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STRUCTURAL STUDY OF PEROVSKITE-TYPE FINE PARTICLES BY SYNCHROTRON RADIATION POWDER DIFFRACTION

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Abstract

The crystal structures of $BaTiO_3$ and $PbTiO_3$ fine particles have been investigated by powder diffraction using synchrotron radiation high energy X-rays. It is revealed that a $BaTiO_3$ fine particle essentially consists of tetragonal and cubic structure components at 300 K, whereas a $PbTiO_3$ fine particle consists of a tetragonal structure. Adopting a structure model for the $BaTiO_3$ particle that a cubic shell covers a tetragonal core, the thickness of cubic $BaTiO_3$ shell is estimated at almost constant irrespective of particle sizes. Successive phase transitions are detected in 100 nm particles of $BaTiO_3$ near the phase-transition temperatures of a bulk crystal. The changes in diffraction profiles are small, but they are apparent for a most up-to-date powder diffractometry.

Keywords: $BaTiO_3$, crystal structure, fine particle, nanoparticle, $PbTiO_3$, size effect, synchrotron radiation, X-ray diffraction

Introduction

The typical perovskite-type oxide, $BaTiO_3$, is known to show the size effect on the ferroelectric phase transitions. That is, a bulk crystal of $BaTiO_3$ undergoes the successive phase transitions, e.g. cubic to tetragonal at 405 K, tetragonal to orthorhombic at 278 K and orthorhombic to rhombohedral at 183 K. On the other hand, ultrafine particle of $BaTiO_3$, which has a diameter D of the nanometer level, shows no phase transition to remain as a cubic phase at room temperature. The critical size reported is approximately D=100 nm [1–3]. Several models to explain the size effect have been proposed. One plausible is the cubic surface model that a shell of cubic $BaTiO_3$ covers a core of tetragonal $BaTiO_3$ [4], where the volume ratio of the cubic surface is supposed to increase with decreasing the particle size. The thickness of cubic surface

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layer is estimated at approximately 5 nm by conventional X-ray diffraction for $BaTiO_3$ particles prepared by solid-state reaction [5]. However, no estimation has been reported for particles with dimension near the critical size.

In the present paper, the phase transitions of $BaTiO_3$ fine particles of 100 and 700 nm in diameter are investigated by means of powder diffraction using synchrotron radiation high-energy X-rays. The thickness of cubic surface layer at 300 K is estimated for both particles based on the cubic surface model. We have already found the cubic component at 300 K even in simply ground $BaTiO_3$ crystals by synchrotron X-ray diffraction [6]. For comparison, we investigate the existence of cubic component in ground $PbTiO_3$ fine powder in the present study. A bulk crystal of $PbTiO_3$ is also known to undergo the cubic to tetragonal phase transition at 763 K. The crystal structures of cubic and tetragonal $PbTiO_3$ are similar to those of $BaTiO_3$, respectively. The critical size of $PbTiO_3$ is reported as 12.6 nm [7], which is fairly smaller than 100 nm of $BaTiO_3$.

Experimental

The $BaTiO_3$ particles of 100 and 700 nm were obtained from Sakai Chemical Industry Co. Ltd. and KCM Corporation, respectively. The former was synthesized by hydrothermal method, while the latter by solid-state reaction. Beforehand, the heat treatment at 400°C was made to eliminate impurities from particles. The average particle sizes were confirmed by the TEM observation prior to the X-ray experiments [8]. The $PbTiO_3$ powder was the 4 N chemical reagent obtained from Soekawa Chemicals, which was simply ground to fine powder in a mortar to give homogeneous intensity distributions on the X-ray Debye-Scherrer pattern.

Synchrotron radiation X-ray powder-diffraction experiments were carried out on the Large Debye–Scherrer Camera installed at BL02B2 in SPring-8 [9]. High energy X-rays with wavelength $\lambda=0.58$ and 0.41 Å were used as incident X-rays for $BaTiO_3$ and $PbTiO_3$, respectively. The sample was sealed into a quartz-capillary of 0.1 mm in inside diameter. The diffraction patterns were recorded on the imaging plate of the camera in transmission geometry. Sample temperatures were controlled on the camera by the N_2 gas flow system. These experimental conditions enable us to collect accurate powder diffraction data with high angular resolution. For example, we have collected accurate powder diffraction patterns of standard $PbTiO_3$ and $BaTiO_3$ powder samples to elucidate the charge density distributions to be compared with results of the first principles calculations [10].

Results and discussion

An example of powder diffraction pattern of the $BaTiO_3$ 100 nm particles at 300 K is shown in Fig. 1 together with the Debye-Scherrer film image. We were able to obtain most precise diffraction data with good counting statics up to higher angle, as shown in the inset in Fig. 1.

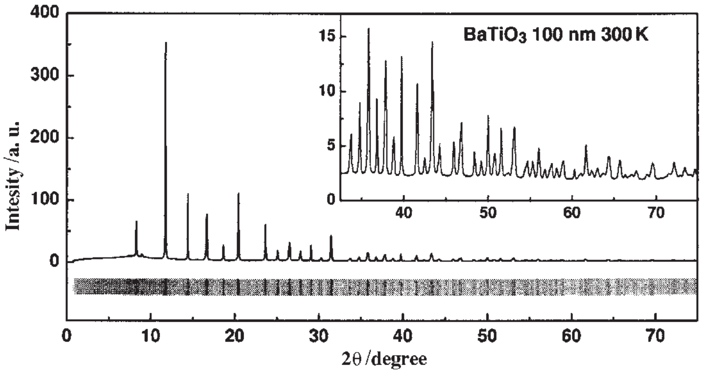

Fig. 1 Powder diffraction pattern of $BaTiO_3$ 100 nm particles in diameter and the Debye–Scherrer film image at 300 K. The close-up in the higher angle region is shown in the inset

The Rietveld refinements of $BaTiO_3$ fine particles were carried out for the data up to 75° in 2θ, which corresponds to the 0.48 Å range in *d* spacing, assuming the composite crystal-structure model of the tetragonal and cubic structures of $BaTiO_3$. The fitting results were enlarged and shown in Fig. 2 in the region between 16.35 and 16.85° in 2θ. The reliability factor (*R* factor) based on the weighted profile, R_{wp}, for the data of $BaTiO_3$ 700 nm particles (Fig. 2a) was 3.97%, which was better than the *R* factor, R_{wp}=4.56%, of the single tetragonal-structure model. The ratio of constituent unit-cell numbers of the cubic to tetragonal component was 7 to 93. On the other hand, R_{wp} was 2.90% for the data of $BaTiO_3$ 100 nm particles (Fig. 2b). The ratio of the cubic to tetragonal component was 37 to 63. The majority was still the tetragonal

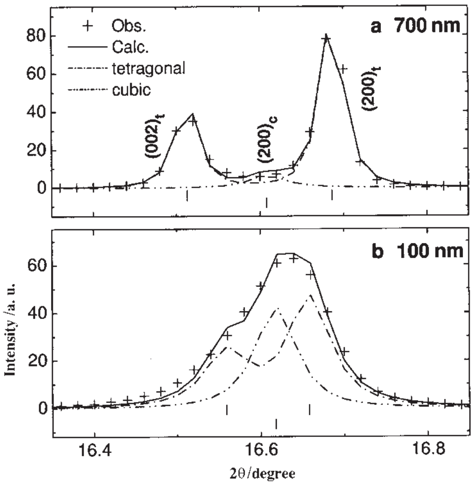

Fig. 2 The results of Rietveld refinement for $BaTiO_3$ fine particles. a – 700 nm and b – 100 nm at 300 K

component. However, the ratio of cubic structure that is stable even at 300 K is significantly high in the 100 nm particles compared with the 700 nm particles.

Let us deduce the thickness of cubic surface based on the proposed structure-model for a $BaTiO_3$ fine particle. We can calculate the volume ratio of the cubic to tetragonal component from the ratio of constituent unit-cell numbers of the cubic to tetragonal component and their lattice constants. Assuming that the particle shape is sphere and the size is the same for all particles (no dispersion), the thickness of cubic surface layer could be estimated from the volume ratio and diameter. The resultants are 7.6(8) and 8.4(6) nm for the 100 and 700 nm particles, respectively, which were almost constant irrespective of not only synthesized methods but also particle sizes within an acceptable error range. We may presume to estimate the critical size of a $BaTiO_3$ fine particle newly at approximately 15 nm, where the tetragonal core disappears and the cubic shell occupies the whole particle.

The phase transitions of $BaTiO_3$ 700 and 100 nm particles were investigated at temperatures from 100 to 450 K. The changes in the observed diffraction patterns indicated that successive phase transitions certainly occurred in both fine particles. Typical four patterns of the 700 nm particles, which are highly similar to those in the cubic, tetragonal, orthorhombic and rhombohedral phases of ground bulk crystals, are shown in Fig 3(a). Corresponding diffraction patterns of the 100 nm particles are shown in Fig. 3(b) at the same temperatures. Although the changes in diffraction profiles of the 100 nm particles are small, apparent changes in asymmetry on the diffraction profiles are detected below 300 K in Fig. 3(b). On the other hand, these phase transitions in the 100 nm particles are not observed by the low temperature capacity measurements [8]. Both the 700 and 100 nm particles are transformed into the cubic

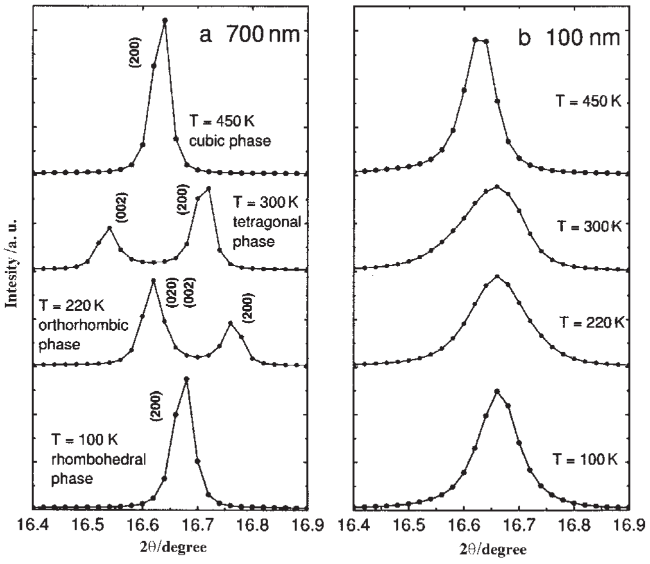

Fig. 3 Typical diffraction patterns for the successive phase transitions of $BaTiO_3$ fine particles. a – 700 nm, b – 100 nm

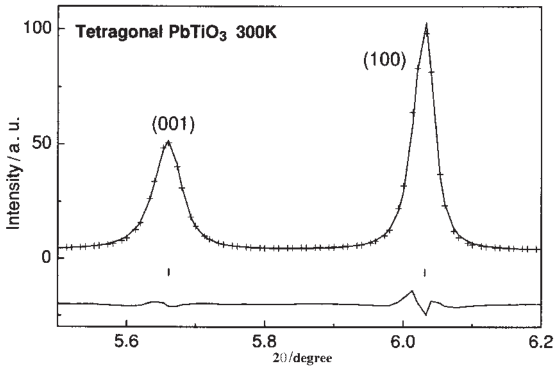

Fig. 4 The results of Rietveld refinement for $PbTiO_3$ fine particles at 300 K

phase at 450 K. However, the particle sizes affect the coherent length on X-ray diffraction. The resultant peak-profile of the cubic phase of 100 nm particles is broader than that of 700 nm particles.

X-ray diffraction experiments were also done for the $PbTiO_3$ fine powder, and the Rietveld refinement was carried out in the same manner. A part of the fitting result for the 300 K data is enlarged and shown in Fig. 4. In this case, the single tetragonal-structure model gave the best fitting. The R factor obtained was so excellent as R_{wp}=2.25%. Although the size-effect of $PbTiO_3$ is essentially similar to that of $BaTiO_3$, the reported critical size of $PbTiO_3$ is fairly small compared with that of $BaTiO_3$ [7]. If the cubic component is included in the $PbTiO_3$ fine powder, they could be detected as the corresponding peak between the (001) and (100) reflections in Fig. 4. We consider that no small particles with sizes near the critical size are made in simply grinding the $PbTiO_3$ powder, which exhibits a striking contrast to the easily detection of cubic component in simply grinding $BaTiO_3$ powder.

Conclusions

The validity of the surface cubic model has been verified as a plausible origin of the size effect of $BaTiO_3$ fine particles by a most up-to-dated synchrotron radiation powder diffraction technique. The successive phase transitions of $BaTiO_3$ 100 nm particles have been also detected in the diffraction data with unprecedented accuracy and detail.

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