XAFS analysis of particle size effect on local structure in BaTiO₃

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The local structure of several samples of BaTiO₃ prepared by solution-gelation method with different particle sizes has been investigated using XAFS. Although the macroscopic crystal structure changes from tetragonal to cubic at room temperature when the particle size is smaller than 100 nm, Raman and XAFS spectroscopy measurements obtain that Ti atoms are displaced from the center of cubic symmetry for all the samples studied. Results of both EXAFS and XANES measurements of the local structure around Ti atoms show that the magnitude of the Ti atom off-center displacement does not depend on the particle size.

Keywords: Ferroelectrics, phase transitions, X-ray absorption fine-structure.

1. Introduction

BaTiO₃ undergoes phase transitions from cubic to tetragonal at 393 K to orthorhombic at 278 K and to rhombohedral structure at 183 K when temperature decreases, as determined by neutron diffraction [Kwei, 1993]. Recent results of the X-Ray Absorption Fine Structure (XAFS) measurements by Ravel *et. al.* [Ravel, 1998] explained the average structure transformations in BaTiO₃ by a disordering of domains wherein the local structure remains rhombohedral at all temperatures. Their results confirmed a dominant order-disorder component to the structural phase transitions in this system, previously believed to be purely displacive.

While the effects of temperature and pressure on the local structure of perovskites have been recently studied, the effect of the particle size has not received sufficient attention, mainly due to the experimental difficulties in sample preparation. The question is how it affects the local structure. In this paper we report the effect of particle size on the local structure of BaTiO₃.

The samples with average grain size of ca. 20 nm, ca. 35 nm and ca. 70 nm were prepared by solution-gelation method. Their structure was characterized by Raman and infrared spectroscopy, x-ray diffraction (XRD), differential scanning calorimetry and electron microscopy [Frey, 1996]. Structure of nanocrystalline BaTiO₃ was obtained to be cubic by x-ray diffraction for all the samples at room temperature, yet Raman spectra indicated the orthorhombic phase [Frey, 1996]. Structure of samples with larger grain sizes (> 100 nm) were obtained to be tetragonal by both the XRD and Raman spectroscopy. Overall, these results suggest that the tetragonal-cubic and orthorhombic-tetragonal transformations shift to lower and to higher

temperatures, respectively, with decreasing grain size. Room temperature measurements of the local structure of the samples with grain size smaller and larger than 100 nm are, therefore, particularly interesting.

2. Experiment

The powder samples with average grain size $d \approx 20$ nm, $d \approx 35$ nm and d ≈ 70 nm were prepared by solution-gelation method. Grain sizes were determined by high-resolution scanning electron microscopy (Hitachi S-800). The size distribution in all cases did not exceed 15 nm. Commercial powder (Cerac) was used to prepare a sample with an average particle size $d \approx 10$ µm by grinding and sieving it through a 200 mesh. These samples were pulverised on a Scotch tape and several layers were stacked to accumulate the total thickness x of the samples corresponding to $\Delta\mu x \approx 0.5$, where $\Delta\mu$ is a jump of absorption coefficient at the Ti K edge energy. The XAFS data were taken at the National Synchrotron Light Source on beamline X16C in transmission using the sagitally focusing double crystal Si (111) monochromator. In order to eliminate higher harmonics, the crystals were detuned by 30% for the Ti K-edge measurements. The energy resolution $\Delta E = E \, \Delta\Theta \cot\Theta = 1eV$ at the Ti K edge energy (4966 eV) was estimated using the vertical angular divergence of $\Delta\Theta = 10^{-4}$ rad at the X16C monochromator position (distance to the source 12 m, pre-mono slits opened 1mm vertically). The XANES range was taken with 0.5 eV energy step around the Ti K edge energy (4966 eV) while the EXAFS range was measured with 2 eV energy step from the Ti K edge to the Ba L_3 edge (5247 eV). XAFS data measured earlier by Ravel *et. al.* [Ravel, 1998] at Ti K edge of BaTiO₃ powder (Aldrich) at different temperatures: 80 K, 450 K and 590 K were used as a reference for the present work.

3. Results

The normalized XAFS spectra were obtained by subtracting the background $\mu_0(k)$ from the measured absorption coefficient $\mu(k)$ using the AUTOBK method [Stern, 1995]. The energy origin, E_0 = 4980 eV, was chosen at the middle of the absorption edge jump. The k^2 - weighted $\chi(k)$ of the samples with different particle size at room temperature, as well as the data with 10 µm particles measured at different temperatures are shown in Fig. 1. The Fourier transform magnitudes of the above data sets are shown in Fig. 2. The useful k range is relatively narrow due to the presence of the Ba L_3 edge at 5247 eV. The energy range between the Ti K and Ba L_3 edges defines the maximum available k value as $k_{max} = 8.2$ Å⁻¹.

Visual inspection of the data (Figs. 1 and 2) leads to the following conclusions. First, besides a very small difference in amplitude, room temperature EXAFS $\chi(k)$ of all the samples with different particle size shows no significant changes. The changes in the amplitude in Fig. 1 (a) are higher than the statistical noise between two measurements of the same sample. These changes, however, are smaller than those occurred during heating the sample with a 10 µm particle size from 80 K to 590 K. In this temperature range, the average structure of BaTiO₃ exhibits several phase transitions from rhombohedral to orthorhombic to tetragonal to cubic at elevated temperatures. Ravel *et. al.* [Ravel, 1998], however, obtained from their EXAFS and XANES analyses that the local structure remains rhombohedral at all temperatures. Decrease of amplitude of the EXAFS signal with
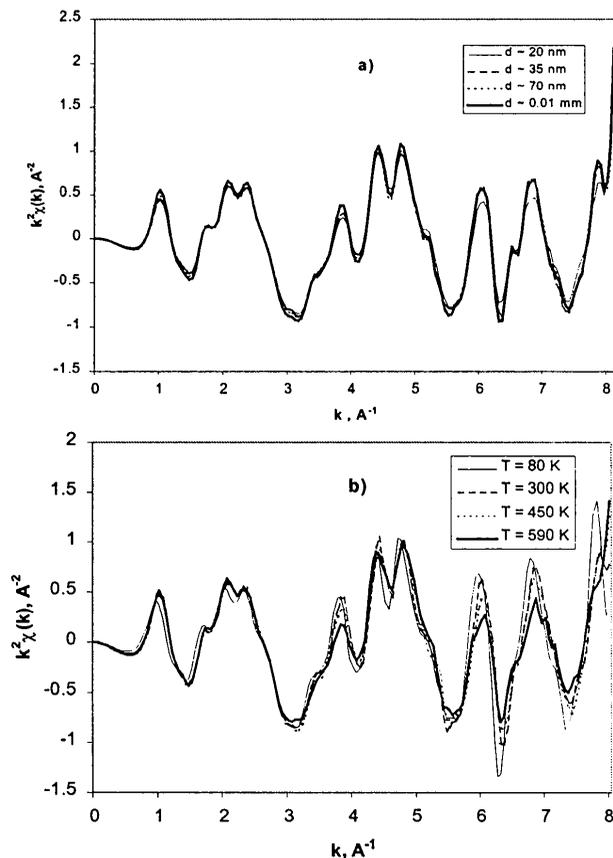
Figure 1
k^2-weighted $\chi(k)$ for the samples with (a) different particle sizes at 300 K and (b) 10 μm particle size at different temperatures (Ravel, 1998).

temperature (Figs. 1 (b) and 2 (b)) is explained in Ref. [Ravel, 1998] by an increasing amount of bond lengths disorder with temperature. The fact that the changes between the EXAFS signals measured for different particle sizes are smaller than the changes occurred in the sample with a macroscopic particle size at different temperatures means that the local structure of the samples with all the particle sizes measured is essentially the same within the experimental resolution.

The presence of Ba L_3 edge near the Ti K edge complicates the situation since the available data range is relatively short: 12 independent points correspond to the data range of 2 Å^{-1} < k < 8.2 Å^{-1} and 1.3 Å < r < 4.0 Å. The number of fit variables necessary to solve the local structure of this system through the 4th nearest neighbor is 13, as shown in the case of isostructural $KNbO_3$ [Frenkel, 1997]. This means that the information amount contained in the Ti K edge EXAFS data in $BaTiO_3$ is too low for solving the structure around Ti atom. We tried to obtain the direction of the Ti off-center displacement from the fit of FEFF6 theory to the data using the first shell signal only. However, the discrimination in favor of one of the displacement directions we assumed in the model: [111], or [110] or [100], or no displacement at all, was not possible to make based on the quality of fits obtained using each model for FEFF calculations. Therefore, solving the structure around Ti K edge using fitting methods is not possible in this case.

To resolve the structure around Ti atom Ravel, *et. al.*, analyzed Ti K edge x-ray absorption coefficient in XANES
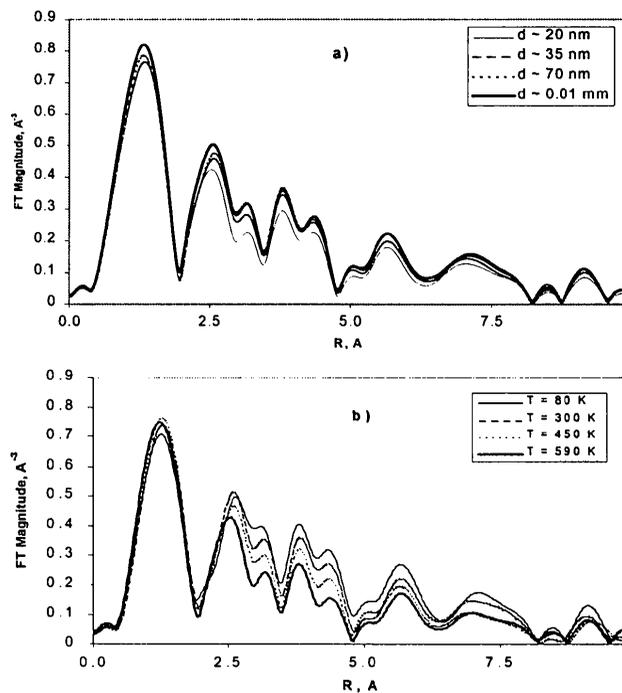

Figure 2
Magnitudes of Fourier transforms of k^2-weighted $\chi(k)$ for the samples with (a) different particle sizes at 300 K and (b) 10 μm particle size at different temperatures (Ravel, 1998).

region, between 4960 and 4970 eV. This range corresponds to the energy range of the $1s \rightarrow 3d$ dipole-forbidden transitions and should, therefore, give a small or no contribution to the XANES of a Ti K edge which is dominated by a dipole mechanism. The presence of a large peak in that range of spectrum is, therefore, a signature of mixing of p character from the surrounding oxygen octahedron with the d character of Ti atom d states. As obtained by Kraizman *et. al.* [Kraizman, 1995] for different titanium containing perovskites, the off-center displacement $\vec{d}$ of the Ti atom from the center of oxygen octahedron is related to the area

A under the peak in the XANES spectrum: $A \propto \langle (\hat{\varepsilon} \cdot \vec{d})^2 \rangle$,

where $\hat{\varepsilon}$ is a unit vector in a direction of the polarization of x-rays, and angle brackets represent an average over relative orientations of $\hat{\varepsilon}$ and $\vec{d}$.

Difference between the distorted ($BaTiO_3$) and undistorted (e. g., $EuTiO_3$) perovskites is very large in the $1s \rightarrow 3d$ transition region of the Ti K edge XANES spectra [Ravel, 1998]. Figure 3 shows XANES region of the Ti K edge data of $BaTiO_3$ for different particle sizes and temperatures. All the data were normalized by edge step and aligned in energy. The area of XANES region decreases with temperature, consistent with a concomitant decrease in the magnitude of the Ti atom off-center displacement (by 9% in the measured temperature range [Ravel, 1998]). All the curves in Fig. 3 (b) are above the reference curve for the $EuTiO_3$ which corresponds to a zero displacement case.

Our XANES measurements for the samples with different particle sizes are shown in Fig. 3 (a). The changes in the region corresponding to the $1s \rightarrow 3d$ between all the samples are clearly smaller than the changes occurred at different

temperatures in a sample with 10 µm particle size (Fig. 3 (b)). Since it has been shown that the local structure of the latter remained non-cubic far above the ferroelectric-paraelectric transition temperature [Ravel, 1998], it is, therefore, evident that in the samples with different particle sizes Ti atoms also occupy off-center positions. Using the results of Ref. [Ravel, 1998] for the magnitudes of $\bar{d}$ at different temperatures, we estimate the size of the off-center displacements in all the samples with different particle sizes to be of ca. 0.10(3) Å.
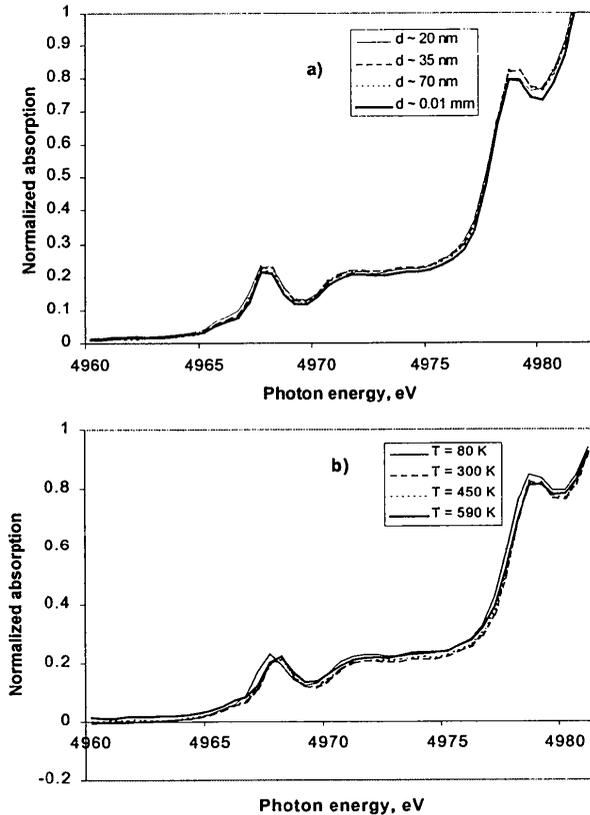

Figure 3
XANES region for the samples with (a) different particle sizes at 300 K and (b) 10 µm particle size at different temperatures (Ravel, 1998).

These XANES measurements, therefore, confirmed our conclusions made from inspection of the raw EXAFS data measured for different particle sizes. The advantage of using XANES to complement the EXAFS data in deciding whether the changes in the local structure occurred or not between the sample with different particle size is that the EXAFS data alone would not provide the unique answer. Indeed, for the spatial resolution of 0.06 Å, as in the case of the Ti K EXAFS data, the small differences in the radial distribution function between different samples may be not resolved in the EXAFS data. Thus, the similarities in the EXAFS data of the different samples are a necessary but not sufficient evidence of the similarities in the local structures in this case. The similarities in both XANES *and* EXAFS ranges indicate that the locally non-centrosymmetric structure, indeed, preserves in all the samples.

Interestingly, comparing the amplitudes of the EXAFS signals in r space (Fig. 2 (a)) one notices that the amplitudes are lower for the samples with smaller particles. As already mentioned above, this difference is larger than that caused by

statistical noise in the data. In this case of the samples with the same local structure, the change in the amplitudes of EXAFS signals with particle size could be related to either the change in the average coordination number with the particle size, or the change in the mean squared bond lengths disorder in the samples, or σ^2, or both. The deviation of the average coordination number from its bulk value should be only few per cents if the particle size exceeds ca. 10 unit cells, therefore, the much larger effect we observed in Fig. 2 (a) is most likely due to the increase of σ^2 with the decreasing particle size. In general, σ^2 is a superposition of dynamic (due to bonds thermal vibration) and static terms. For the same local structure, the amplitude of thermal vibrations is temperature dependent, and, therefore, should be equal for all the 300 K samples with different particle sizes. Therefore, to explain the difference between the amplitudes of the different samples measured at 300 K, the amount of bond lengths static disorder should be the highest in the samples with the smallest particle sizes. In the case of an infinite long-range order, the static contribution to σ^2 should be very small in an ordered structure. In our case, however, the smallest particle (20 nm) has significant fraction of bonds near the particle surface to the total fraction of bonds between Ti central atom and its nearest neighbors. These surface bonds are most strongly disordered and their contribution to the total σ^2 increases with a decrease of the particle size.

4. Conclusions

Previous polarized XANES measurements in the BaTiO$_3$ single crystal demonstrated that the Ti atoms are displaced in approximately [111] direction at all temperatures. Our measurements of the powdered samples can not provide information about the direction of the Ti atom off-center displacement. Combining EXAFS and XANES measurements, however, we demonstrated that the local structure was the same for all the particle sizes measured and it was indistinguishable from the 10 µm size sample where the local displacements are in [111] direction. The fact that the XRD measurements obtain that the average structure is cubic for the particle sizes smaller than 100 nm means that the average structure is obtained by disordering of locally non-centrosymmetric domains. These results agree with the Raman spectroscopy measurements [Frey, 1996], where the distortions from the cubic structure were also observed in the sample with the smallest particle size.

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