Size Effect on Dielectric Properties of Barium Titanate Fine Particles

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High density, impurity-free, and defect-free Barium titanate ($BaTiO_3$) fine particles with various sizes from 20 to 1000 nm were prepared by the 2-step thermal decomposition method of barium titanyl oxalate and post-heating treatments. The crystal structures of these particles were evaluated using XRD measurement and Raman scattering measurement. The dielectric properties of these particles were evaluated using a powder dielectric measurement method. This method consists of two procedures *i.e.*, (1) a dielectric measurement of slurry that consists of particles and a suitable dispersion medium (propylene carbonate) and (2) a calculation of the dielectric constant of a slurry model by a finite element method. As a result, the dielectric constant of $BaTiO_3$ fine particles strongly depended on their particle size. The dielectric constant of $BaTiO_3$ fine particles with a size around 140 nm exhibited a dielectric maximum. It is found that the tetragonality strongly affects the dielectric constant of the $BaTiO_3$ fine particles.
Key words: $BaTiO_3$ fine particle, dielectric property, size effect, slurry, finite element method

1. INTRODUCTION

Ferroelectric barium titanate ($BaTiO_3$) fine particles have been used as raw materials for electronic devices such as multilayered ceramic capacitors (MLCC). Recently, with the demands on miniaturization and higher capacitance, the downsizing of MLCC has been developed and accelerated. In the future, it is expected that the thickness of dielectric layers in MLCC will become less than 0.5 μm and the particle size of the $BaTiO_3$ will decrease from a few hundred nm to a few ten nm. However, in ferroelectrics, it is known that the dielectric properties are dependent on a size.[1-4] This phenomenon is called "size effect" in ferroelectrics, and it is anticipated that it will cause problems when MLCC will be developed in the future. Therefore, the size effect in ferroelectrics such as $BaTiO_3$ is one of the most important phenomena from the industrial and scientific viewpoints.

In $BaTiO_3$ bulk ceramics, many researchers have reported the grain size dependence of the dielectric properties.[1-3] Some of them have reported that the dielectric constant of the bulk ceramics with a certain grain size exhibited maximum. However, various values of size with dielectric maximum were reported. On the other hand, recently, a new dielectric measurement method for particles was developed, and the particle size dependence of dielectric constant in $BaTiO_3$ fine particles was estimated.[5] It was reported that the dielectric constant of $BaTiO_3$ particles with a size around 70 nm exhibited maximum. However, the preparation processes of some $BaTiO_3$ powders were different, and that might affect the dielectric properties significantly. This is because the dielectric property can depend on so many factors.

As the factors which affect the dielectric property, a density, impurities, defects, stresses, size and crystal structure etc. are considered. The size effect is considered as a phenomenon in which only size affects the crystal structure and the crystal structure affects the dielectric property. Therefore, in order to explain the size effect, the relationship among the particle size, the dielectric property and the crystal structure should be investigated.

The objective in this study is to investigate the relationship among the particle size, the crystal structure and the dielectric property for $BaTiO_3$ fine particle. For this objective, high density, impurity-free, and defect-free $BaTiO_3$ fine particles with various sizes from 20 to 1000 nm were prepared systematically by the 2-step thermal decomposition method of Barium titanyl oxalate[6] and post-heating treatments. Moreover, the crystal structures and dielectric constants of these particles were estimated.

2. EXPERIMENTAL

2.1 Sample preparation and characterization

Barium titanyl oxalate ($BaTiO(C_2O_4)_2 \cdot 4H_2O$) powder was prepared by Fuji Titanium Co., Ltd. Its Ba/Ti atomic ratio was 1.000 and the amount of the impurity was less than 0.02 %. The details were described elsewhere.[7] Using this powder, $BaTiO_3$ particles with various particle sizes were prepared by the 2-step thermal decomposition method and post-heating treatments. At first, the thermal decomposition at the 1st step was performed at 500 °C for 3 hours in air, and resulted in the formation of the intermediate compounds with almost amorphous structure. At the following 2nd step, this compound was annealed at 650 °C for 3 hours in the vacuum of 10^{-2} torr, and resulted in the formation of the $BaTiO_3$ particles. Moreover, this particles ware annealed at various temperatures from 700 °C to 1100 °C for 3 hours in air, to control particle sizes of $BaTiO_3$.

These particles were characterized using the following methods. The crystal structures of the products ware investigated using a powder X-ray diffractometer (XRD) (RINT2000, Rigaku, Cu-kα, 50 kV, 30 mA) and a laser Raman scattering spectrometer (Raman) (NRS-2100, JASCO, 514 nm, 100 mW). The average particle sizes and the crystallite sizes were estimated using a transmission electron microscope (TEM) (JEM-2010F, JEOL) and a XRD, respectively. The impurities in the products ware analyzed using a Fourier transform infrared spectrometer (FT-IR) (SYSTEM 2000 FT-IR, Perkin Elmer) and by differential thermal analysis with thermogravimetry (TG-DTA) (TG-DTA2000, Mac Science).

2.2 Dielectric measurement of particles

The dielectric constant of $BaTiO_3$ particles were estimated using a powder dielectric measurement method. This method consists of two procedures *i.e.*, (1) a dielectric measurement of slurry that consists of particles and a suitable dispersion medium and (2) a calculation of the dielectric constant of a slurry model by a finite element method (FEM).

At first, the $BaTiO_3$ slurries ware prepared. The $BaTiO_3$ particles were mixed with propylene carbonate (ε_r= 66.58 at 20 °C) using the ball mill at a volume fraction of 11 vol%. The dielectric constants of the $BaTiO_3$ slurries were measured at 20.00 ± 0.03°C and 20 MHz. Figure 1 shows a schematic diagram of the dielectric measurement system for the slurry. This system consisted of an impedance analyzer (Agilent, 4294A), a liquid test fixture (Agilent, 16452A) and a thermostat.

On the other hand, the dielectric constant of a slurry model was calculated by FEM. The FEM analysis software ANSYS (ANSYS Inc., version 7.0) was used. For the slurry model, the following two assumptions
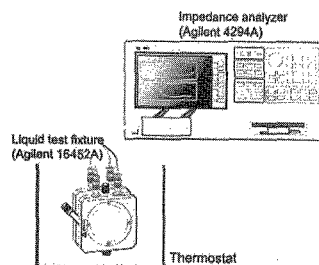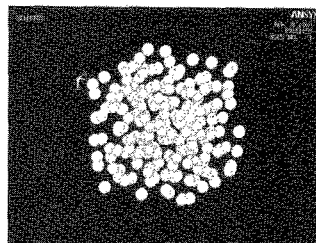
were considered, *i.e.*, (1) one sphere $BaTiO_3$ particle can be regarded as one semi-sphere made of numerous tetrahedrons, and (2) one $BaTiO_3$ sphere must be surrounded by the propylene carbonate tetrahedrons (no contact between the $BaTiO_3$ spheres). Figure 2 shows the inner structure of the used slurry model. 200 $BaTiO_3$ semi-spheres were distributed homogeneously and randomly in the propylene carbonate matrix. The number of elements and nodes of the model were about 270000 and 200000, respectively. The dielectric constant of the model was calculated by the electrostatic field analysis when a certain dielectric constant of the $BaTiO_3$ sphere was assumed. Finally, the calculated dielectric constants of the model were compared with the measured dielectric constant of the slurry, and then the dielectric constant of the $BaTiO_3$ particles was determined.

3. RESULTS AND DISCUSSION

3.1 Preparation of $BaTiO_3$ particles with various sizes and their characterizations

At first, we try to prepare impurity-free and nm-sized $BaTiO_3$ particles using the 2-step thermal decomposition method. At the 1st step, barium titanyl oxalate powder was annealed at 500 °C for 3 hours in air, and then resulted in the formation of white-colored powders with almost amorphous structure. At the following 2nd step, this intermediate compound was annealed at 650 °C for 3 hours in the vacuum of 10^{-2} torr, and resulted in the formation of the $BaTiO_3$ particles. Moreover, this particles ware annealed at various temperatures from 700 °C to 1100 °C for 3 hours in air.

At first, their average particle sizes of these products were using TEM. The results were shown in Table I. This revealed that $BaTiO_3$ fine particles with various sizes from 20 to 1000 nm could be obtained by the 2-steps thermal decomposition method of barium titanyl oxalate and post-heating treatments.

Figure 3 (a) shows the (111) XRD peak of $BaTiO_3$. With the increase of heat-treatment temperature, the full-width at half maximum (FWHM) of the (111) peak decreased and the peak shifted to higher angles. This
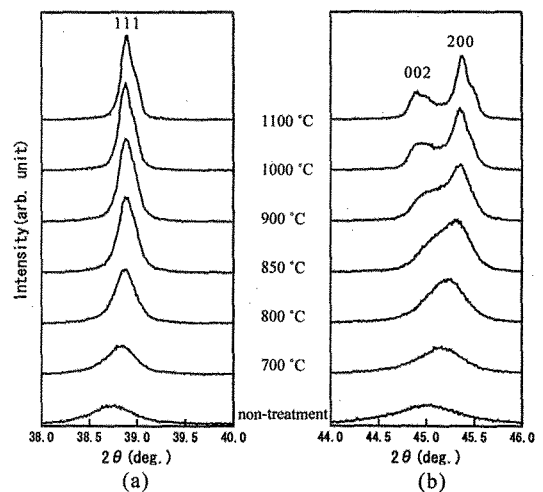

Fig. 1. Schematic diagram of dielectric measurement system for the slurry

Fig. 2. Inner structure of the slurry model used in this study

Fig. 3. XRD patterns of the $BaTiO_3$ particles prepared at various heat-treatment temperatures

Table I.   Characterization results of $BaTiO_3$ particles prepared in this study

Heat-treatment condition	Particle size	Crystallite size	Symmetry	Impurity	Composition	Density
no-treatment	20 nm	20 nm	XRD: P*m-3m* Raman: P*4mm*	lattice: negligible surface: OH⁻, CO_3^{2-}	Ba/Ti = 1.00	5.87 g/cm³ 99.2 %
700 °C, 3 hr.	40 nm	36 nm	XRD: P*m-3m* Raman: P*4mm*	lattice: negligible surface: OH⁻, CO_3^{2-}	Ba/Ti = 1.00	5.88 g/cm³ 98.3 %
800 °C, 3 hr.	85 nm	80 nm	XRD: P*m-3m* Raman: P*4mm*	lattice: negligible surface: OH⁻, CO_3^{2-}	Ba/Ti = 1.00	6.01 g/cm³ 100 %
850 °C, 3 hr.	140 nm	130 nm	XRD: P*4mm* Raman: P*4mm*	lattice: negligible surface: OH⁻, CO_3^{2-}	Ba/Ti = 1.00	5.97 g/cm³ 99.2 %
900 °C, 3 hr.	215 nm	210 nm	XRD: P*4mm* Raman: P*4mm*	lattice: negligible surface: OH⁻, CO_3^{2-}	Ba/Ti = 1.00	5.97 g/cm³ 99.3 %
1000 °C, 3 hr.	430 nm	400 nm	XRD: P*4mm* Raman: P*4mm*	lattice: negligible surface: OH⁻, CO_3^{2-}	Ba/Ti = 1.00	5.99 g/cm³ 99.6 %
1100 °C, 3 hr.	1000 nm	> 1000 nm	XRD: P*4mm* Raman: P*4mm*	lattice: negligible surface: OH⁻, CO_3^{2-}	Ba/Ti = 1.00	5.94 g/cm³ 98.9 %

means that the crystallite size increased and the lattice volume expanded with the increase of heat- treatment temperature. The crystallite sizes estimated using the FWHM of (111) peak were shown as Table I.

Figure 3 (b) shows the (002) and (200) XRD peaks of $BaTiO_3$. The crystal structures of the products annealed over 850 °C clearly assigned to tetragonal *4mm*. On the other hand, the crystal structures of the products annealed below 800 °C assigned to cubic *m-3m*. However, in the case the c/a ratio close to 1.00, cubic *m-3m* symmetry is undistinguishable from tetragonal *4mm* symmetry with low c/a ratio. Therefore, it is not clear that the crystal phases of the products annealed below 800 °C are true cubic phase or not. Figure 4 shows the particle size dependence of the lattice parameters estimated from the positions of (002) and (200) peaks. The positions of (002) and (200) peaks were determined by the peak profile separation using Pearson VII function. It was revealed that a-axis increased and c-axis decreased with the decrease of the particle size. And the lattice volume expanded with the decease of the particle size below 85 nm. Figure 5 shows the particle size dependence of the tetragonality (c/a ratio). Their tetragonality decreased with the decrease of the particle size.

While the crystal structures of the particles with sizes below 85 nm assigned to cubic *m-3m* by XRD measurement, it was assigned to tetragonal *4mm* by a Raman scattering measurement. Raman scattering measurement can clarify the local and dynamic symmetry while XRD measurement can clarify the average and static symmetry. The difference between XRD and Raman observed for these particles was similar to a behavior observed just above Curie temperature (T_c) for $BaTiO_3$ crystals.[8] This similarity suggests that the size effect of $BaTiO_3$ crystallites can be one of the ferroelectric phase transitions.

We also measured the impurities, the density and a Ba/Ti atomic ratio for the $BaTiO_3$ particles prepared in this study. Table I shows these results. FT-IR and TG-DTA measurements revealed that there was no impurity in the $BaTiO_3$ lattice. The relative density of all $BaTiO_3$ particles was almost over 99 %, and this revealed that there were few physical defects such as

voids. On the other hands, the Ba/Ti atomic ratios for the $BaTiO_3$ particles were determined by using the X-ray fluorescence analysis. Their Ba/Ti ratio was always 1.00, and these results suggest that these $BaTiO_3$ particles may be defect-free materials. It should be noted that all $BaTiO_3$ particles in Table I are high density, almost defect-free and impurity-free particles. This means that the suitable sample for the objective in this study could be obtained.

3.2 Particle size dependence of dielectric constants of the $BaTiO_3$ particles

The slurries of the $BaTiO_3$ particles were prepared and the dielectric constants of these slurries were measured as described in the experimental procedure. On the other hand, the dielectric constant of the slurry model was calculated by FEM. From both the measurement results and the calculation results, the dielectric constants of $BaTiO_3$ particles prepared in this study and BT-05 (Sakai Chemical Co., $BaTiO_3$ fine particles with a size of 500 nm) were estimated as shown in Figure 6. This result revealed that the dielectric constant of $BaTiO_3$ fine particles strongly depended on their particle size. While the dielectric constants of $BaTiO_3$ particles with sizes over 430 nm were almost constant at around 1600, those of the particles with sizes below 215 nm increased with the
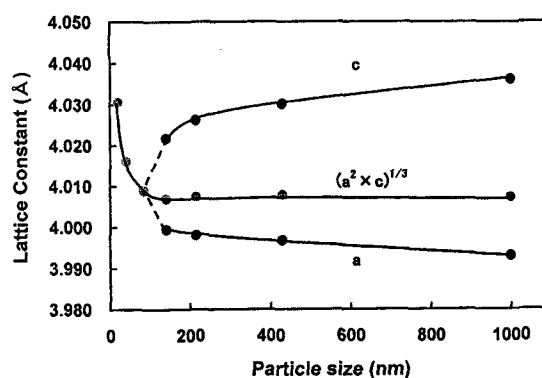

Fig. 4.   Particle size dependence of lattice parameters for $BaTiO_3$ particles

decrease of particle sizes down to 140 nm. Moreover, the dielectric constants of the particles with sizes below 140 nm decreased with decrease of particle sizes. The dielectric constant of BaTiO₃ particles with a size around 140 nm exhibited a dielectric maximum about 5000. The particle size dependence of the dielectric constant estimated in this study is similar to the grain size dependence on the BaTiO₃ bulk ceramics reported by many researchers.

Relationship among the particle size, the crystal structure and the dielectric property is considered. By comparing the results shown in Fig. 5 and Fig. 6, it is found that the tetragonality is related to the dielectric constant of the BaTiO₃ fine particles. The dielectric constant of the particles with sizes over 140 nm increased with the decrease of the c/a ratio. The c/a ratio of the particles with a size of 140 nm *i.e.*, a size with dielectric maximum, equaled to 1.006. It should be noted that the maximum dielectric constant was obtained for the particles with a c/a ratio below 1.011 (BaTiO₃ single crystal value). This result is similar to the result on BaTiO₃ bulk ceramics reported by Arlt *et al.* [4] Currently, it is difficult to explain this reason. However, this study revealed that the tetragonality strongly affected the dielectric constant of BaTiO₃ fine particle. As the next step, in order to explain the origin of the higher dielectric constants, the crystal structures of the particles should be investigated in detail.
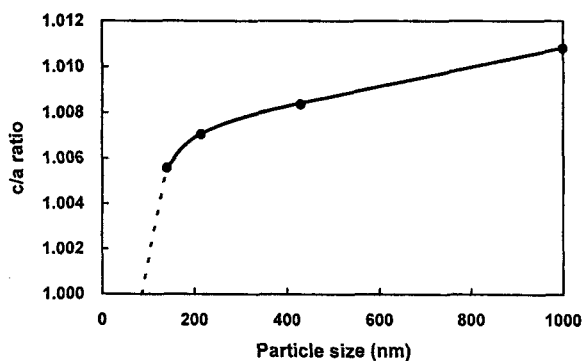
4. CONCLUSIONS

In this study, high density, impurity-free, and defect-free BaTiO₃ particles with various particle sizes from 20 nm to 1000 nm were prepared by the 2-step decomposition method of BaTiO(C₂O₄)₂•4H₂O and post-heating treatments. The crystal structures of these particles were evaluated using XRD measurement and Raman scattering measurement. It was revealed that a-axis increases and c-axis decreases with the decrease of the particle size. And the lattice volume expanded with the decrease of the particle size below 85 nm. The tetragonality of the particle decreased with the decrease of the particle size. While the crystal structure of the particles with sizes below 85 nm assigned to cubic *m-3m* by XRD measurement, it was assigned to tetragonal *4mm* by a Raman scattering measurement. This difference was similar to a behavior observed just above T_c for BaTiO₃ single crystals. The dielectric properties of these particles were evaluated using a dielectric measurement method for particles using BaTiO₃ slurry. As a result, the dielectric constant of BaTiO₃ fine particles strongly depended on their particle size. The dielectric constant of BaTiO₃ fine particles with a size around 140 nm exhibited a dielectric maximum about 5000. From the relationship of the dielectric constant and the tetragonality, it is revealed that the tetragonality strongly affects the dielectric constant of the BaTiO₃ fine particles, and maximum dielectric constant was obtained for the particles with a c/a ratio below 1.011.

Fig. 5. Particle size dependence of tetragonality

Fig. 6.　Particle size dependence of dielectric constant of BaTiO₃ particles

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