The size effect of ferroelectric materials is one of the most important issues to develop next-generation dielectric devices. In this paper, we reviewed our studies on the size effects of barium titanate (BaTiO₃) fine particles and ceramics. In the size effect of BaTiO₃ fine particles, the maximum of dielectric permittivity was observed at a particle size of around 140 nm, and was explained by the composite structure model including a gradient lattice strain layer (GLSL) having a very high permittivity. In contrast, the grain size effect of BaTiO₃ ceramics, where the permittivity showed a maximum at a grain size of about 1.1 μm, was interpreted as the superposition effect of domain-wall contributions and grain boundary effect.

1. Introduction

Crystal structure and dielectric property of ferroelectric materials may depend on the sample size at nano- or submicro-metric scale. This phenomenon is called “size effect” in ferroelectrics, and the study of size effect has become important in recent years with the utilization of nanostructured ferroelectric materials in various dielectric devices. In the case of multilayered ceramic capacitors (MLCCs), the dielectric layer thickness in MLCCs has been continuously reduced to reach below 1 μm in order to increase the capacitance density. The reduction of dielectric layer thickness demands the simultaneous reduction of BaTiO₃ grain size to submicron level. The biggest obstacle to developing high-capacitance MLCCs is the grain size effect of BaTiO₃ ceramics. It is known that the dielectric permittivity of BaTiO₃ ceramics depends on grain size. To develop next-generation dielectric devices, it is indispensable to understand the mechanism of the size effect.

The size effect of ferroelectric materials has confirmed for various specimen forms such as fine particles, thin film, and thin film and thin film depend on particle size, grain size, and film thickness, respectively. It seems that the size effects depend on the specimen forms. Therefore, we should understand the mechanism of the size effect for each specimen form. In this study, we studied the particle size effect of BaTiO₃ fine particles and the grain size effect of BaTiO₃ ceramics. In this paper, we will review our recent achievement in the size effects of BaTiO₃ fine particles and ceramics.

2. Size effect of BaTiO₃ fine particles

The crystal structure and the dielectric property of BaTiO₃ particles depend on impurities and defect concentration in the crystals, which demand us to prepare almost impurity- and defect-free BaTiO₃ particles with various particle sizes at nano- or submicro-metric scale for the investigation of the size effect of BaTiO₃ particles. We have developed a two-step decomposition method of barium titanyl oxalate to synthesize high-quality BaTiO₃ single crystal particles with various particle sizes of 20–430 nm. The size effects of BaTiO₃ single crystal particles measured using slurries fitted by assuming single particle size distributions. Therefore, we employed a new composite structure model for BaTiO₃ nanoparticles shown in Fig. 3, where a BaTiO₃ particle is assumed to consist of three regions, i.e., (i) an inner tetragonal core, (ii) a gradient lattice strain layer (GLSL), and (iii) a surface cubic layer. This model was designed to explain the permittivity of BaTiO₃ particles measured using slurries.
incorporate the lattice relaxation between inner tetragonal core and surface cubic layer.27) Lattice parameters (a-axis and c-axis length) and atomic positions were changed continuously in the GLSL. The open circles and the solid lines are the measured and the calculated profile, respectively. The “F” symbols indicate the calculated crystal structure factor of a particle.

fittings could be obtained using the structure model with the GLSL. Figure 4 shows an example of lattice parameter distribution in the BaTiO3 particle with the particle size of 140 nm. The structure refinement revealed that the lattice parameters of the inner tetragonal core and surface cubic layer did not depend on particle size. Previous studies reported that the c/a ratio of BaTiO3 particles decreased with particle size.1),2),20),21),28) In contrast, this study revealed that the lattice parameters of the inner tetragonal core were almost consistent with that of BaTiO3 bulk single crystal. The particle size dependence of c/a ratio should be interpreted as the decrease in the volume fraction of inner tetragonal core. Figure 5 shows the particle size dependence of the thicknesses of the three regions, R_{I-II}, (R_{II-III}-R_{I-II}), and (D/2-R_{II-III}), where R_{I-II} is the radius of inner tetragonal core, (R_{II-III}-R_{III}) is the thickness of GLSL, and (D/2-R_{I-II}) is the thickness of surface cubic layer. It was found that the surface cubic layer have almost constant thickness of 10–15 nm despite particle size. This means that the ferroelectricity of the BaTiO3 particles should disappear below the particle size of 20–30 nm because the particles loses tetragonal core below this size. The existence of ferroelectric critical size was pointed out in previous studies.1)–5) The ferroelectric critical size, 20–30 nm, determined in this study was consistent with that estimated by the symmetry assignment in XRD analysis.29) In the size effect of BaTiO3 particles, the crystal structures of the three regions did not depend on particle sizes while only the volume fraction of these regions changes with particle size. The ferroelectricity is depressed with decreasing particle size and finally disappears below the critical size. This phenomenon was explained by the decrease in volume fraction of tetragonal core with decreasing particle size.

The composite structure suggests that the dielectric property of BaTiO3 particles is dependent on the particle size. The dielectric permittivity of the surface cubic layer is assumed to be lower than that of the bulk crystal because the surface cubic layer is significantly different from the bulk crystal. The dielectric properties of the surface cubic layer are expected to be lower than those of the bulk crystal because the surface cubic layer is significantly different from the bulk crystal. The dielectric properties of the surface cubic layer are expected to be lower than those of the bulk crystal because the surface cubic layer is significantly different from the bulk crystal.
a paraelectric layer. In contrast, the GLSL may have high permittivity because the GLSL is the static phase transitional layer from the tetragonal phase to the cubic phase. We observed a decreasing of soft-mode frequency, which was the origin of the enhancement of dielectric permittivity, with decreasing particle size. We think that the soft-mode frequency of GLSL is lower than that of the bulk crystal because the GLSL have the static phase transitional structure, and therefore the decreasing of soft-mode frequency is due to the increase of the volume fraction of GLSL. The GLSL enhanced the permittivity of particle while the surface cubic layer depressed it. By assuming the above-mentioned dielectric distribution inside a particle, the particle size dependence of permittivity was simulated as shown in Fig. 1 (calculated). We could reproduce the measured particle size dependence of permittivity, which means that the new composite structure model with the GLSL successfully explained the size effect on the dielectric properties of BaTiO3 particles. The dielectric property of BaTiO3 nanoparticles is dependent on the particle structure. The thin surface cubic layer induces a dielectric maximum at a certain particle size. On the other hand, when the nanoparticles have thick cubic layers, the maximum disappeared and the permittivity decreased with decreasing particle size. The thickness of cubic layers is generally determined by the defect concentration in BaTiO3 nanoparticles. Therefore, BaTiO3 nanoparticles with low defect concentration are required for a high dielectric permittivity.

3. Grain size effect of BaTiO3 ceramics

As is the case for fine particles, the dielectric property of BaTiO3 ceramics depends on many factors, e.g., impurities, defect concentration, crystallinity, density, and residual stress, as well as grain size. Therefore, in order to discuss the size effect of BaTiO3 ceramics, we need fine-grained BaTiO3 ceramics with low impurity concentration, low defect concentration, high crystallinity, high density, and low residual stress. However, it is generally difficult to prepare such BaTiO3 ceramics using a conventional sintering method. In this study, highly dense BaTiO3 ceramics with micrometer- and nanometer-sized grains were fabricated by the two-step sintering method and aerosol deposition (AD) method, respectively. The two-step sintering is a promising technique for obtaining highly dense ceramics without significant grain growth. The AD method is an attractive technique for the fabrication of dense thick films with nanosized grains. This method is based on the impaction phenomenon of submicrometer ceramic particles that are accelerated in aerosol gas up to velocities of several hundreds of m/s. During impact onto the substrate, these particles are fractionated to nanosized pieces, thereby forming dense ceramic films. The AD method is a unique technique that enables nanograinized ceramic fabrication at room temperature.

In the two-step sintering method, BaTiO3 powder with an average particle size of 100 nm was used as a raw powder for preparing BaTiO3 ceramics. BaTiO3 powder was isostatically pressed without a binder at 200 MPa and 200°C. The resulting green compacts were heated to $T_1 = 1320-1380°C$ at 5-25°C/min, immediately cooled to various lower temperatures ($T_2 = 1100-1380°C$) at 30°C/min, and isothermally sintered for 10 h. The sintering conditions for obtaining high-density ceramics without significant grain growth were decided on the basis of the shrinkage behaviors of the ceramics during the increase in temperature. Using the two-step sintering method, we obtained highly dense BaTiO3 ceramics with grain sizes of 0.6-13 μm (Fig. 6). In the AD method, BaTiO3 powder with an average particle size of 500 nm was used as raw powders for preparing AD thick films. BaTiO3 thick films were deposited on SrTiO3 single-crystal substrates by the AD method described in detail elsewhere. An AD thick film clamped on a substrate is under high residual stress and thereby the permittivity of perovskite-type ferroelectric films is considerably lower than that empirically predicted. Therefore, freestanding thick films are indispensable to the investigation of the size effect of perovskite-type ferroelectric ceramics. In this study, to obtain crystallized freestanding BaTiO3 thick films, the as-deposited AD films were heated to 600°C at 300°C/h. During the annealing process, the magnitude of the interfacial stress between the film and substrate increased with increasing temperature because of the mismatch in the thermal expansion coefficient between the film and substrate materials. The magnitude of thermal stress was higher than the adhesion strength between the film and substrate; therefore, we obtained freestanding thick films by the annealing process. The freestanding BaTiO3 thick films were reannealed at 800-1250°C for 1 h in order to control their grain size. Grain size increased with increasing temperature and was controlled from 20 to 830 nm (Fig. 7).

![Fig. 6. FE-SEM images of fractured surfaces of BaTiO3 ceramics prepared by two-step sintering.](image)

![Fig. 7. FE-SEM images of fractured surfaces of freestanding BaTiO3 thick films using AD method.](image)

![Fig. 8. (Color online) Grain size dependences of dielectric permittivity ($\varepsilon_r$) and piezoelectric $d_{33}$ coefficient of BaTiO3 ceramics.](image)
Spontaneous polarizations of the domains had simple lamellar structures in the grain. Directions of the elastic energy due to the stress from grain boundaries. For fine-grained ceramics, the elastic energy was relatively high; therefore, the 90° domains were introduced in the BaTiO3 grains for reducing domain size. The results of Raman spectroscopy indicated by Arlt et al.6,51 Therefore, the 90° domain configurations in grains (a) and grain size dependence of 90° domain width in BaTiO3 ceramics (b). Most of the domains had simple lamellar structures in the grain. Directions of spontaneous polarizations (P3) are indicated by arrows in illustrations.

Figure 8 shows the grain size dependences of dielectric permittivity and piezoelectric d33 coefficient at 25°C.52,43,45,50 The permittivity of BaTiO3 ceramics increased with decreasing grain size when the grain size was more than 1.1 μm, whereas it decreased when the grain size was below 1 μm. The maximum permittivity of the BaTiO3 ceramics was 8,000 for a grain size of 1.1 μm. Moreover, the piezoelectric d33 coefficient after poling treatment also increased with decreasing grain size in micron range, and the d33 coefficient for a grain size of 1.2 μm exhibited a maximum of 460 pC/N. It is possible to obtain very high permittivity and piezoelectric coefficient by controlling the grain size of BaTiO3 ceramics.

The increase in permittivity with decreasing grain size at the micron level was caused by domain-wall contributions as proposed by Arlt et al.42,51 Therefore, the 90° domain configurations of the BaTiO3 ceramics were observed by a field emission scanning electron microscopy (FE-SEM) after chemical etching of sample surface as shown in Figure 9(a).52,43 The observations revealed that most of the domains had simple lamellar structures. The 90° domain width decreased with decreasing grain size, as shown in Figure 9(b). The correlation between domain width and grain size was theoretically explained by Arlt et al. The 90° domains were introduced in the BaTiO3 grains for reducing the elastic energy due to the stress from grain boundaries. For fine-grained ceramics, the elastic energy was relatively high; therefore, fine 90° domains were introduced in the BaTiO3 grains.

To understand the domain-wall contributions to the permittivity, ultra wide range dielectric spectra22-56 of the BaTiO3 ceramics were measured. In the frequency range up to 5 MHz, the dielectric permittivity of the ceramics was determined by the conventional capacitance measurement. In the frequency range up to a few GHz, a planar-electrode method was employed.57 In the THz region, complex permittivity was determined by analyzing reflectivity data taken by a Fourier-transform infrared (FT-IR) spectrometer using Four-Parameter-Semi-Quantum (FPSQ) model.55,53,55 Figure 9(a) shows the grain size dependences of permittivities determined by the conventional capacitance measurement and the FPSQ model. The 90° domain configurations in grains (a) and grain size dependence of the permittivities determined by the conventional capacitance measurement and the FPSQ model. Moreover, the ionic polarizability also increased with decreasing grain size. The 90° domain structure induces a lattice strain into the BaTiO3 lattices around the domain wall.42 The crystal lattices on the 90° domain walls may have approximately cubic symmetry and they are extended in one direction with separating from the domain walls to possess the spontaneous lattice strains of the tetragonal phase. This region is quite similar to the GLSL proposed in the last section and should have a high permittivity due to the ionic polarization, because it has the static phase transitional structure from tetragonal phase to cubic phase. Therefore, the high domain-wall density enhanced the ionic polarizability as well as the orientational polarizability. The increase in permittivity and piezoelectric coefficient with decreasing grain size to 1 μm is due to the 90° domain-wall contributions.

In contrast, for grain sizes below 1 μm, the orientational and ionic polarizabilities decreased with decreasing grain size. At the same time, we confirmed decreases in spontaneous polarization and Curie temperature, that meant the ferroelectricity decreased with decreasing grain size below 1 μm.53 The domain-wall contributions suppressed with decreasing grain size in spite of reducing domain size. The results of Raman spectroscopy indicate...
icated that the crystal lattice of nanograined BaTiO$_3$ ceramics was under high compressive stress, which explained a variety of phenomena with decreasing grain size below 1 μm. We believe the compressive stress is associated with the stress from grain boundaries. This means the permittivity of BaTiO$_3$ ceramics decreased by the grain boundary effect. Therefore, we can conclude that the grain size effect of BaTiO$_3$ ceramics is interpreted as the superposition effect of the domain-wall contributions and the grain boundary effect. The dielectric and piezoelectric properties of BaTiO$_3$ ceramics are determined by the 90º domain and grain boundary structures.

4. Summary

Our studies on the size effects of BaTiO$_3$ fine particles and ceramics were reviewed in this paper. The size effect of BaTiO$_3$ fine particles, where the permittivity showed a maximum at a particle size of around 140 nm, was explained by the composite structure model including GLSL having a very high permittivity. This means the permittivity of BaTiO$_3$ ceramics, where the permittivity showed a maximum at a grain size of about 1.1 μm, was interpreted as the superposition effect of the domain-wall contributions and the grain boundary effect. The size effects of BaTiO$_3$ fine particles and ceramics have different origins. However, they agree in that the dielectric properties are determined by the nanostuctures. For developing next-generation dielectric devices, it is very important to control the dielectric and piezoelectric properties of ferroelectric materials by highly controlling their nanostuctures.

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