**Skewness: Important parameter to affect the dielectric properties of BaTiO$_3$**

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**ABSTRACT**

Recent electric vehicle multilayer ceramic capacitors (MLCCs) adopt submicron-sized solid-state synthesized BaTiO$_3$ for dielectric layers for high reliability. Unlike BaTiO$_3$ nanoparticles synthesized by the hydrothermal method, particle size distribution control becomes demanding with the solid-state synthesis. Here, BaTiO$_3$ with 260 and 390 nm average particle sizes were synthesized using a solid-state method, and the dielectric properties of the samples sintered at 1100, 1150, and 1200°C were studied in terms of particle size distributions. Notably, BaTiO$_3$ samples sintered with 260 nm particles with smaller grain sizes and lower tetragonality exhibited higher dielectric properties than those prepared with 390 nm particles. The reasons behind the high dielectric performance were found in the lower skewness of the 260 nm particles, which produced a higher density of the sintered sample. For electric vehicle MLCC BaTiO$_3$, engineering their skewness is as important as controlling their grain size or tetragonality for high dielectric performance.

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**1. Introduction**

With the advent of the Fourth Industrial Revolution, the demands for multilayer ceramic capacitors (MLCCs), which are essential components tailoring charge supply in electronics, are exponentially increasing [1–3]. For the conventional MLCCs adopted in mobile phones, miniaturization, thin dielectric layers, and high capacitance have been important requirements. However, recent developments in MLCCs incorporated within electric vehicles have primarily focused on high reliability [4,5].

BaTiO$_3$ is the most widely used material in the dielectric layers, and the thickness of the layers is closely related to the initial BaTiO$_3$ particle size. Ultra-fine BaTiO$_3$ particles (< 100 nm) synthesized by the hydrothermal method contain nano-sized intergranular pores, and these pores are known to cause delamination of electrodes in MLCCs during sintering [6,7]. On the other hand, larger BaTiO$_3$ particles (> 200 nm) prepared by the solid-state reaction have superior crystallinity [8]. Therefore, the larger BaTiO$_3$ particles are preferred in electric vehicle MLCCs to secure reliability in contrast to the ultra-fine hydrothermal BaTiO$_3$ particles [3].

Using large BaTiO$_3$ particles prepared by solid-state reactions is also advantageous in terms of capacitance as it guarantees large grain sizes after sintering: the larger the grain, the higher the capacitance (up to ~1 μm) [9–12]. In addition to the grain size [13,14], tetragonality (c/a ratio) [15], and particle size distribution are major parameters that determine the dielectric properties of BaTiO$_3$ dielectric layers [16]. However, the number of studies on the particle size distribution effect on dielectric properties of BaTiO$_3$ is limited. Although many numerical and experimental studies have shown that narrow particle size distribution is beneficial for higher density in sintered sample, these studies were only conducted on single or binary compounds such as tungsten metal and Al$_2$O$_3$ [17–20].

Here we demonstrate that skewness of the particle size distribution is another important parameter to engineer besides average particle size and standard deviation for high dielectric properties of BaTiO$_3$ layers. Two different BaTiO$_3$ particles with different particle size distributions were prepared via solid-state reaction (260 and 390 nm). Dielectric properties of BaTiO$_3$ bulk samples produced from the two different BaTiO$_3$ particles were investigated in terms of grain size, tetragonality, and skewness of particle size distributions. We found that minimizing the skewness can be as effective in improving dielectric properties as increasing grain size or tetragonality.
2. Experimental methods

2.1. Synthesis

BaTiO$_3$ particles were synthesized via solid-state reactions from high purity BaCO$_3$ (>99.5%, Ditto Technology Co., Inc., Gunpo, Republic of Korea) and TiO$_2$ (>99.5%, Ditto Technology) powders. Two different TiO$_2$ powders of different average particle sizes (~50 and 70 nm) were used to synthesize two sets of BaTiO$_3$ particles of varying particle size distributions. BaCO$_3$ and TiO$_2$ (~50 and 70 nm) were weighed stoichiometrically and mixed homogeneously by ball-milling them with zirconia balls (3 mm and 5 mm in diameter) in ethanol at 2,000 RPM for 12 hours. After drying the ball-milled powder in a vacuum oven at 70°C for 10 hours, the dried powder was pulverized using a mortar. Two different pulverized powders (one with 50 nm and the other with 70 nm TiO$_2$) were calcinated at 1000°C for 2 hours. Disk-type powder compacts were fabricated by applying isostatic pressure to the calcinated powders (250 MPa for 5 minutes) using a cold isostatic press (CIP; Sansho Industry, Osaka, Japan). The disk-type powder compacts were sintered at 1000, 1150, and 1200°C for 2 hours to produce BaTiO$_3$ bulk samples with different grain sizes.

2.2. Characterization

Particle size distributions of calcinated BaTiO$_3$ particles (one with 50 nm and the other with 70 nm TiO$_2$) were measured by a particle size analyzer (PSA; Model ELSZ-2000ZS, Otsuka, Osaka, Japan). The size and morphology of the calcinated particles and corresponding sintered grains were observed with a scanning electron microscope (SEM; Model S-4500, Hitachi, Tokyo, Japan). The average grain sizes of BaTiO$_3$ bulk samples were estimated from polished and chemically etched surfaces by applying the equivalent circle diameter (ECD) method to processed SEM images via the Olympus stream program. The densities of BaTiO$_3$ bulk samples were obtained by using the Archimedes principle. The crystal structures and phases of BaTiO$_3$ bulk samples sintered at 1000, 1150, and 1200°C were characterized by an X-ray diffractometer (XRD; Smartlab, Rigaku, Tokyo, Japan) using Cu Ka1 radiation. Temperature-dependent dielectric properties (30–200°C) of the bulk samples were measured at 1 kHz using a precision LCR meter (E4980A, Keysight, California, USA) and a test chamber (Nanoionics Korea, Seoul, Republic of Korea).

3. Results and discussion

Figures 1(a,b) show SEM images of BaTiO$_3$ particles synthesized via the solid-state method. Figure 1(a) presents the BaTiO$_3$ particles synthesized with 50 nm TiO$_2$, and Figure 1(b) presents those synthesized with 70 nm TiO$_2$. The BaTiO$_3$ particles prepared with smaller TiO$_2$ particles (50 nm) are smaller than those prepared with larger TiO$_2$ particles (70 nm). Figures 1(c,d) show the corresponding BaTiO$_3$ particle size distributions measured by the light scattering method (presented in bar-type graphs). The dashed lines in Figures 1(c,d) are the reconstructed normal distribution curves whose means and standard deviations are the same as those obtained from the bar-type graphs. The measured BaTiO$_3$ particle size distributions in Figures 1(c,d) were analyzed with Minitab to obtain average particle size, standard deviation, and skewness. Firstly, the average particle sizes of the BaTiO$_3$ particles were approximately 260 nm and 390 nm for the BaTiO$_3$ particles synthesized with 50 nm and 70 nm TiO$_2$, respectively. Secondly, the BaTiO$_3$ particles with a smaller average particle size have a narrower standard deviation (43 nm in Figure 1(c)) than those with a larger average particle size (65 nm in Figure 1(d)). Although the standard deviations of 260 nm and 390 nm BaTiO$_3$ particles are different, their geometric standard deviation, which is a measure for dispersion in a distribution, is similar (~1.17) [21]. Lastly, the asymmetries of particle size distributions of 260 nm and 390 nm BaTiO$_3$ particles about their mean particle sizes were evaluated by calculating the skewness, a measure of the asymmetry of the probability distribution of a real-valued random variable about its mean.

\[
S_k = \frac{n}{(n-1)(n-2)} \sum_{i=1}^{n} \left( \frac{x_i - \bar{x}}{s} \right)^3 \tag{1}
\]

Equation (1) shows how the skewness ($S_k$) can be calculated using the variable ($x_i$), mean ($\bar{x}$), standard deviation ($s$), and the number of variables ($n$). Qualitatively, a more significant deviation of measured distribution (bar-type graphs in Figures 1(c,d)) from its normal distribution (dashed-line graphs in Figures 1(c, d)) indicates a higher skewness. It is observed that the 390 nm BaTiO$_3$ particles (Figure 1(d)) are more skewed than 260 nm BaTiO$_3$ particles (Figure 1(c)). Quantitatively, the skewness of 260 nm and 390 nm BaTiO$_3$ particles were estimated to be 0.67 and 0.95, respectively. Therefore, 260 nm and 390 nm BaTiO$_3$ particles with a comparable relative standard deviation but different skewness are prepared. Properties of 260 nm and 390 nm BaTiO$_3$ particles are listed in Table 1.

Figures 2(a-f) show SEM images of the polished and chemically etched surfaces of BaTiO$_3$ bulk samples fabricated by sintering 260 nm and 390 nm BaTiO$_3$.
particles at 1100°C, 1150°C, and 1200°C. In line with the BaTiO₃ average particle sizes (260 nm and 390 nm), the sintered bulk samples were named BT260 (260 nm) and BT390 (390 nm), respectively. The average grain sizes of BT260 (Figures 2(a,c,e)) and BT390 (Figures 2(b, d,f)) are observed to increase with sintering temperature. The average grain sizes of BT260 and BT390 sintered at different temperatures were estimated (equivalent circle diameter (ECD) method) and plotted in Figure 2(g). While the average grain size of BT260 increases linearly as the sintering temperature is raised from 1100°C to 1200°C, that of BT390 increases at an accelerated rate with increasing sintering temperatures. After sintering at 1100°C, the average grain size of BT390 (~700 nm) is only 7.5% larger than that of BT260 (~650 nm). In contrast, the average grain size of BT390 after sintering at 1200°C (~1.4 μm) is 45% larger than that of BT260 sintered at the same temperature (~0.97 μm). We suspect that the rapid grain growth of BT390 may have to do with the number of pores present in the compacted powders. Even after sintering at 1100°C, we can observe that the number of pores present in BT390 (Figure 2(b)) is higher than in BT260 (Figure 2(a)). From this fact, we can infer that the compacted powder of BT390 must have included more pores than those within the compacted powder of BT260. The more room for grain growth, the faster the rate of growth [22]. Although varying in degrees, the average grain sizes of BT390 are larger than those of BT260 in all sintering temperatures.

Figure 2(h) shows relative densities of BT260 and BT390 sintered at 1100°C, 1150°C, and 1200°C. The relative densities of both BT260 and BT390 increase with increasing sintering temperatures. However, the relative densities of BT390 are lower than those of BT260 at all sintering temperatures. The discrepancies are decreased with higher sintering temperatures. No sintering aids such as SiO₂ or glass frit are added in BT260 and BT390 to minimize the number of parameters affecting the dielectric

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Scanning electron microscopy (SEM) images of BaTiO₃ particles with average particle sizes of (a) 260 nm, (b) 390 nm, and particle size distributions of BaTiO₃ with average particle sizes of (c) 260 nm, (d) 390 nm.

| Average particle size (nm) | Standard deviation (nm) | Geometric standard deviation | Skewness |
|----------------------------|--------------------------|-----------------------------|----------|
| 260                        | 43                       | 1.1741                      | 0.67     |
| 390                        | 65                       | 1.1742                      | 0.95     |

**Table 1.** Properties of particle size distributions of 260 nm and 390 nm BaTiO₃ particles.
properties of BT260 and BT390. The increase in the relative density with sintering temperature resembles that observed previously in the average grain size change (Figure 2(g)). However, the relative densities of BT260 are still higher than those of BT390 at all sintering temperatures.

Figure 2. SEM images of polished and chemically etched surfaces of BaTiO$_3$ bulk samples fabricated by sintering 260 nm (BT260) and 390 nm BaTiO$_3$ particles (BT390) at (a,b) 1100°C, (c,d) 1150°C, and (e,f) 1200°C, respectively. (g) Average grain sizes and (h) relative densities of BT260 and BT390 sintered at 1100°C, 1150°C, and 1200°C.
Figures 3(a, b) show X-ray diffraction (XRD) patterns of (a) BT260 and (b) BT390 sintered at 1100°C, 1150°C, and 1200°C for 2θ from 20° to 80°. XRD patterns of (c) BT260 and (d) BT390 for 2θ from 43° to 47°. (e) Gaussian fitting of the XRD pattern for BT390 sintered at 1200°C. (f) Sintering temperature-dependent tetragonality (c/a ratio) of BT260 and BT390.

Figures 3(a, b) show X-ray diffraction (XRD) patterns of BT260 (Figure 3(a)) and BT390 (Figure 3(b)) sintered at 1100°C, 1150°C, and 1200°C. All the diffraction peaks of BT260 and BT390 can be closely matched to the BaTiO$_3$ reference peaks given in Figures 3(a, b) regardless of the sintering temperatures. Therefore, we can conclude that the BT260 and BT390 are BaTiO$_3$ single phases.
Figure 4. Temperature-dependent dielectric constants measured at 1 kHz for BT260 and BT390 sintered at (a) 1100°C, (c) 1150°C, and (e) 1200°C. Temperature-dependent dielectric loss measured at 1 kHz for BT260 and BT390 sintered at (b) 1100°C, (d) 1150°C, and (f) 1200°C.
Tetragonality of a sintered BaTiO$_3$ bulk is estimated from 2θ values of the two adjacent peaks corresponding to (002) and (200) near 2θ ~45°. Figures 3(c,d) show the XRD peaks corresponding to (002) and (200) for BT260 and BT390 sintered at 1100°C, 1150°C, and 1200°C. To accurately determine the peak positions corresponding to (002) and (200), the XRD patterns were measured for every 0.01°. In addition, the Gaussian curve fitting method was employed to identify the 2θ value at which the XRD pattern peaks, as present in Figure 3(e). Figure 3(f) is the estimated tetragonality of BT260 and BT390 sintered at different temperatures. The tetragonality of both BT260 and BT390 increase with sintering temperatures. While the tetragonality of BT260 increases linearly with the sintering temperatures, that of BT390 drastically increases when sintered at 1200°C. Except for 1150°C where tetragonality of BT260 (1.0092) and BT390 (1.0091) are similar, BT390 has a greater tetragonality than BT290 at other sintering temperatures. Hence, it can be deduced that the degree of unit cell distortion is higher in BT390 when compared to that in BT260 [21].

Figures 4(a-f) present temperature-dependent ε and losses of BT260 and BT390 sintered at 1100°C, 1150°C, and 1200°C, respectively. All the dielectric properties measurements were carried out at 1 kHz from 30°C to 190°C. The ε peaks observed near 130°C for both samples are due to a transition from tetragonal to cubic phase [23]. As the sintering temperature is increased, the ε of both BT260 and BT390 are improved. For example, the maximum ε of BT260 and BT390 are improved by 60% and 90%, respectively, when the sintering temperature is increased from 1100°C to 1200°C. The dielectric losses of BT260 and BT390 are comparable for all sintering temperatures except at 1200°C (Figure 4(f)), where the loss of BT260 is slightly higher than BT390 for measuring temperatures lower than 130°C. Even the highest loss is below 0.11. Therefore we can conclude that the dielectric properties of BT260 are higher than those of BT390 at all sintering temperatures.

BT260 had a smaller average particle size before sintering (Figures 1(c,d)), a smaller grain size after sintering (Figure 2(g)), and lower tetragonality (Figure 3(c)) than those of BT390, except for the density (Figure 2(h)). Hence, the observed higher dielectric constant of BT260 is attributed to its higher sample density than that of BT390. The density is closely related to the average particle size, geometric standard deviation, and skewness of the particle size distribution. Firstly, for submicron-sized BaTiO$_3$ particles, it is difficult to generalize the relationship between the average particle size and the corresponding density because first different sintering conditions change the relationship, and second, particle size distribution information is in most cases not provided in the literature. According to Zhou et al. BaTiO$_3$ of 260 nm average particle size had a relative density (after sintering) of about 15% lower than that of 820 nm particle size [24]. We suspect that the higher density of BT260 than BT390, contrary to what Zhou et al. reported, may have to do with the particle size distribution difference between the two samples. Secondly, it was confirmed that the geometric standard deviations of both 260 nm and 390 nm BaTiO$_3$ particles were comparable (Table 1). Lastly, the skewness of 260 nm BaTiO$_3$ particles was lower than that of 390 nm BaTiO$_3$ particles. Therefore, the low skewness of 260 nm BaTiO$_3$ particles overcomes their small average particle size and produces sintered samples with higher density than BT390, which in turn resulted in the high dielectric properties. The density of a sintered sample is known to be inversely proportional to the skewness of the initial particle distribution [17]. For example, the skewness of 260 nm BaTiO$_3$ particles was approximately 30% lower than that obtained for 390 nm BaTiO$_3$ particles. The 30% decrease in skewness leads to 10% improvement in the sample density sintered at 1100°C. In other words, engineering skewness of the particle size distribution is as important as controlling grain size or tetragonality for the high dielectric performance of BaTiO$_3$.

4. Conclusions

We demonstrated that the skewness of particle size distribution is an important parameter to improve the dielectric performance of BaTiO$_3$ layers in MLCCs. From two sets of BaTiO$_3$ particles whose average particle sizes were 260 nm and 390 nm, average grain size, density, and tetragonality were obtained after sintering them at 1100°C, 1150°C, and 1200°C. The average grain size and tetragonality of the samples sintered with 260 nm BaTiO$_3$ particles (BT260) were smaller than those of the samples sintered with 390 nm particles (BT390) at all sintering temperatures. Nonetheless, the dielectric performance of BT260 was higher than that of BT390 because of its higher density. The higher density of BT260 is attributed to its lower skewness. Therefore, minimizing the skewness of BaTiO$_3$ particle distribution is another effective route for the high dielectric performance of BaTiO$_3$ samples prepared with particles synthesized via the solid-state method.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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