, confirming the complete remove of carbon contamination after SPS process. The XRD pattern of all samples are almost similar except for 1100 °C. The tetragonal structure of BaTiO₃ was characterized by two peaks (0 0 2) and (2 0 0) between 44–46°, whereby cubic structure showed single peak (2 0 0). The XRD patterns of BaTiO₃ between 44–46° are shown in figure 5. The as-received BaTiO₃ was a single phase cubic structure of BaTiO₃, while sintered BaTiO₃ at 1100 °C revealed a tetragonal structure, as shown in figure 5. Meanwhile, the structure of BaTiO₃ sintered at 900 and 1000 °C was not a pure cubic, however, it has tendency as tetragonal structure. Thus, the structure of BaTiO₃ sintered at 900 and 1000 °C were mixed cubic and tetragonal. These results implied that the structure of BaTiO₃ was influenced by the grain size. For instance, crystals structure and microstructure of BaTiO₃ sinter at 1100 °C was tetragonal and coarse grain, respectively. In contrast, the crystal structure and microstructure of as-received powder of BaTiO₃ was cubic and fine particle, respectively. The dielectric properties of BaTiO₃ were affected by tetragonality of the structure [19]. Tetragonality of BaTiO₃ is a ratio between lattice parameter of c- and a-axis, where c/a higher than 1.008 is preferred for MLCC industry [19]. Tetragonality of BaTiO₃ in the present study were 1.0068, 1.0072 and 1.0088 for sintering temperature 900, 1000 and 1100 °C, respectively. Higher tetragonality of BaTiO₃ sinter at 1100 °C is due to the tetragonal phase, while also influenced by the grain size.
Figure 5. XRD patterns of spark plasma sintered of BaTiO$_3$ at 44 – 46$^\circ$, showing the transformation from cubic to tetragonal phase. The solid line and dashed line represent cubic and tetragonal peaks, respectively.

4. Conclusions
Dense BaTiO$_3$ was successfully fabricated by spark plasma sintering furnace. The dense BaTiO$_3$ were obtained at sintering temperature 1000 – 1100 $^\circ$C with relative density higher than 95%. Moreover, dense and fine-grained BaTiO$_3$ was obtained at 1000 $^\circ$C. On the contrary, density lower than 90% was reached by conventional sintering of BaTiO$_3$ even though higher temperature was used. These results indicated the effectiveness of spark plasma sintering to obtain dense and fine-grained BaTiO$_3$. However, the fine-grained BaTiO$_3$ had lower tetragonality compared to BaTiO$_3$ sintered at 1100 $^\circ$C. Tetragonality of BaTiO$_3$ sinter at 1100 $^\circ$C was 1.0088, which is suitable for MLCC industry. Furthermore, the study regarding the fine-grained microstructure while maintain higher tetragonality is needed in the future.

5. References
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