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Size and Temperature Induced Phase Transition Behaviors of Barium Titanate Nanoparticles

Takuya Hoshina[1], Hirofumi Kakemoto[1], Takaaki Tsurumi[1], Satoshi Wada[1] and Masatomo Yashima[2]

[1]Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan
Fax: 81-3-5734-2514, e-mail: hoshina@cim.ceram.titech.ac.jp

[2]Department of Materials Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan
Fax: 81-045-924-5630, e-mail: yashima@materia.titech.ac.jp

High density, almost impurity-free and defect-free barium titanate ($BaTiO_3$) fine particles with various sizes from 20 to 1000 nm were prepared by 2-steps thermal decomposition of barium titanyl oxalate and post-heating treatment. In order to clarify the size effect on $BaTiO_3$ particles, the crystal structures of these particles were investigated as a function of the size using synchrotron radiation XRD measurement and Raman scattering measurement. As a result, the ferroelectric (tetragonal–cubic) phase transition observed around 30 nm. Moreover, the temperature dependences of the crystal structures for these particles were investigated. As a result, the temperature of tetragonal–cubic phase transition was constant despite particle sizes, but the volume change temperature shifted to low temperature with decreasing particle sizes. The $BaTiO_3$ nanoparticles have a complicated phase transition mechanism.

Key words: Barium titanate, Size effect, Fine particles, Synchrotron radiation XRD, Raman scattering

1. INTRODUCTION

Ferroelectric $BaTiO_3$ 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. However, in ferroelectrics, it was known that ferroelectricity decreases with decreasing particle and grain sizes, and disappears below certain critical sizes [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.

Recently, the size dependence of dielectric properties for the $BaTiO_3$ particles was reported [5-6]. In this report, high density, almost impurity-free and defect-free $BaTiO_3$ fine particles with various sizes from 20 to 1000 nm were prepared by 2-step thermal decomposition method and post-heating treatment, and the dielectric constants of the particles were measured by powder dielectric measurement method. As the result, the dielectric constant of $BaTiO_3$ particles with a size around 140 nm exhibited a dielectric maximum of around 5000.

In this study, to clarify an origin for the size dependence of the dielectric constants for the $BaTiO_3$ particles, the crystal structures of the $BaTiO_3$ particles were investigated as a function of the size using synchrotron radiation XRD measurement and Raman scattering measurement. Moreover, the temperature dependences of the crystal structures for the particles were investigated.

2. EXPERIMENTAL

2.1 Sample preparation

The $BaTiO_3$ particles with various sizes were prepared by 2-step thermal decomposition of barium titanyl oxalate ($BaTiO(C_2O_4)_2\ 4H_2O$) and post-heating treatment [5-6]. The barium titanyl oxalate powder was prepared by Fuji Titanium Co., Ltd. [7] Its Ba/Ti atomic ratio was 1.00 and the amount of the impurity was less than 0.02 %. 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, these particles were annealed at various temperatures from 700 °C to 1100 °C for 3 hours in air, to control particle sizes of $BaTiO_3$. The average particle sizes were estimated using transmission electron microscope (TEM) (JEM-2010F, JEOL, Inc.). The impurities in the products were analyzed using Fourier transform infrared spectrometer (FT-IR) (SYSTEM 2000 FT-IR, Perkin Elmer, Inc.) and differential thermal analysis with thermogravimetry (TG-DTA) (TG-DTA2000, Mac Science).

2.2 Crystal structure analysis by synchrotron radiation XRD

High intensity synchrotron radiation XRD data was collected using the large Debye-Sherrer camera installed at beam line BL02B2 in the synchrotron radiation facility, SPring-8. High energy X-ray with wavelength of 0.50 Å was used as incident X-ray. The $BaTiO_3$ particles were sealed into a glass capillary of 0.2 mm inside diameter. The diffraction pattern was recorded on the imaging plate of the camera with transmission

geometry. Sample temperature was controlled by N_2 gas flow system. The observed diffraction data was analyzed by Rietveld method. In this study, a single phase model was applied to refine the crystal structure, *i.e.*, it was assumed that whole particle was composed of a tetragonal single phase (P*4mm*) or a cubic single phase (P*m-3m*).

2.3 Phonon analysis by Raman scattering measurement

Raman scattering measurement was performed using laser Raman spectrometer, NRS-2100 (JASCO, Inc.). The Ar laser with wavelength of 514.5 nm was used as the excitation laser. The laser power was about 10 mW/cm^2. The measurement range was 100 to 1000 cm^{-1}. Sample temperature was controlled by a thermostat hot stage (Linkam LK600PM, Linkam Scientific Instruments, Ltd.).

3. RESULTS AND DISCUSSION

3.1 Characterization of prepared $BaTiO_3$ particles

It is considered that the crystal structure and the dielectric property of the particles also depend on many factors, *e.g.*, density, impurities and defects. Therefore, in order to investigate the intrinsic size effect of the $BaTiO_3$ particles, high density, almost impurity-free and defect-free $BaTiO_3$ particles with various sizes are required.

In this study, we obtained $BaTiO_3$ particles with various sizes from 20 nm to 1000 nm by 2-step thermal decomposition of $BaTiO(C_2O_4)_2$ $4H_2O$ and post-heating treatment. 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, the Ba/Ti atomic ratios of these particles were 1.00 and the relative densities of these particles were over 99 %. The details of characterization results were described elsewhere [5-6].

3.2 Size induced phase transition behavior of $BaTiO_3$ particles

It is known that it is difficult to assign the crystal symmetry of $BaTiO_3$ nanoparticles into either cubic or tetragonal symmetry using conventional XRD equipment owing to line broadening and low XRD intensity. To solve the problem, accurate diffraction patterns for the $BaTiO_3$ nanoparticles were collected using synchrotron radiation high-energy X-ray. The crystal symmetry of the nanoparticles was determined by comparing the FWHM of (002) refraction with that of (111) refraction at 24 °C and 160 °C [6]. As a result, the crystal symmetries of the $BaTiO_3$ particles with 20 nm and 30 nm were assigned to cubic P*m-3m* while these of the particles over 40 nm were assigned to tetragonal P*4mm* at 24 °C. This result revealed that the critical size of $BaTiO_3$ particles, which is the size of ferroelectric phase transition from tetragonal to cubic at room temperature, exists around 30 nm. Figure 1 shows the size dependence of lattice parameters estimated by Rietveld analysis of synchrotron radiation XRD data. With decreasing particle sizes, *c*-axis gradually decreased while *a*-axis gradually increased

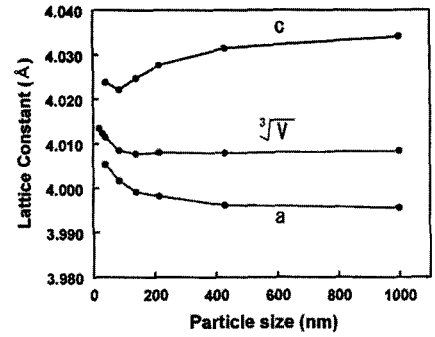

Fig. 1. Size dependence of lattice parameters for $BaTiO_3$ particles

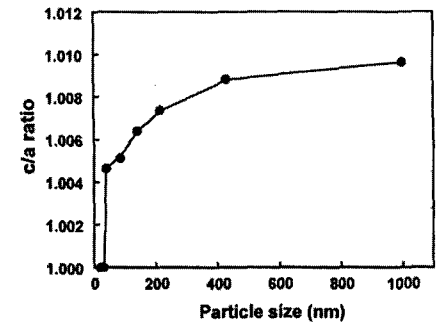

Fig. 2. Size dependence of tetragonality for $BaTiO_3$ particles

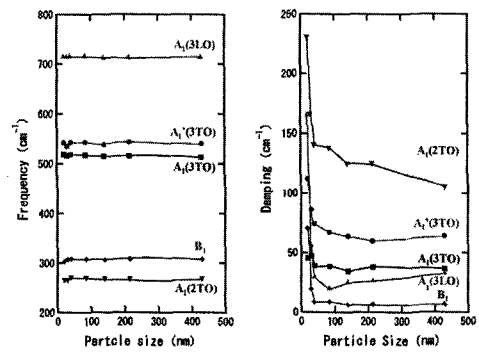

Fig. 3. Size dependence of optical phonon resonance frequencies and damping factors for $BaTiO_3$ particles

over 85 nm. Moreover, with decreasing particle sizes, the cell volume increased below 140 nm. Figure 2 shows the size dependence of tetragonality (*c*/*a* ratio) for the $BaTiO_3$ particles. With decreasing particle sizes, the *c*/*a* ratio gradually decreased over 40 nm, and drastically decreased down to 1.00 around 30 nm.

XRD measurement can clarify the average and static symmetry while Raman scattering measurement can clarify the local and dynamic symmetry. From the Raman scattering measurement in this study, the local and dynamic symmetry of $BaTiO_3$ particles with the sizes from 20 to 1000 nm was assigned to tetragonal P*4mm*. From the measurement in the range from 100 to 1000 cm^{-1}, the three kinds of optical phonon modes of P*4mm* $BaTiO_3$, *i.e.*, "Last" mode (A_1(2TO), A_1(2LO)), "O_4 torsional" mode (B_1) and "O_6 displacive" mode

(A_1(3TO), A_1 (3TO), A_1(3LO)) was observed. The soft mode ("Slater" mode) wasn't observed. The Raman spectrum was fitted using Gaussian type function, and then the resonance frequency and the damping factor for the each mode except the soft mode were determined by the peak position and the FWHM of Raman peak, respectively. Figure 3 shows the size dependence of the resonance frequency and the damping factor for the $BaTiO_3$ particles. Despite particle sizes, the resonance frequency of each optical mode except the soft mode was almost constant. On the other hand, the damping factor of each optical mode increased with decreasing particle sizes. Especially, the damping factors significantly increased around 30 nm.

3.3 Temperature induced phase transition behavior of $BaTiO_3$ nanoparticles

Temperature dependences of the crystal structure for the $BaTiO_3$ particles with 430 nm, 140 nm, 40 nm and 30 nm were investigated. Figure 4 shows the Temperature dependence of lattice parameters for the $BaTiO_3$ particles with 430 nm, 140 nm and 40 nm. For the $BaTiO_3$ particles with 430 nm, the temperature induced phase transition behavior was similar to that of the $BaTiO_3$ single crystal. The temperature of tetragonal (T)–cubic (C) phase transition was around 135 °C. At this temperature, a volume change was observed. For the particles with 140 nm, the T-C phase transition temperature (I) was around 135 °C, but the volume change temperature (II) was around 110 °C. Moreover, for the particles with 40 nm, the volume change temperature (II) was around 70 °C while the T-C phase transition temperature (I) was around 135 °C. For the particles with 30 nm, no phase transition was observed. Figure 5 shows the temperature dependence of tetragonality for the $BaTiO_3$ particles with 430 nm, 140 nm and 40 nm. To date, many researchers reported the decrease of Curie temperature (T-C phase transition temperature) with decreasing sizes for ferroelectrics particles [3-4], but it wasn't observed in this study. However, the previous reports has some problem, *i.e.*, the amount of impurities and defects changed with sizes of $BaTiO_3$ particles, and it was difficult to assign the crystal symmetry of $BaTiO_3$ with low *c/a* ratio using conventional XRD measurement. It is considered that the intrinsic size effect could be investigated in this study by the synchrotron radiation XRD measurement of almost impurity-free and defect-free $BaTiO_3$ particles. The T-C phase transition temperature (I) was constant despite particle sizes, but the volume change temperature (II) shifted to low temperature with decreasing particle sizes.

On the other hand, the temperature dependences of phonon modes were also investigated. Figure 6 shows the temperature dependence of the resonance frequency and the damping factor for the $BaTiO_3$ particles with 430 nm, 140 nm, 40 nm and 30 nm. For all the particles, the damping factor of each optical mode increased with increasing temperature while the resonance frequency of each optical mode except the soft mode was almost constant despite temperature. Figure 7 shows the damping factor of A_1(2TO) mode for the $BaTiO_3$ particles with 430 nm, 140 nm, 40 nm and 30 nm. This figure revealed that the damping factors significantly increased close to the line of the particles with 30 nm around the temperature corresponding to the volume change temperature (II). Thus, it became clear that the $BaTiO_3$ nanoparticles have a complicated phase transition behavior by synchrotron radiation XRD and Raman scattering measurement.

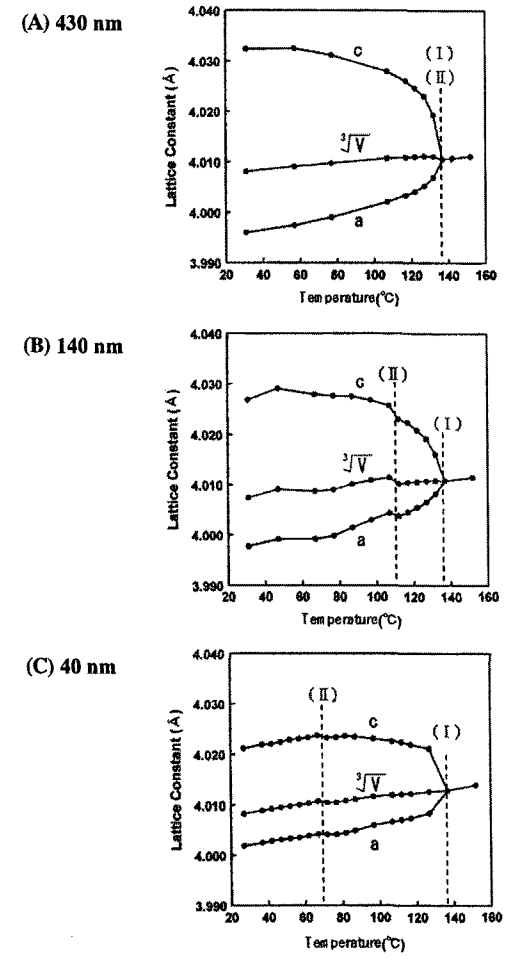

Fig. 4. Temperature dependence of lattice parameters for $BaTiO_3$ particles: (A) 430 nm, (B) 140 nm and (C) 40 nm

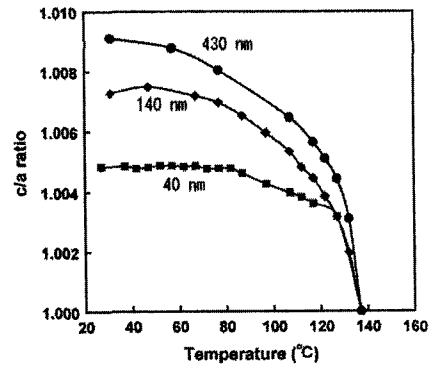

Fig. 5. Temperature dependence of tetragonalities for $BaTiO_3$ particles with 430 nm, 140 nm, 40 nm and 30 nm

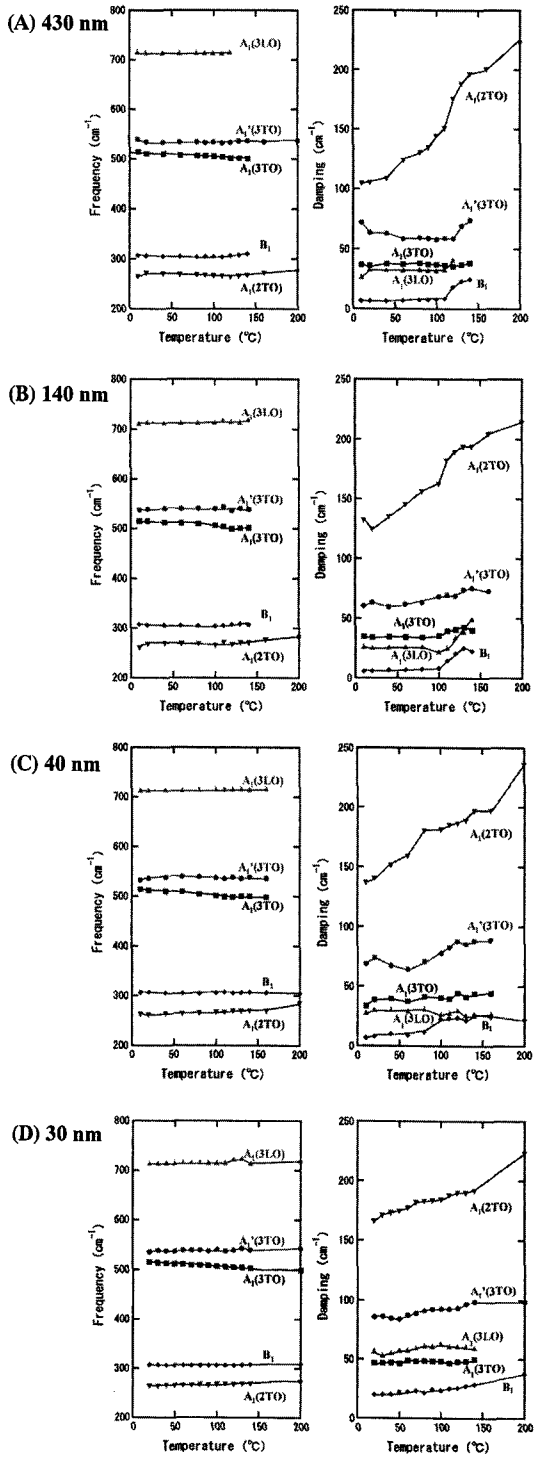

Fig. 6. Temperature dependence of optical phonon resonance frequencies and damping factors for $BaTiO_3$ particles: (A) 430 nm, (B) 140 nm, (C) 40 nm and (D) 30 nm

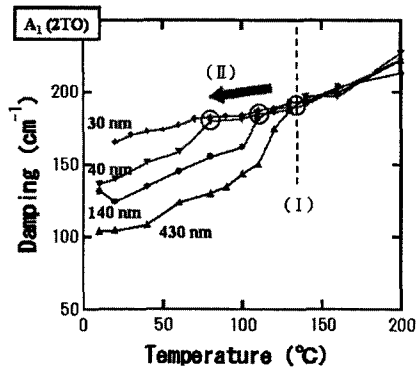

Fig. 7. Temperature dependence of A_1(2TO) mode damping factors for $BaTiO_3$ particles with 430 nm, 140 nm, 40 nm and 30 nm

4. CONCLUSIONS

In this study, high density, almost impurity-free and defect-free $BaTiO_3$ fine particles with various sizes from 20 to 1000 nm were prepared by 2-steps thermal decomposition of barium titanyl oxalate and post-heating treatment. In order to clarify the size effect on $BaTiO_3$ particles, the crystal structures of these particles were investigated as a function of the size using synchrotron radiation XRD measurement and Raman scattering measurement. As a result, the ferroelectric phase transition observed around 30 nm. Moreover, the temperature induced phase transition for the $BaTiO_3$ nanoparticles were investigated. As a result, the temperature of tetragonal–cubic phase transition was constant despite particle sizes, but the volume change temperature shifted to low temperature with decreasing particle sizes. The $BaTiO_3$ nanoparticles have a complicated phase transition mechanism.

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