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SIZE EFFECT ON CRYSTAL STRUCTURE AND CHEMICAL BONDING NATURE IN $BaTiO_3$ NANOPOWDER

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The size effect on the crystal structure including the chemical bonding nature has been investigated for several kinds of $BaTiO_3$ nanopowder with the particle sizes down to 50 nm in diameter, by means of powder diffraction using high-energy synchrotron radiation. The Rietveld refinement reveals that the $BaTiO_3$ nanopowder consists of tetragonal and cubic structure components at 300 K. The feature of coexistence can be illustrated by the core/shell model for the particle, in which the shell with a cubic structure covers the core with a tetragonal structure. The thickness of the cubic shell is almost constant irrespective of the particle sizes, and is estimated as approximately 8 nm. Hence, the critical particle-size, where the entire particle is covered with the cubic shell, is suggested as 16 nm. The charge density distributions of the $BaTiO_3$ nanopowder in the cubic phase at 410 K are revealed by the maximum entropy method. Changes in the bonding electron density and the ionic valence expected are not observed clearly even in the 50 nm crystal compared with the bulk crystal.

Keywords: *$BaTiO_3$, charge density, crystal structure, maximum entropy method, powder diffraction, Rietveld method, size effect, synchrotron radiation*

Introduction

Barium titanate, $BaTiO_3$, is a perovskite-type oxide well known to show ferroelectricity with a tetragonal structure at room temperature. For the bulk crystal, the cubic-tetragonal phase transition occurs at 403 K. However, with nanosizing the $BaTiO_3$ crystal at room temperature, the dielectric constant significantly decreases and finally the ferroelectricity vanishes [1–3]. The critical size reported was approximately 100 nm [4–6], where the $BaTiO_3$ nanocrystal was considered to exhibit a cubic structure at room temperature. Such size effect is also observable in other measurements [7]. We have been also studying the size effect by measuring the heat capacity [8] and crystal structure [9].

As a structure model of the $BaTiO_3$ nanoparticle to give a plausible explanation for the size effect, so-called core/shell model is proposed to show that the surface layer with a cubic structure covers the particle core with a tetragonal structure [10]. In the previous structural study, we have investigated the validity of the core/shell model experimentally for several kinds of $BaTiO_3$ nanopowder with the particle sizes down to 100 nm in diameter, near the critical size, by using the high resolution of synchrotron radiation (SR) powder diffraction [9]. Essentially all kinds of $BaTiO_3$ nanopowder consisted of tetragonal and cubic structure components coexisting at 300 K. Based on the core/shell model, the obtained thickness of the cubic shell was almost constant irrespective of the particle sizes. It was approximately 8 nm, so that we proposed that the critical size must be approximately 16 nm.

In the present study, we extend the sample varieties toward the ultrafine nanoparticle using the $BaTiO_3$ nanopowder with the particle size of 50 nm. The core/shell model is examined for the new sample by analyzing the high-energy SR powder diffraction data by the Rietveld method. Furthermore, we investigate the charge density distributions in $BaTiO_3$ nanopowder with sizes of 50 and 700 nm by the maximum entropy method (MEM) [11] to discuss the size effect from a viewpoint of chemical bonding nature. The MEM is a powerful tool to reveal the bonding nature in the charge density distributions. We have already reported the accurate charge density distributions of $BaTiO_3$ powders with the particle sizes over 1 μm using the same method [12].

Experiment

Powder sample of $BaTiO_3$ with average particle size of 50 nm in diameter produced by the radio frequency

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plasma method was obtained from Nisshin Flour Milling Co. Ltd. The particle sizes were confirmed by TEM observation and surface area measurement. The powder diffraction experiments were carried out on the Large Debye-Scherrer Camera installed at BL02B2 in the SR facility, SPring-8 [13]. High-energy X-rays with wavelength λ=0.58 Å were used as incident X-rays. Diffraction patterns from the sample sealed into a glass capillary of 0.1 mm inside diameter were recorded on the imaging plate of the camera with transmission geometry. Sample temperatures were controlled by the N_2 gas flow system at 300 and 410 K, near room temperature and above the phase transition temperature, respectively. These experimental combinations enabled us to obtain accurate powder diffraction data with a high angular resolution. The previous experimental procedure was followed in the present study, and the experimental detail is shown in the previous paper [9].

Results and discussion

Observed diffraction patterns are analyzed by the Rietveld method for the data up to 75° in 2θ, which corresponds to 0.48 Å in *d* spacing. The 50 nm sample data at 300 K are successfully refined for the composite crystal-structure model of the tetragonal and cubic structures of $BaTiO_3$. The fitting results of the (002) and (200) reflections are shown in Fig. 1 with the result of 700 nm sample data previously obtained [9]. The peak of 50 nm sample looks like a single peak originated from a cubic structure. However, the profile is asymmetry and the composite structure model gave the best fitting result. The crystal structure observed in the 50 nm sample is properly regarded as a pseudo-cubic structure, which exhibits lower ferroelectricity due to the reduction of long-range dipole-dipole interactions.

The volume ratio of the cubic component to the entire sample, V_{cubic}/V_{total}, and the tetragonality of the tetragonal component, c_t/a_t, where a_t and c_t are lattice constants of the tetragonal component, are calculated for the 50 nm sample from the refined lattice constants in the Rietveld analysis. Both data are added to the previous data [9], and they are all summarized in Figs 2 and 3, respectively. Adopting the core/shell model, the volume ratio, V_{cubic}/V_{total}, is expressed by the equation, $V_{cubic}/V_{total} = [(D/2)^3-(D/2-t)^3]/(D/2)^3$, where D is the particle diameter and t the thickness of surface layer with a cubic structure. As shown in Fig. 2, the data point of 50 nm sample is also well fitted by the equation curve with t=8 nm. We speculate that the volume ratio is still increasing with decreasing the particle size below 50 nm, and reaches the value, V_{cubic}/V_{total}=1.0, at the critical size, D=16 nm, where the surface layer with a cubic structure occupies the whole particle. The tetragonality of the tetragonal component is decreasing with decreasing the particle size as shown in Fig. 3. It also seems to approach the value, c_t/a_t=1.000, at the critical size of D=16 nm.

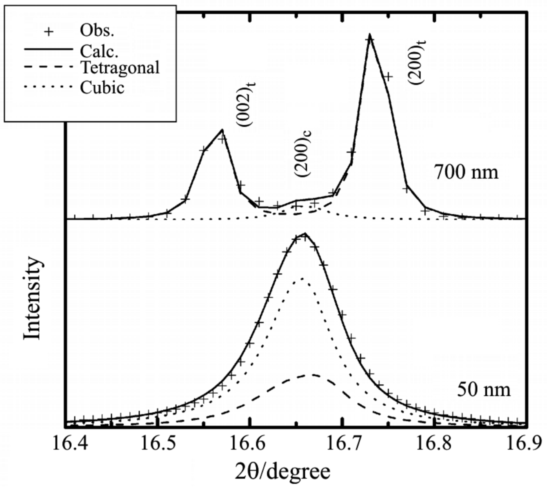

Fig. 1 Enlarged Rietveld profile fitting patterns of (002) and (200) reflections at 300 K of $BaTiO_3$ nanopowder with the sizes of 700 and 50 nm. The composite structure model of the tetragonal and cubic structures gives the best fit. The reliability factors, R_{wp}=3.97 and 5.06% for the 700 and 50 nm sample data, respectively

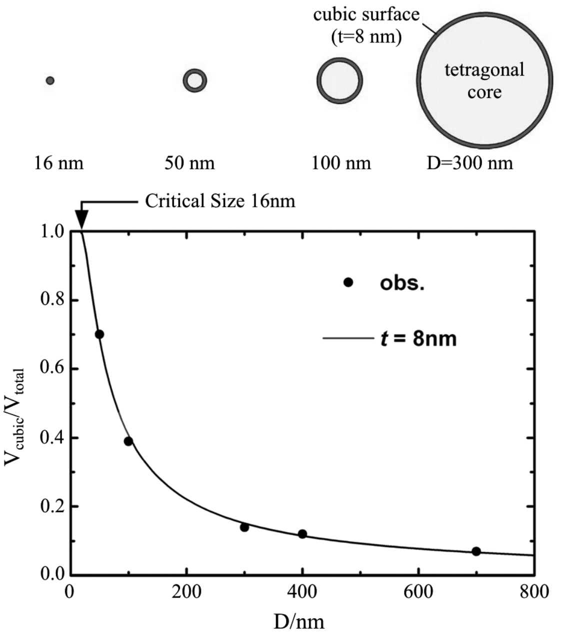

Fig. 2 Size effect on the volume ratio of the cubic component to the entire sample of $BaTiO_3$ nanopowders at 300 K, V_{cubic}/V_{total}. The solid curve is drawn by the equation, $V_{cubic}/V_{total}= [(D/2)^3-(D/2-t)^3]/(D/2)^3$, based on the core/shell model illustrated for the $BaTiO_3$ nanoparticle, where D is the particle diameter and t=8 (nm) the constant thickness of surface layer with a cubic structure

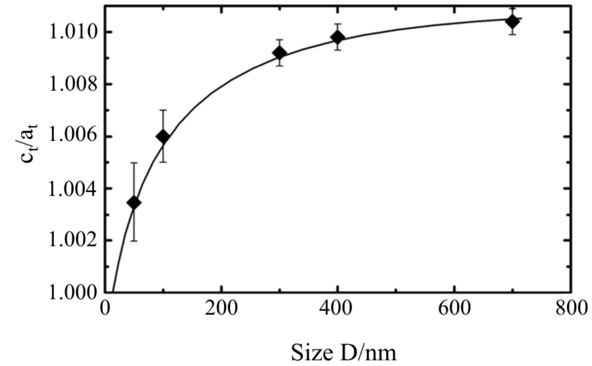

Fig. 3 Tetragonality, c_t/a_t, of the tetragonal component in $BaTiO_3$ nanopowders at 300 K as a function of the particle size in diameter D, where a_t and c_t are lattice constants of the tetragonal component

The diffraction patterns of the 50 and 700 nm samples at 410 K, above the phase transition temperature of $BaTiO_3$ bulk crystals, are also analyzed by the Rietveld method. The crystal structure model consisting of only a cubic component gave the best fit. The lattice constants obtained from 50 and 700 nm data are 4.014(1) and 4.010(1) Å, respectively. It has been found that the crystal slightly expands in the smaller 50 nm particle. At this stage, we considered that the unit-cell expansion implies the weakening of covalency on the Ti–O bond, which must be the essential factor related to the ferroelectric instability in $BaTiO_3$. In order to investigate the size effect from such a viewpoint of chemical bonding nature, the charge density distributions in the cubic phase at 410 K are investigated for the 50 and 700 nm sample data by the MEM/Rietveld analysis. The 91 independent observed structure-factors up to 75º in 2θ were derived by the Rietveld analyses for both data, and used in the MEM analyses. The reliability factors for the Rietveld analysis were R_I=2.42% and R_{wp}=5.34% for the 50 nm sample data. For the 700 nm sample data, R_I=2.99% and R_{wp}=5.45%. The MEM analyses were carried out with the unit cell divided into 80×80×80 pixels. The reliable factors for the MEM charge densities of the 50 and 700 nm samples based on the structure factors, R_{MEM}, were 0.72 and 1.26%, respectively.

The MEM charge density analyses reveal that the Ba atom is ionic while a clear covalent bond is formed on the Ti–O bond in both samples. The minimum charge density, ρ_{min}, on the Ba–O bond obtained in each sample is 0.2 e/Å^3 the same level as the background level, which gives evidence on the ionic nature of the Ba atom. The ρ_{min} on the Ti–O bond is 0.7 and 0.6 e/Å^3 in the 50 and 700 nm sample, respectively. The density is almost the same level, and no clear change in covalency on the Ti–O bond can be observed in the 50 nm sample, although appearance of an ionic nature on the Ti–O bond was expected in the 50 nm sample as the crystal expanded in the small dimensions. The ionic valence of each constituted atom is calculated by counting the numbers of electrons around the atoms adopting the Mulliken scheme as follows: $Ba^{+1.4(3)}$, $Ti^{+2.4(3)}$ and $O^{-1.2(3)}$ for the 50 nm sample and $Ba^{+1.7(3)}$, $Ti^{+2.4(3)}$ and $O^{-1.3(3)}$ for the 700 nm sample. Almost no difference is also found within errors. Furthermore, both charge density distributions of the nanopowder are very similar to the previously reported charge density distributions of the ordinary powder sample having the bonding nature of the bulk crystal [12], as ρ_{min} on the Ba–O and Ti–O is 0.2 and 0.6 e/Å^3, respectively, and the ionic valence, $Ba^{+1.8(3)}$, $Ti^{+2.1(3)}$ and $O^{-1.3(3)}$. The bonding nature may be changed in much smaller nanoparticle.

Conclusions

The validity of the core/shell model is verified experimentally as a plausible model for the size effect on $BaTiO_3$ using the nanopowder with sizes down to 50 nm by SR powder diffraction technique. The size effect on the bonding nature is not clearly observed in this study. It is considered that the size effect on $BaTiO_3$ nanopowders is not mainly caused by the change in bonding nature, at least down to the size of 50 nm. The other factors such as the surface with a cubic structure and the reduction of long-range dipole-dipole interactions in the small dimensions are clue to the size effect on $BaTiO_3$ nanopowders.

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