

## Domain Size Effect on Dielectric Properties of Barium Titanate Ceramics

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Barium titanate (BaTiO<sub>3</sub>) ceramics with various grain sizes were prepared by a conventional sintering method and a two-step sintering method. The permittivity of the ceramics increased with decreasing the grain size down to 1.1 μm on average. The BaTiO<sub>3</sub> ceramics with an average grain size of 1.1 μm had a high permittivity of 7,700. The transmission electron microscopy (TEM) observation revealed that the 90° domain density increased with decreasing the grain size. The domain size of the ceramics with the highest permittivity of 7,700 was approximately 100 nm. From an ultra wide range dielectric spectroscopy, it was found that the high domain density enhanced the orientational polarizability due to the domain-wall vibration and the ionic polarizability due to the lattice vibration. It was clarified that the increase of the permittivity with decreasing the grain size was due to the domain size effect. [DOI: 10.1143/JJAP.47.7607]

KEYWORDS: barium titanate, two-step sintering, dielectric property, domain size, size effect, wide range dielectric spectroscopy, polarization

### 1. Introduction

BaTiO<sub>3</sub> is typical ferroelectrics with high permittivity and have been used as the materials for dielectric devices such as multilayered ceramic capacitors (MLCC). Recently, with the demands on miniaturization and higher capacitance of MLCC, fine grained dielectric layers with high permittivity have been required. In ferroelectrics, it is known that the dielectric permittivity depend on the grain size. This phenomenon is called the size effect in ferroelectrics, many researchers reported the size dependence of the permittivity for BaTiO<sub>3</sub> ceramics.<sup>1–4</sup> It was generally recognized that the permittivity of BaTiO<sub>3</sub> ceramics increased with decreasing the grain size in micron level while that decreased in submicron level. For the development of the dielectric and piezoelectric devices in the next generation, it is indispensable to understand the mechanism of the size effect of BaTiO<sub>3</sub> ceramics. Arlt *et al.*<sup>1</sup> reported that the 90° domain size decreased with decreasing the grain size and the permittivity increased by the contribution of 90° domain wall. However, the mechanism of the domain contribution has not been fully clarified. In order to understand the mechanism, it is important to measure the permittivity of the fine grained BaTiO<sub>3</sub> ceramics without internal stress and impurity.

Recently, Chen *et al.*<sup>5</sup> proposed a two-step sintering method for preparing fine grained ceramics. This method is effective to prepare fine grained BaTiO<sub>3</sub> ceramics without internal stress and impurity, while the hot-press sintering and the spark plasma sintering method are unsuitable for stress- and impurity-free BaTiO<sub>3</sub> ceramics, respectively. Polotai *et al.*<sup>6</sup> and Wang *et al.*<sup>7</sup> used the two-step sintering method to control grain size and improve the density of the BaTiO<sub>3</sub>. Karaki *et al.*<sup>8</sup> reported that the BaTiO<sub>3</sub> ceramics with an average grain size of 1.6 μm prepared by the two-step sintering had a high permittivity of 6,000 and high piezoelectric  $d_{33}$  constant of 460 pC/N.

In this study, to clarify the size effect on dielectric properties of BaTiO<sub>3</sub> ceramics, the permittivity and the 90° domain contribution were investigated as a function of the

grain size for the BaTiO<sub>3</sub> ceramics prepared by a conventional sintering method and a two-step sintering method. Moreover, we clarified the polarization mechanism of the domain contribution by an ultra wide range dielectric spectroscopy.

### 2. Experimental Procedure

BaTiO<sub>3</sub> ceramics with various grain sizes were prepared by a conventional sintering method and a two-step sintering method. Hydrothermal synthesized BaTiO<sub>3</sub> powder with average particle size of 100 nm (BT-01, Sakai Chemical) was used as raw powder of the BaTiO<sub>3</sub> ceramics. The Ba/Ti atomic ratio of the powder was approximately 0.998. The BaTiO<sub>3</sub> powder was isostatically pressed without binder at 200 MPa and 20 °C. In the conventional sintering method, the green compacts were sintered at various temperatures (1260–1380 °C) for 2 h. In the two-step sintering method, the green compacts were heated at 10 °C/min to 1320 °C, then immediately cooled at 30 °C/min to various lower temperatures (1150–1320 °C) and isothermally sintered for 15 h.

The crystal structures of the BaTiO<sub>3</sub> ceramics with various grain sizes were investigated using X-ray diffraction (XRD) system (Bruker AXS D8 ADVANCE, Cu K $\alpha$ , 35 kV, 300 mA). The densities of the ceramics were measured by the Archimedes method. The grain sizes of the ceramics were measured using scanning electron microscopy (SEM; JEOL JSM-5310, 20 kV). The domain configurations of the ceramics were observed using transmission electron microscopy (TEM; Philips CM30, 300 kV and JEOL 200CX, 160 kV) after Ar ion milling of the samples.

The dielectric properties of the ceramics in a wide frequency range from kHz to THz were evaluated using three kinds of measurement methods. In the frequency range up to 5 MHz, the dielectric permittivity of the ceramics was determined by the conventional capacitance measurement. Au electrodes were formed on the two facing surfaces of the ceramic plates. The capacitance and the loss tangent ( $\tan \delta$ ) were measured with an impedance analyzer (Agilent 4294A). In the frequency range up to a few GHz, a planar-electrode method<sup>9</sup> was employed. Micro-planer-electrodes were designed and formed on the polished ceramic surface

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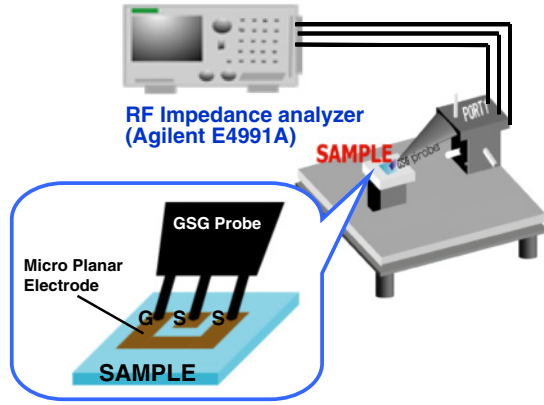


Fig. 1. (Color online) Measurement system of permittivity in frequency range from MHz to GHz.

by a liftoff process using an electron-beam lithography. Figure 1 shows the measurement system consisting of an impedance analyzer (Agilent E4991A) and a ground–source–ground (GSG) probe (Cascade Microtech). The complex permittivity was determined from the admittance between the source and the ground ports with the help of electromagnetic field simulation (Sonet Software). In the THz region, complex permittivity was determined using an infrared (IR) reflection method. IR reflectivity of the ceramics with the polished surface was measured using two IR spectrometers. A Fourier-transform infrared (FT-IR) spectrometer (JASCO FARIS-1) was used to measure the far IR reflectivity in the wavenumber range from 10 to 700  $\text{cm}^{-1}$ . A silicon bolometer unit (Infrared Laboratory) was used as a detector below 100  $\text{cm}^{-1}$  while triglycine sulfate detector was used in the range from 100 to 700  $\text{cm}^{-1}$ . On the other hand, a conventional FT-IR spectrometer (Shimadzu FTIR-8600PC) was used to measure the reflectivity in the range from 700 to 1500  $\text{cm}^{-1}$ .

Four-parameter-semi-quantum (FPSQ) model<sup>10)</sup> gives the relation between the complex permittivity ( $\epsilon^*$ ) due to ionic polarization and the optical phonon parameters:

$$\epsilon^*(\omega) = \epsilon_{\infty 1} \prod_j \frac{\omega_{j\text{LO}}^2 - \omega^2 + i\gamma_{j\text{LO}}\omega}{\omega_{j\text{TO}}^2 - \omega^2 + i\gamma_{j\text{TO}}\omega}, \quad (1)$$

where  $\omega$  is the angular frequency,  $\epsilon_{\infty 1}$  is the complex permittivity due to electric polarization,  $\omega_{j\text{LO}}$  and  $\omega_{j\text{TO}}$  are resonance frequencies of  $j$ -th longitudinal optical (LO) and transverse optical (TO) modes, respectively,  $\gamma_{j\text{LO}}$  and  $\gamma_{j\text{TO}}$  are damping factors of LO and TO modes, respectively. The IR reflectivity ( $R$ ) has the following relation with the complex permittivity:

$$R(\omega) = \left| \frac{\sqrt{\epsilon^*(\omega)} - 1}{\sqrt{\epsilon^*(\omega)} + 1} \right|^2. \quad (2)$$

On the other hand, it is empirically known that the dielectric relaxation due to orientational polarization has following relation:

$$\frac{\epsilon^*(\omega) - \epsilon_{\infty 2}}{\epsilon_0 - \epsilon_{\infty 2}} = \sum_{k=1} g_k \left( \frac{1}{1 + i\omega\tau_k} \right), \quad (3)$$

where  $\epsilon_{\infty 2}$  is the complex permittivity due to ionic polarization given by eq. (1),  $\epsilon_0$  is the low-frequency permittivity and  $g_k$  is distribution of the relaxation time ( $\tau_k$ ). We have

combine eqs. (1) and (3) to fit the observed permittivity from kHz to GHz region and IR reflectivity in THz region. The following  $F(x_i)$  was minimized using nonlinear least-squares calculation:<sup>11)</sup>

$$F(x_i) = [\epsilon_{\text{obs}}^*(\omega) - \epsilon_{\text{cal}}^*(\omega)]^2 + [R_{\text{obs}}(\omega) - R_{\text{cal}}(\omega)]^2, \quad (4)$$

where  $x_i$  is the fitting parameters in eqs. (1) and (3), i.e.,  $\epsilon_{\infty 1}$ ,  $\omega_{j\text{LO}}$ ,  $\omega_{j\text{TO}}$ ,  $\gamma_{j\text{LO}}$ ,  $\gamma_{j\text{TO}}$ ,  $g_k$ , and  $\tau_k$ , the suffixes “obs” and “cal” indicate “observed” and “calculated” values, respectively. From the dielectric spectroscopy of BaTiO<sub>3</sub> ceramics with various grain sizes, we discuss the domain effects on dielectric properties of BaTiO<sub>3</sub> ceramics.

### 3. Results and Discussion

The grain size of BaTiO<sub>3</sub> ceramics was controlled by choosing sintering temperature in the conventional sintering method and the two-step sintering method. Table I shows the average grain size and the relative density of BaTiO<sub>3</sub> ceramics prepared in this study. The sintering temperature to obtain dense BaTiO<sub>3</sub> ceramics was lower in the two-step sintering method than the conventional method. It means that the two-step sintering method was effective to prepare the fine-grained BaTiO<sub>3</sub> ceramics. In fact, the grain size was controlled in the range from 1.1 to 5.9  $\mu\text{m}$  in the two-step sintering method while that was controlled in the range from 2.2 to 13  $\mu\text{m}$  in the conventional method. Figure 2 shows the microstructure of the BaTiO<sub>3</sub> ceramics with an average grain size of 1.1  $\mu\text{m}$  prepared by the two-step sintering method.

Figure 3 shows the grain size dependence of the permittivity at 1 kHz. The permittivity of the BaTiO<sub>3</sub> ceramics increased with decreasing the grain size. This result was consistent with those of Arlt *et al.*<sup>1)</sup> and Kinoshita *et al.*<sup>2)</sup> The highest permittivity value of the BaTiO<sub>3</sub> ceramics in this study was 7,700 for a fine grain size of 1.1  $\mu\text{m}$ . It was

Table I. Average grain size and relative density of BaTiO<sub>3</sub> ceramics prepared by (a) conventional sintering method and (b) two-step sintering method.

(a)		
Sintering temperature (°C)	Ave. grain size ( $\mu\text{m}$ )	Relative density (%)
1260	2.2	93.5
1280	2.3	94.7
1300	3.0	96.8
1320	6.3	97.5
1340	6.2	97.4
1360	7.0	96.1
1380	13	97.7
(b)		
Sintering temperature (°C)	Ave. grain size ( $\mu\text{m}$ )	Relative density (%)
1150	1.1	94.5
1170	1.4	95.0
1200	1.6	98.2
1250	3.4	96.9
1270	4.4	94.7
1300	4.6	97.0
1320	5.9	96.0

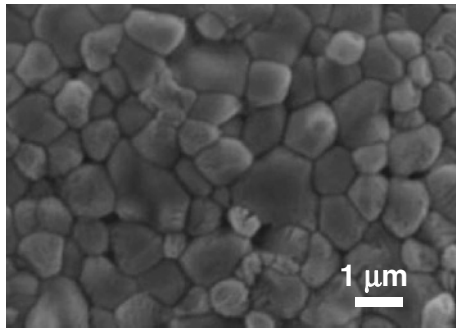
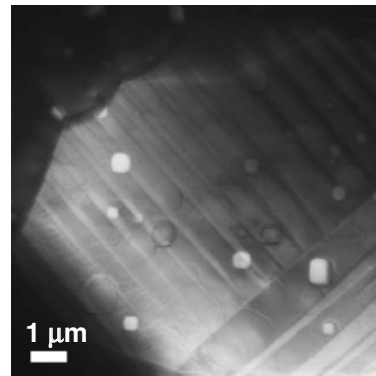
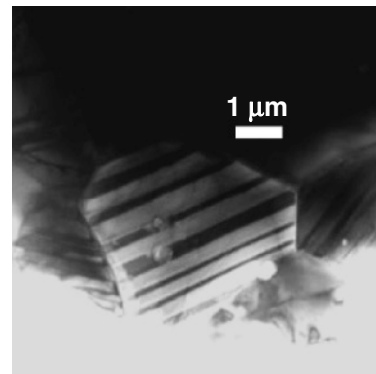


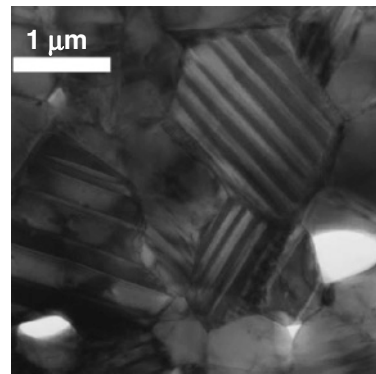
Fig. 2. SEM images of the BaTiO<sub>3</sub> ceramics with average grain size of 1.1 μm prepared by two-step sintering method.



(a)



(b)



(c)

Fig. 4. TEM image of BaTiO<sub>3</sub> ceramics with average grain size of (a) 13, (b) 6.2, and (c) 1.1 μm.

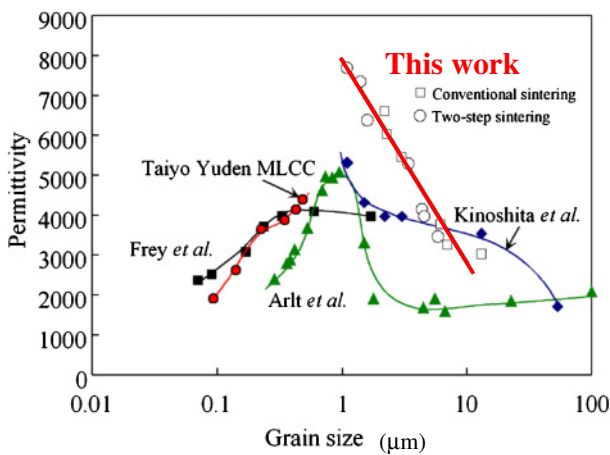


Fig. 3. (Color online) Grain size dependence of the permittivity of BaTiO<sub>3</sub> ceramics.

found that it was possible to obtain a very high permittivity by the grain size control.

The increase of the permittivity was seemed to be caused by the domain contribution as mentioned by Arlt *et al.*<sup>1)</sup> Therefore, the domain configurations of the BaTiO<sub>3</sub> ceramics were observed by TEM as shown in Figs. 4(a)–4(c). The 90° domain configurations in the grains were clearly observed. The TEM observations revealed that the 90° domain size decreased with decreasing the grain size. The relationship between the grain size and the domain size of BaTiO<sub>3</sub> ceramics was consistent with those of previous several reports.<sup>1,12,13)</sup> Figure 5 shows the domain size dependence of the permittivity of the BaTiO<sub>3</sub> ceramics. The permittivity of the BaTiO<sub>3</sub> ceramics increased with decreasing the domain size as expected. The domain size of the BaTiO<sub>3</sub> ceramics which gives the highest permittivity of 7,700 was approximately 100 nm. It is possible to obtain BaTiO<sub>3</sub> ceramics with a very fine domain size around 100 nm using the two-step sintering method. The relationship between the domain size and the permittivity suggested that the high dielectric permittivity was caused by the fine domain configuration.

To understand the domain contribution to the permittivity, ultra wide range dielectric spectra of the BaTiO<sub>3</sub> ceramics were measured. Figures 6(a) and 6(b) show the dielectric spectra of the BaTiO<sub>3</sub> ceramics with a coarse grain (13 μm) and a fine grain (1.4 μm), respectively. In Fig. 6(a), the Debye-type dielectric relaxation observed in the frequency

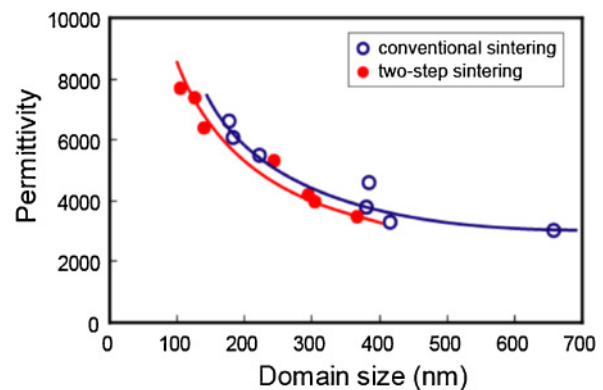


Fig. 5. (Color online) Domain size dependence of permittivity of BaTiO<sub>3</sub> ceramics.

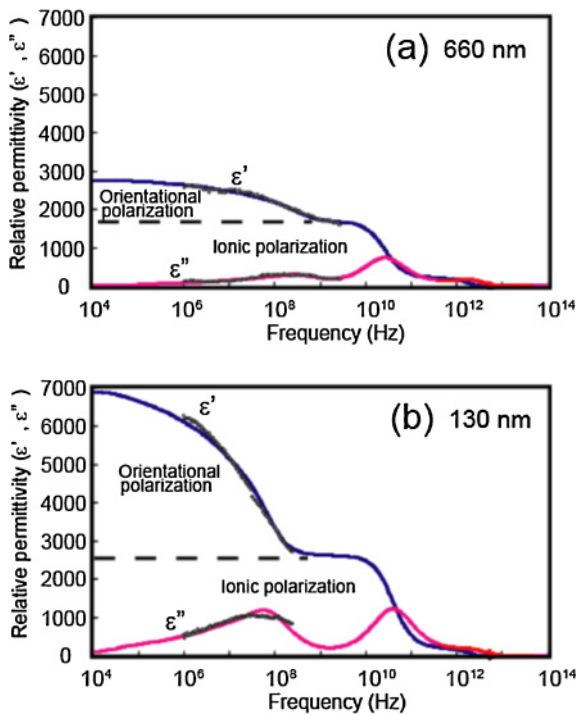


Fig. 6. (Color online) Dielectric spectra of the BaTiO<sub>3</sub> ceramics with (a) coarse grains (13 μm) and (b) fine grains (1.4 μm).

range from kHz to GHz is attributable to the orientational polarization due to the domain-wall vibration by the electric fields as mentioned in a previous report.<sup>14</sup> The permittivity due to the ionic polarization was about 1,600 for the coarse grained BaTiO<sub>3</sub> ceramics, which was consistent with the averaged permittivity of mono-domain BaTiO<sub>3</sub> crystals.<sup>15</sup> The permittivity of BaTiO<sub>3</sub> ceramics was determined by the orientational polarization due to the domain-wall vibration as well as the ionic polarization due to the lattice vibration. Therefore, the domain effect should give the change of the Debye-type dielectric relaxation. For the BaTiO<sub>3</sub> ceramics with a fine grain (1.4 μm) as shown in Fig. 6(b), the orientational polarizability due to the domain-wall vibration was enhanced by the high domain density. It was clarified that the increase of the permittivity is mainly due to the domain contribution. However, it should be noted that the ionic polarizability also increased with decreasing the grain and domain size. The permittivity due to the ionic polarization was about 2,700 for the BaTiO<sub>3</sub> ceramics with grain size of 1.4 μm. To understand this phenomenon, the crystal structures of the BaTiO<sub>3</sub> ceramics were investigated using XRD measurement. Figure 7 shows XRD profiles around the 002 and 200 reflections of the BaTiO<sub>3</sub> ceramics with various domain sizes. The XRD intensity between the 002 and 200 reflections increased with decreasing the domain size, while the peak positions were independent on the domain size. This suggested that the region which has various *c/a* ratios intrinsically existed in the BaTiO<sub>3</sub> grain. The 90° domain structure induces the lattice strain into the BT lattices around the domain wall. 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 gradient lattice strain region should

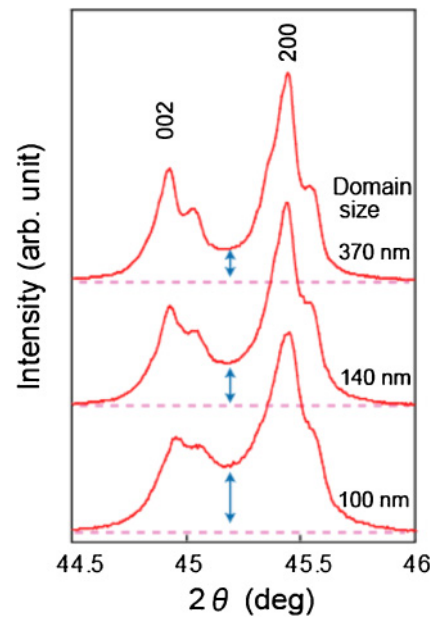


Fig. 7. (Color online) XRD profiles around 002 and 200 reflections of the BaTiO<sub>3</sub> ceramics with various domain sizes.

have a high permittivity due to the ionic polarization, because it has the static phase transitional structure from tetragonal phase to cubic phase. High domain density enhanced the ionic polarizability as well as the orientational polarizability. The increase of permittivity with decreasing grain size is due to the domain size effect.

As shown in Fig. 3, several studies reported that the permittivity decreased with decreasing the grain size when the grain size is below ~1 μm. We infer the domain contribution would decrease if the domain size becomes smaller than a certain value. However, the origin of the domain size dependence of the permittivity for the grain size below submicrometer is not still known. For the future work, it would be necessary to study on the dielectric properties of BaTiO<sub>3</sub> ceramics with grain sizes below submicrometer using the wide range dielectric spectroscopy.

#### 4. Conclusions

In this study, BaTiO<sub>3</sub> ceramics with various grain sizes were prepared by the conventional sintering method and the two-step sintering method. The permittivity of the ceramics increased with decreasing the grain size down to 1.1 μm. The BaTiO<sub>3</sub> ceramics with a grain size of 1.1 μm and a domain size of 100 nm had a high permittivity of 7,700. It is thought that the BaTiO<sub>3</sub> ceramics with the high permittivity should have a high piezoelectric property. The ultra wide range dielectric spectroscopy revealed that the orientational polarizability due to the domain-wall vibration and the ionic polarizability due to the lattice vibration were enhanced by the high domain density. It was clarified that the increase of permittivity with decreasing the grain size was due to the domain size effect. These results suggested that it is possible to control the permittivity of BaTiO<sub>3</sub> ceramics by controlling the domain configuration when the grain size is down to 1.0 μm. We believe the knowledge obtained in this study will be useful for the development of BaTiO<sub>3</sub> based dielectric devices.

## Acknowledgements

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