Size dependence of THz region dielectric properties for barium titanate fine particles

**Satoshi Wada · Hiroaki Yasuno · Takuya Hoshina ·
Hirofumi Kakemoto · Yoshikazu Kameshima ·
Takaaki Tsurumi**

Abstract Barium titanate (BaTiO$_3$) crystallites with various particle sizes from 22 to 500 nm were prepared by the two-step thermal decomposition method of barium titanyl oxalate. Various characterizations revealed that these particles were impurity-free, defect-free, dense BaTiO$_3$ particles. The powder dielectric measurement clarified that the dielectric constant of BaTiO$_3$ particles with a size of around 58 nm exhibited a maximum of over 15,000. To explain this size dependence, the THz region dielectric properties of BaTiO$_3$ fine particles, especially Slater mode frequency, were measured using the far infrared (FIR) reflection method. As the result, the lowest Slater mode frequency was obtained at 58 nm. This tendency was completely consistent with particle size dependence of the dielectric constant.

Keywords THz region dielectric property · Barium titanate · Fine particle · Infrared reflection

1 Introduction

Ferroelectric barium titanate (BaTiO$_3$) fine particles have been used as raw materials for electronic devices such as multilayered ceramic capacitors (MLCC). With the miniaturization of electronic devices, the downsizing of MLCC has been developed. As a result, it is expected that the thickness of dielectric layers in MLCC will become less than 0.5 μm. Consequently, the particle size of the BaTiO$_3$ raw materials will decrease to a few 10 nm. However, in ferroelectric fine particles, it was known that ferroelectricity decreases with decreasing particle and grain sizes, and disappears below certain critical sizes; this is called the "size effect" in ferroelectrics [1–8]. Therefore, the size effect in the BaTiO$_3$ is one of the most important phenomena for the industry and science.

To date, some researchers investigated the size effect of BaTiO$_3$ using particles [3, 4, 6]. Recently, Wada et al. [9] reported a unique particle size dependence that dielectric maximum of 15,000 was observed at 68 nm. This result suggested that the high dielectric constant of 15,000 should be originated from a change of dielectric polarization mechanism, i.e., (1) an appearance of new dipolar polarization at microwave region or (2) a change of the optic phonon behavior at THz region by downsizing of the BaTiO$_3$ particles. Therefore, it is very important to investigate the dielectric properties at THz region [10]. However, there was no report to measure the size dependence of THz region dielectric properties for the fine particles.

In this study, the THz region dielectric properties of the BaTiO$_3$ fine particles were measured by using an infrared reflection method. Moreover, the size dependence of the Slater mode frequency was investigated.

2 Experimental procedure

Barium titanyl oxalate [BaTiO(C$_2$O$_4$)$_2$·4H$_2$O] were prepared by Fuji Titanium Co., Ltd. Its Ba/Ti atomic ratio was 1.000 and the amount of the impurity was less than 0.02mass% [11]. To prepare defect-free, impurity-free BaTiO$_3$ nanoparticles, the two-step thermal decomposition method [12] was used in this study. As a result, BaTiO$_3$ particles with various particle sizes ranging from 22 to 500 nm were prepared.

S. Wada (✉) · H. Yasuno · T. Hoshina · H. Kakemoto ·
Y. Kameshima · T. Tsurumi
Department of Metallurgy and Ceramics Science,
Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro,
Tokyo 152-8552, Japan
e-mail: swada@ceram.titech.ac.jp

The crystal structure was investigated using a powder X-ray diffractometer (XRD) (RINT2000, Rigaku, Cu-kα, 50 kV, 30 mA). The average particle sizes and crystallite sizes were estimated using a transmission electron microscope (TEM) (CM300, Philips, 300 kV) and XRD. The impurity in the products was analyzed using a Fourier transform infrared spectrometer (FT-IR) (SYSTEM 2000 FT-IR, PerkinElmer) and by differential thermal analysis with thermogravimetry (TG-DTA) (TG-DTA2000, Mac Science). The absolute density of the BaTiO$_3$ powders was measured using a pycnometer, and the relative density was calculated using a theoretical density estimated from lattice parameters by the XRD measurement. The Ba/Ti atomic ratios for the BaTiO$_3$ particles were determined by using the X-ray fluorescence analysis. The dielectric constants for these BaTiO$_3$ particles were measured by using the powder dielectric measurement method [13].

For the far infrared (FIR) reflection measurement, 3D colloidal sphere array (colloidal crystal) was prepared using these BaTiO$_3$ fine particles from 22 to 500 nm. A dense BaTiO$_3$ colloidal crystal was prepared from a BaTiO$_3$ slurry [10]. The FIR reflection spectra from 5 to 1,200 cm^{-1} were measured at 25 °C by using two FT-IR spectrometers, i.e., FARIS-1 (JASCO Co., 5~700 cm^{-1}) and FTIR-8600PC (Shimadzu, 400–1,200 cm^{-1}). Especially, the FIR reflection measurement using FARIS-1 was performed in vacuum to neglect the absorption peaks of H$_2$O in air. A special attachment for a reflection measurement was used, and an incident angle and a reflection angle to the sample surface were fixed at 11°. Aluminum-evaporated film on the glass was used as a reference. These two spectra were connected at 650 cm^{-1}.

3 Results and discussion

3.1 Preparation and characterization

BaTiO$_3$ fine particles with various particle sizes from 22 to 500 nm were prepared by the two-step thermal decompo-
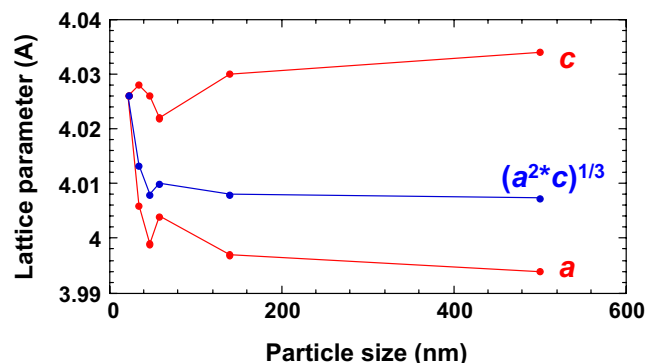
sition method. The crystal structure of these BaTiO$_3$ particles over 30 nm was assigned to tetragonal *4mm* by XRD measurement while that of the BaTiO$_3$ particles below 30 nm was assigned to cubic *m-3m*. On the other hand, Raman scattering measurement revealed that all of BaTiO$_3$ particles prepared in this study were assigned to tetragonal *4mm* symmetry. Investigation of impurity in these particles using both TG-DTA and FT-IR measurements revealed that no impurity was detected in the BaTiO$_3$ lattice while hydroxyl and carbonate groups were detected only on the surface. Moreover, their relative densities were always over 97% despite particle sizes. Therefore, in this study, the impurity-free, defect-free, dense BaTiO$_3$ fine particles from 22 to 500 nm were successfully prepared.

3.2 Size dependence of crystal structure

The crystal structures of these BaTiO$_3$ fine particles were refined using Rietveld method. Based on our results, it was clarified that all of the BaTiO$_3$ fine particles were composed of two parts, i.e., (1) surface cubic layer and (2) bulk tetragonal layer. The structure refinement revealed that the thickness of the BaTiO$_3$ fine particles prepared in this study was around 1–2 nm. This thickness was much smaller than that of commercial BaTiO$_3$ fine particles reported by Aoyagi et al. [14]. The size dependence of lattice parameters and tetragonality (c/a ratio) in the bulk layer were also calculated as shown in Figs. 1 and 2. As mentioned before, the critical size at the size-induced phase transition was around 30 nm. However, despite the tetragonal *4mm* phase, the discontinuous change for the lattice parameter and tetragonality was clearly observed at 58 nm. At present, it is difficult to explain this origin, but we believe that this discontinuous change should be related to the existence of the surface cubic layer.

3.3 Size dependence of dielectric property

The dielectric constants of these particles were measured using suspensions by the powder dielectric measurement
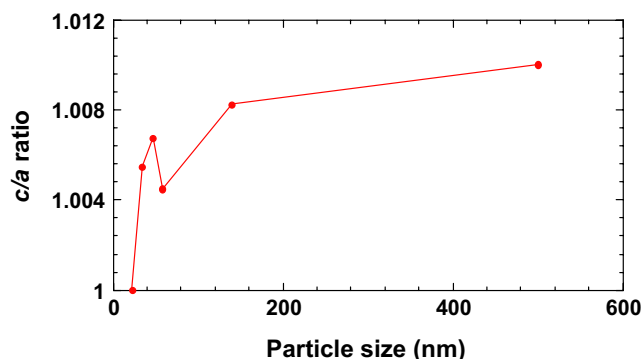

Fig. 1 Particle size dependence of lattice parameters and cell volume for the bulk tetragonal layer of the BaTiO$_3$ fine particles

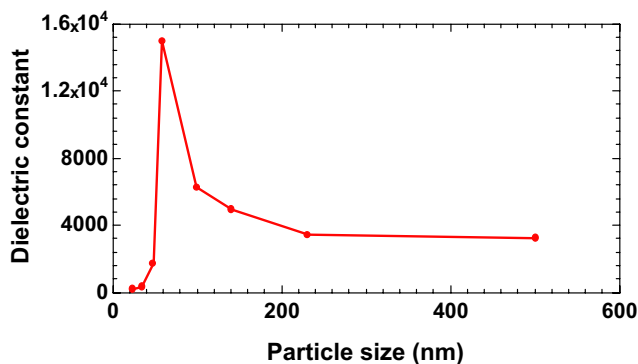Fig. 2 Particle size dependence of tetragonality for the bulk tetragonal layer of the BaTiO$_3$ fine particles

Fig. 3 Particle size dependence of dielectric constant for the BaTiO$_3$ fine particles [9]

Fig. 5 Particle size dependence of normalized slope S of FIR reflection spectra below 100 cm^{-1} for the BaTiO$_3$ fine particles

method [9]. Figure 3 shows particle size dependence of dielectric constants measured at 20 °C and 20 MHz. With decreasing particle size, the dielectric constant was almost constant at around 3,000 down to 200 nm. Below 200 nm, the dielectric constant increased with decreasing particle size, and at 58 nm, the dielectric maximum around 15,000 was clearly observed. This result was almost consistent with a previous report [9]. Below 58 nm, the dielectric constant drastically decreased with decreasing particle size. The results similar to this unique size dependence were reported for several BaTiO$_3$ ceramics [2, 8] and particles [9, 15]. Therefore, it is important to consider this origin of dielectric maximum at a certain size. In general, for BaTiO$_3$, it was known that the high dielectric constant over 3,000 can be originated from the phonon behavior, i.e., Slater mode frequency with the lowest frequency [16]. In this study, the dielectric maximum around 15,000 was observed at 58 nm. To explain this high dielectric constant, there are two hypotheses, i.e., (1) an appearance of new dipolar polarization at microwave region and (2) a softening of the optic Slater mode frequency. To confirm the origin, the THz region dielectric properties must be measured for these BaTiO$_3$ fine particles.
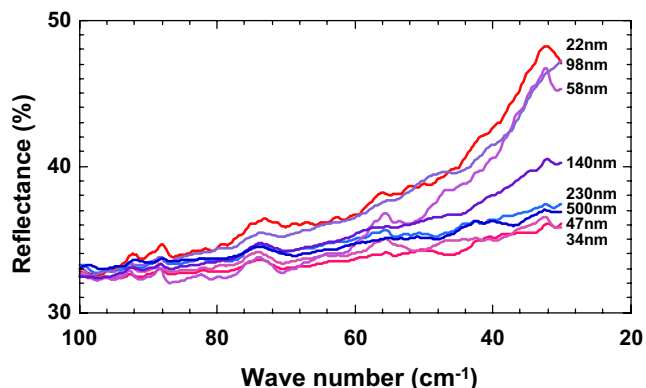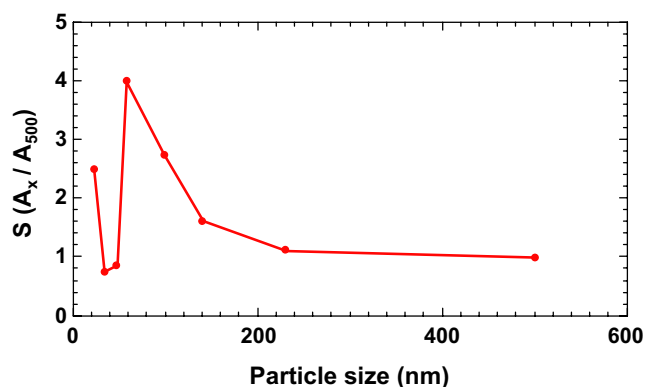
3.4 Size dependence of phonon behavior

To explain this size dependence, the THz region dielectric properties of BaTiO$_3$ fine particles were measured using the FIR reflection method with the dense BaTiO$_3$ colloidal crystals. As a result, the high intensity reflection spectra below 100 cm^{-1} for the BaTiO$_3$ fine particles were successfully obtained for the first time. As well known, the Slater mode was an overdamped phonon mode, and the slope of the curve below 100 cm^{-1} increased with decreasing Slater transverse optic (TO) mode frequency [17, 18]. Figure 4 shows the particle size dependence of FIR spectra below 100 cm^{-1} measured at 25 °C. These slope was fitted using a second-order equation of $y = A * x^2 + B * x + C$ (A, B, C : constant), and we defined the slope of the curve using A value. Finally, all A values were divided by the A_{500} value obtained for the BaTiO$_3$ fine particles with 500 nm, and were normalized as $S = A/A_{500}$. Figure 5 shows the size dependence of the normalized slope S. Moreover, it should be noted that the reciprocal of the S value can be proportional to the Slater TO mode frequency. [17, 18] However, in this study, owing to the light scattering
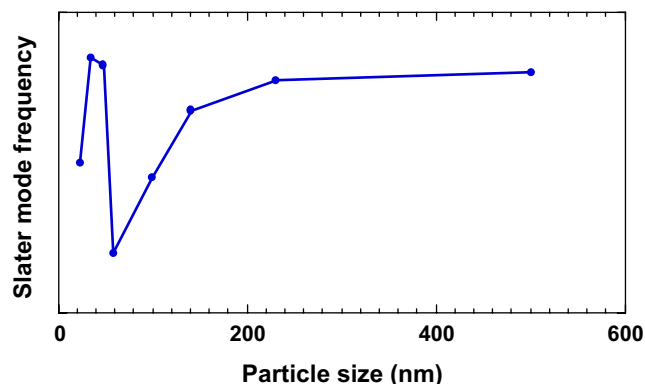

Fig. 4 Particle size dependence of FIR reflection spectra below 100 cm^{-1} for the BaTiO$_3$ fine particles

Fig. 6 Particle size dependence of relative values of the Slater TO mode frequency for the BaTiO$_3$ fine particles

reflection, it was difficult to determine the absolute value for the Slater TO mode frequency. Thus, Fig. 6 shows the size dependence of the relative value obtained from Fig. 5 for the Slater TO mode frequency. Despite the tetragonal *4mm* region over 30 nm, the minimum value for the Slater TO mode frequency was clearly observed at 58 nm, which revealed that the softening of the Slater TO mode occurred for the $BaTiO_3$ fine particles prepared in this study. Therefore, this result suggested that the high dielectric constant around 15,000 at 58 nm can be originated from the softening of the Slater TO mode.

4 Conclusions

The impurity-free, defect-free, dense $BaTiO_3$ fine particles were successfully prepared using the two-step thermal decomposition method. It was confirmed that these particles intrinsically had the surface cubic layer with thicknesses around 1–2 nm. It is possible that this thin surface layer affected the whole crystal structure and phonon behavior of the $BaTiO_3$ fine particles. As a result, the dielectric maximum can be observed at 58 nm. This is just a hypothesis, and much precise study must be required to explain this mechanism.

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