

Powder characterization and electrical properties of BaTiO₃ produced by several powder synthesis methods

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BaTiO₃ powder, with an average particle diameter of about 170 nm, was fabricated by three synthesis methods (solid state, hydrothermal and co-precipitation), and the variation in properties of the sintered specimens depended on the particle size distribution and shape of the synthesized powder. The electrical properties of the synthesized BaTiO₃ were investigated in terms of crystallite size and tetragonality, based on the powder characteristics. Crystallite sizes of the specimens calculated by Debye-Scherrer equation were 31.2 nm, 31.5 nm, and 33.6 nm for the solid state, hydrothermal, and co-precipitation methods, respectively. The tetragonality (c/a ratio) obtained from the Rietveld refinement method increased from 1.0064 to 1.0075, and to 1.0079 with increasing crystallite size. The high tetragonality causing amplification of the dipole moment enhanced the dielectric constant, and the dielectric constant for the specimen produced by co-precipitation method had the highest value of 5813, due to its highest value of the tetragonality.

Key words: BaTiO₃, Synthesis method, Crystallite size, Tetragonality, Dielectric constant.

Introduction

The demand for high performance and miniaturized multilayer ceramic capacitors (MLCC) has been growing with the continuous development of electronic devices. Previous research has focused on barium titanate (BaTiO₃), which is a key material of the MLCCs. Previous studies have used different powder synthesis methods to produce BaTiO₃ [1-3].

There are some typical BaTiO₃ synthesis methods such as solid state method including the processing of solid precursors [4]; a hydrothermal method, having both liquid and solid precursors [5]; and a co-precipitation method from liquid precursors [6]. The crystallizability of BaTiO₃ changes according to the type of raw material used for synthesis, temperature, or pressure, as well as through other factors [2, 7, 8]. Therefore, the crystallite size or crystal structure are expected to vary with the dielectric values for specimens synthesized through the solid state, hydrothermal, and co-precipitation methods.

The crystal structure consists of ferroelectric domains that have a single crystallographic plane of rotation twins. The residual strain energy at the domain wall is more easily released with increasing domain size, which leads to a change in the lattice parameter. This residual strain energy is one of the major factors that

increase the tetragonality of the lattice, where the tetragonality is measured by the c/a axis ratio in crystal [9-12]. In the perovskite structure of BaTiO₃, movement of the positive charge on the Ti⁴⁺ ion located on the B-site increases with increased tetragonality and causes amplification of the dipole moment, which results in improved dielectric properties [13].

In the current study, BaTiO₃ powders were fabricated by solid state, hydrothermal, and co-precipitation methods, and the crystallite size and tetragonality from final powders having similar particle diameters were quantitatively examined. The current investigation also focuses on the dielectric material development for MLCCs through verifying the relation between crystal structure and electric properties.

Experimental Procedure

BaCO₃ (Aldrich, 99%) and TiO₂ (Aldrich, 99.9%) were mixed, with a molar ratio of Ba/Ti = 1, and ball milled. The final BaTiO₃ powder was obtained after calcining at 1000 °C. For the hydrothermal process, Ba(OH)₂ · 8H₂O (Aldrich, 99%) and TiCl₄ (Aldrich, 99.9%) were mixed in deionized water and stirred with H₂O₂ (Junsei, Guaranteed reagent). The mixed solution was added to aqueous ammonia and the resultant precipitate was centrifuged, washed, and dried. For the co-precipitation method, BaCl₂ · 2H₂O (Aldrich, 99%) and TiCl₄ (Aldrich, 99.9%) were stirred with H₂C₂O₄ (Aldrich, 99.99%), and BaTiO₃ powder was obtained

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through precipitation during heat treatment. 1.0 mol% MgO (Aldrich, 98%), 0.05 mol% V_2O_5 (Junsei, 99.0%), 1.5 mol% SiO_2 (Aldrich, 99.9%), and 0.05 mol% MnO_2 (Aldrich, 99%) were added to each of the individual synthesized $BaTiO_3$ powders. After milling for 24 h, each powder was sieved and pressed at a pressure of 1000 psi in a disk type mold ($\Phi 20$), and the samples were sintered at 1320 °C for 2 h in a reducing atmosphere.

The particle size distribution of the powders synthesized by the three methods was measured using a particle size analyzer (PSA, Malvern, Nano-S90), and the particle shapes, as well as the microstructures of the sintered specimens, were imaged by field emission scanning electron microscopy (FE-SEM, Hitachi, S4700). Crystal structure analysis was conducted with an X-ray diffractometer (XRD, Philips, Xpert Pro) and the crystallite sizes were calculated by using the Debye-Scherrer formula. Tetragonality (c/a) and lattice parameter were obtained from the diffraction peaks corresponding to the (002) and (200) planes using a Rietveld refinement method. The electrical properties were measured after Ag paste was applied to the sintered specimens. The dielectric constant and the temperature stability were measured over a temperature range from -55 °C to 150 °C using a LCR meter (Agilent, E4980A) at 1 kHz / 1.0 V.

Results and Discussion

Figure 1 shows the particle size distributions and

shapes of $BaTiO_3$ powder synthesized by solid state, hydrothermal, and co-precipitation methods. Powder synthesized by the solid state reaction was composed of average 172.6 ± 42.9 nm particles with partial agglomerates above 1 μm , and generally had irregular shapes (Fig. 1(a, d)). Powder produced by the hydrothermal method exhibited uniform diameters of 182.5 ± 46.9 nm (Fig. 1(b, e)). $BaTiO_3$ powder synthesized by co-precipitation had a particle size of 166.0 ± 65.5 nm. No agglomerate and irregular shapes were observed from the co-precipitation process (Fig. 1(c, f)). There are some differences in particle shape and size distribution among the three methods, but the mean particle size of these powders is similar, at approximately 170 nm.

Figure 2 shows SEM images of the polished and thermally etched surfaces of the $BaTiO_3$ specimens produced by the solid state, hydrothermal, and co-precipitation methods after sintering at 1320 °C. The grain size and shape of the individual sintered specimens were different because of the difference in grain growth rate of the initial powder. For the solid state method, growth of 30 to 50 times greater than the initial particle size is observed, and it has a relatively lower grain growth, as compared to the other two methods. Inhomogeneous grain growth from the agglomerates in the initial powder was also observed. Intermediate phases in the chemical reaction, such as Ba_2TiO_4 and $BaTi_3O_7$, remained in the specimen and restricted the movement of the grain boundaries. These phases may be a factor in delaying grain growth [14].

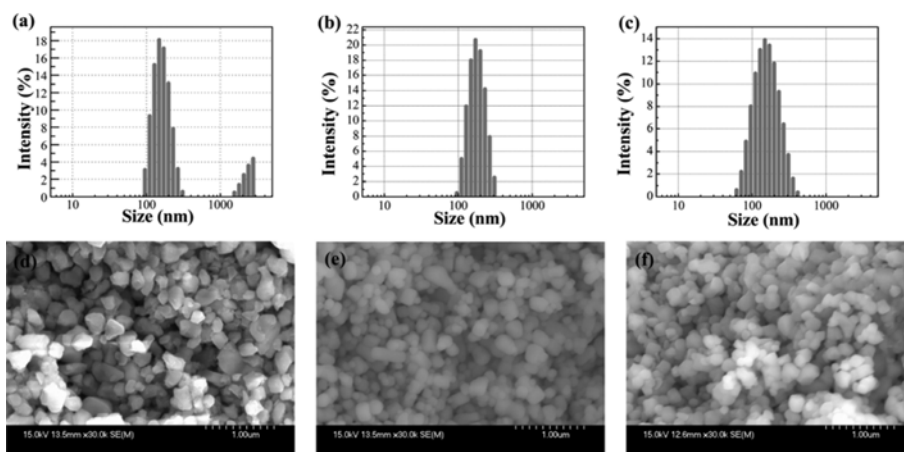


Fig. 1. Particle size distribution and scanning electron microscopy images of $BaTiO_3$ powders synthesized by (a, d) the solid state method, (b, e) the hydrothermal method, and (c, f) the co-precipitation method.

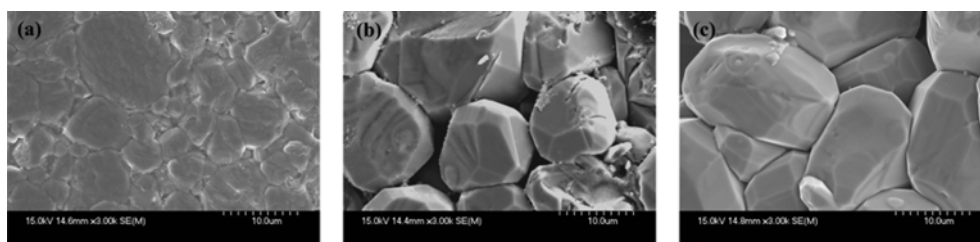


Fig. 2. Microstructure of $BaTiO_3$ synthesized by (a) the solid state method; (b) the hydrothermal method; and (c) the co-precipitation method.

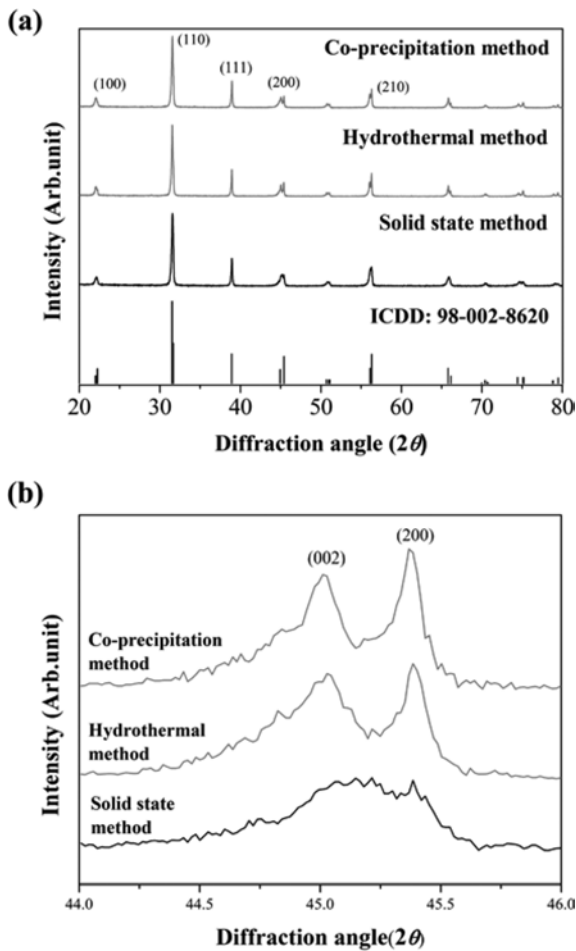


Fig. 3. X-ray diffraction patterns of the BaTiO₃ specimens according to various synthesis methods: (a) whole patterns of sintered BaTiO₃ powders and (b) detailed patterns of 44°–46°.

For the two liquid methods (hydrothermal and co-precipitation), a marked increase in grain size was found. In Fig. 2(b), BaTiO₃ specimen prepared by the hydrothermal method shows homogeneous grains, which have grown about 50 to 100 times greater than the initial particles, and some pores were also observed. For the co-precipitation method (Fig. 2(c)), the grain growth is significant, with an increase of 100 to 150 times, and a dense structure is present as well. These results indicate that the grain growth in liquid methods is accelerated after dissociation of the hydroxyl ions, which causes the internal stress [9, 15]. The co-precipitation method, with its relatively broad particle size distribution, especially leads to an improved densification behavior, due to the gap filling ability of the fine particles, as compared to the hydrothermal method [16].

Figure 3 shows the XRD patterns of the BaTiO₃ specimens. These tests were performed in order to verify the structural properties of individual specimens with different grain growth rates. In the range of $2\theta = 10^\circ$ – 80° , all diffraction patterns of the BaTiO₃ specimens correspond with the perovskite structure, and no secondary phase is observed (Fig. 3(a)). From

these XRD patterns, the average crystallite size can be calculated using the Debye-Scherrer equation [17].

$$t = 0.9\lambda / B \cos \theta_B \quad (1)$$

Where t is the crystallite size, λ is the wavelength, B is the corrected full width at half maximum (FWHM), and θ_B is the diffraction angle. The FWHM of the reflection peak increases with decreasing crystallite size. The (110) reflection with the highest intensity was used to estimate the crystallite size, and the FWHMs for specimens synthesized by the solid state, hydrothermal, and co-precipitation methods were 0.2644° , 0.2518° , and 0.2459° , respectively. The co-precipitation specimen has the lowest FWHM value, as compared to the specimens from the other two synthesis methods, because of its increased crystallinity due to its larger grain growth. Crystallite sizes calculated by equation (1) were 31.2 nm, 32.8 nm, and 33.6 nm for the solid state, hydrothermal, and co-precipitation methods, respectively.

Quantitative analysis for the crystal structure of BaTiO₃ specimens was conducted to investigate the correlation between crystallite size and electrical properties. As shown in Fig. 3(b), the diffraction peaks that corresponded to the (002) and (200) planes observed in the 2θ ranges from 44° to 46° , the tetragonal ratio for the BaTiO₃ phase, can be determined. The lattice parameters and the tetragonality of BaTiO₃ were quantitatively calculated from the diffraction peaks using a Rietveld refinement method. The (002) and (200) peaks represent the a - and c -axis of lattice parameters of the perovskite structure, and separation of the peaks occurs due to the tetragonal nature of the phase fraction. As shown in Table 1, the tetragonality values of specimens produced by the solid state, hydrothermal, and co-precipitation methods were 1.0064, 1.0075, and 1.0079, respectively. This increase in the tetragonality coincides with that of the crystallite size obtained using equation (1). Perovskite crystal structures consist of ferroelectric domains with a single crystallographic plane of a rotation twin, and the domain wall area increases with decreasing crystallite size. Space charge effects occur as a consequence of the difference between the thickness and the strain of individual domain walls. If the crystallite size is small, spontaneous polarization decreases with an increase in the space charge effect. In contrast, for large domain

Table 1 Lattice parameters and tetragonality of the synthesized BaTiO₃ powder ceramics according to different synthesis methods.

Synthesis method	Lattice parameter		Tetragonality (c/a)
	a (Å)	c (Å)	
Solid state	4.0001	4.0258	1.0064
Hydrothermal	3.9962	4.0265	1.0075
Co-precipitation	3.9973	4.0289	1.0079

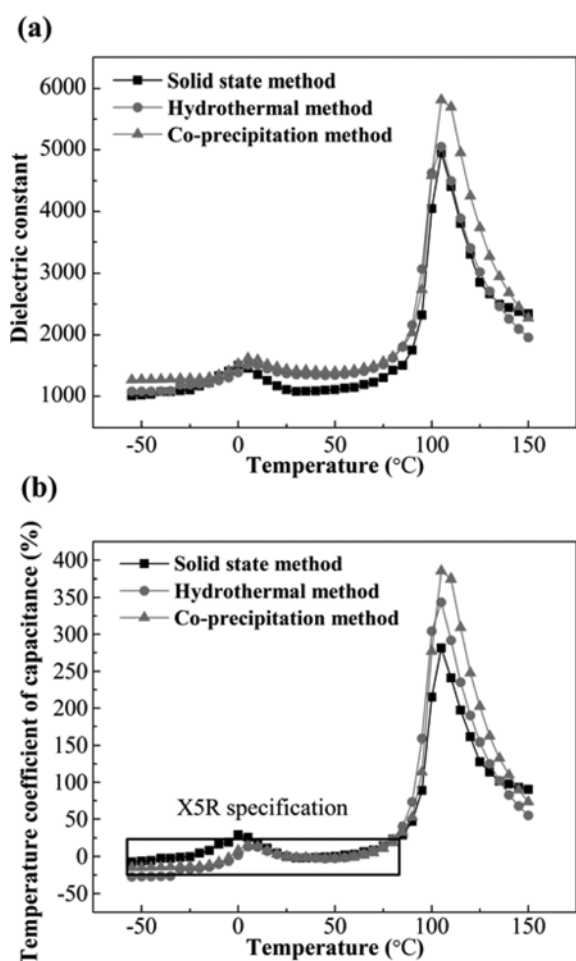


Fig. 4. (a) Temperature dependence of dielectric constant and (b) temperature coefficient of capacitance (%) of BaTiO₃ specimens synthesized by three different synthesis methods.

sizes, the residual strain at the domain wall is more easily relieved, which leads to high polarization and results in high tetragonality [9-12].

Figure 4 shows the temperature dependence of the dielectric constant and the temperature coefficient of capacitance (TCC) value of the ceramics synthesized by the solid state, hydrothermal, and co-precipitation methods. For the TCC values, all of the specimens met the X5R specification (-55°C to 85°C , $\Delta C \pm 15\%$) (Fig. 4(b)). Over the full temperature range of -55°C to 150°C , the solid state specimen has the lowest dielectric constant among the three materials, and the difference in the permittivity of the three specimens is clearly discernible near the Curie temperature. Maximum values of permittivity near the Curie temperature were 3804, 5048, and 5813 for the solid state, hydrothermal, and co-precipitation methods, respectively. The sample produced by the co-precipitation method has the highest value that corresponds with the highest tetragonality, as shown in Table 1. In the perovskite structure of BaTiO₃, distortion of the TiO₆ octahedron increases with increasing tetragonality; i.e., with increasing asymmetry of the lattice [13].

Conclusions

The BaTiO₃ powders for MLCCs were fabricated by a solid state, a hydrothermal, and a co-precipitation method, and the electrical properties of BaTiO₃ were investigated in terms of crystallite size and tetragonality, based on their powder characteristics. Synthesized powders had similar particle diameters of about 170 nm. Accelerated grain growth and densification were observed in the powder produced by the co-precipitation method, which had a relatively broad particle size distribution. Inhomogeneous grain growth was observed in the powder synthesized by the solid state method, including agglomerates. Crystallite sizes were 31.2 nm, 31.5 nm, and 33.6 nm for the solid state, hydrothermal, and co-precipitation methods, respectively. The smaller the crystallite size, the larger the domain walls will be, which leads to restrictions on changes to the lattice parameters. Hence, the tetragonality result obtained from a Rietveld refinement method was in agreement with the ordering of the crystallite size. The highest tetragonality of 1.0079 for the BaTiO₃ ceramic produced by the co-precipitation method had the highest dielectric constant of 5813 among specimens synthesized by these three methods.

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