

# XAFS Study of Local Structure Change in Perovskite Titanates

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## Abstract

The Ti K-edge EXAFS for PbTiO<sub>3</sub> measured in the temperature range including the critical temperature (763 K) due to the phase transition from tetragonal to cubic phase is discussed from the local point of view. Three kinds of atomic pairs, shorter Ti-O(1), medium Ti-O(2) and longer Ti-O(3) were analyzed independently. The interatomic distance of Ti-O(3) changes at  $T_c$  discontinuously and shows a “displacive” type transition. On the other hand, EXAFS shows that the lattice distortion remains even in cubic phase, which indicates “order-disorder” type transition. The peak intensity at the pre-edge region in XANES, which indicates the distortion of Ti atoms along the  $c$ -axis of the oxygen octahedron, corresponds to the distortion obtained from EXAFS analysis.

## 1. Introduction

X-ray absorption fine structure (XAFS) has become a technique to study local structures as a complementary technique to diffraction methods which are based on long-range order [1]. PbTiO<sub>3</sub> has long been considered as “displacive” type ferroelectrics: The perovskite PbTiO<sub>3</sub> shows tetragonal structure at  $T < T_c$  ( $=763$  K) (lattice parameters  $a = b = 3.89$  Å and  $c = 4.15$  Å at 300 K [2]) and cubic structure at  $T > T_c$  ( $a = b = c = 3.905$  Å at 773 K). On the other hand, if the local distortion does not change with temperature across  $T_c$  the transition is “order-disorder” type. In this case, only the orientations of the distortion within a small domain change with temperature; the orientation is arranged along the preferable direction below  $T_c$ , but it is disordered above  $T_c$ .

The local structural change of PbTiO<sub>3</sub> has been extensively studied by Sicron *et al.* using XAFS of both Pb L<sub>III</sub> and Ti K-edges [3, 4]. These results show that an essential element of “order-disorder” is present even in this normally pure ferroelectric crystal, which displays a soft mode and a dielectric constant of typical “displacive” type ferroelectrics. Recently, a more detailed study by Pb L<sub>III</sub> edge EXAFS for PbTiO<sub>3</sub> has been carried out [5] where three kinds of atomic pairs Pb-O(1,2,3) are analyzed independently. Shorter atomic pairs of Pb-O(1,2) show “order-disorder” type behavior, on the other hand, the longest Pb-O(3) shows “soft mode” behavior [5].

In this paper, we study the local structural change around Ti atoms in PbTiO<sub>3</sub> crystal through  $T_c$  in more detail. Actually, there exist three types of Ti-O pairs by tetragonal distortion; longer and shorter interatomic distances along the  $c$ -axis and a medium Ti-O pairs perpendicular to the  $c$ -axis. Our results show that the local distortion remains above  $T_c$  in which PbTiO<sub>3</sub> shows cubic phase.

## 2. Experimental and Data Analyses

The powder sample of PbTiO<sub>3</sub> (99.99%) was purchased from Soeakwa Co. Ltd. and was checked by X-ray powder diffraction to assure its crystal structure. The powder was mixed with BN and

was dry pressed for producing a pellet that could be easily handled and placed within the furnace. X-ray absorption spectra of Ti K-edge (4.95 keV) were measured at BL9A of Photon Factory (KEK) in transmission mode. A Si(111) double crystal monochrometer was used. The temperature range for measurement was from 300 K to 923 K.

The EXAFS analysis was performed according to XANADU code [6] and it is given only briefly here. The normalized EXAFS interference function,  $\chi(k)$ , was multiplied by a Hamming window function to reduce the ripples in the Fourier-transformed spectra in  $r$ -space. The  $k$ -range for the Fourier transform was from 2.95 to  $8.8$  Å<sup>−1</sup>.

## 3. Results and Discussion

We discuss here the result for Ti K-edge XAFS. Figure 1 shows the EXAFS oscillation functions,  $k^2\chi(k)$ , of Ti K EXAFS for PbTiO<sub>3</sub> crystal at various temperatures obtained by transmission measurement. Although the signal in the transmitted ionization chamber is not so large due to the absorption by Pb atoms, satisfactory data quality has been obtained up to  $8.5$  Å<sup>−1</sup> for EXAFS analyses even at high temperatures. As the temperature increases the amplitude of the EXAFS function decreases gradually. Figure 2 shows the Fourier transforms of Ti K EXAFS for PbTiO<sub>3</sub> crystals at various temperatures as shown in Fig. 1. The peak intensity decreases as temperature increases and change of the fine structure is observed. The atoms are distorted along the  $c$ -axis at tetragonal phase: There are three kinds of Ti-O atomic pairs; shorter Ti-O(1), medium Ti-O(2) and longer Ti-O(3) as shown in Fig. 3. The peaks from 1 to  $2$  Å include three Ti-O pairs. In the case of Ti K-edge we tried to perform 3 shell-fitting in order to obtain the structural parameters and reasonable results were obtained. Our unknown parameters for the fitting are  $r$  and  $\sigma^2$  for each shell and the total number of them is 6.

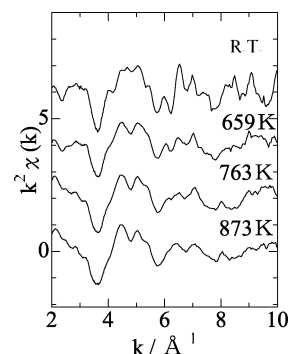


Fig. 1. EXAFS oscillation functions,  $k^2\chi(k)$ , of Ti K-edge EXAFS for PbTiO<sub>3</sub> crystal at various temperatures.

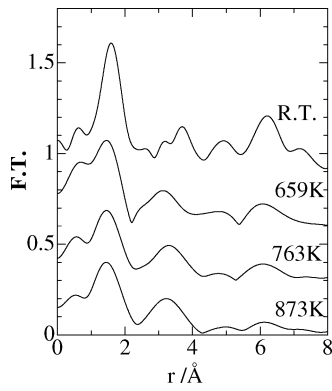


Fig. 2. Fourier transforms of Ti K-edge EXAFS for PbTiO<sub>3</sub> crystals at various temperatures as shown in Fig. 1.

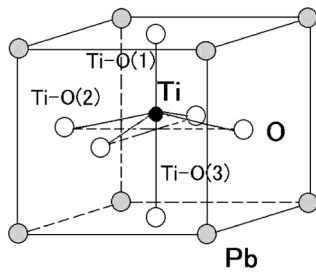


Fig. 3. Schematic structure of PbTiO<sub>3</sub> in the tetragonal phase. The central atom is Ti (Black circles), white circles represent O atoms and gray circles represent Pb atoms.

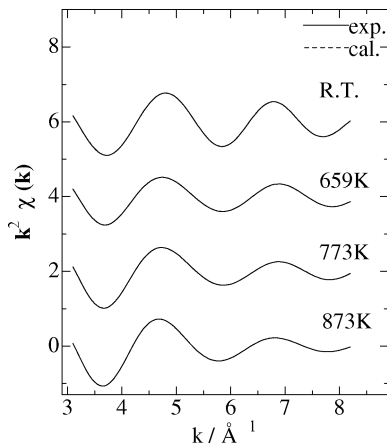


Fig. 4. Example of the quality for 3-shell fitting in the present study at various temperatures.

Figure 4 shows an example of the quality of 3-shell fitting in the present study at various temperatures. The fitting results reproduce the experimental spectra well. Figure 5 shows the contributions of each shell as a function of  $r$  which is obtained from the theoretical fitting for the Ti K-edge of PbTiO<sub>3</sub>. Figure 6 shows the variations of three kinds of Ti-O interatomic distances with temperature. We also easily find the tetragonal distortion below  $T_c$  as shown in Pb L<sub>III</sub>-edge EXAFS [5]. For example in the tetragonal phase at 300 K, the distance for Ti-O(1) is about 1.8 Å, that for Ti-O(2) is about 2.0 Å and that for Ti-O(3) is 2.4 Å. From these values we can estimate the distortion of Ti atoms with O atoms in the tetragonal phase. The distortion of Ti atoms from O atoms for  $c$ -axis is about 0.35 Å at 300 K for the tetragonal phase, which is the same value as that obtained by Sicron *et al.* [3, 4].

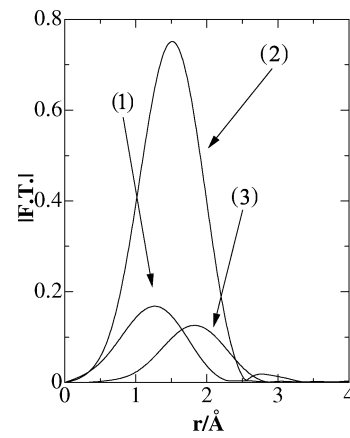


Fig. 5. The contributions of each shell in Ti K-edge fitting for PbTiO<sub>3</sub> as a function of  $r$  at 300 K.

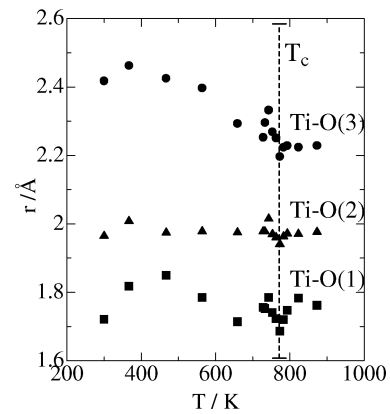


Fig. 6. Variations of three kinds of Ti-O interatomic distances with temperature.

The interatomic distance of Ti-O(2) is almost constant in the whole temperature range including  $T_c$ . That of Ti-O(3) decreases as temperature increases up to  $T_c$  and does not change with temperature at  $T > T_c$ . As for Ti-O(1), we find complex behavior between Ti-O(2) and Ti-O(3). That is: the longest Ti-O(3) shows typical “displacive” behavior and Ti distortion remains at temperatures above  $T_c$ . These phenomena are quite similar to the result of Pb-O obtained from Pb L<sub>III</sub>-edge EXAFS study [5]. At  $T > T_c$ , the interatomic distance for Ti-O(1) is 1.75 Å, that for Ti-O(2) is 2.0 Å, and that for Ti-O(3) is 2.25 Å. This difference in Ti-O distance shows that atomic distortion remains at the cubic phase.

Figure 7 shows X-ray absorption near edge structure (XANES) of Ti K-edge for PbTiO<sub>3</sub> at various temperatures. We can find two clear peaks (A and B) before the edge. The origins of these two peaks are assigned to the transition from 1s to 3d<sub>xy</sub> and 3d<sub>z<sup>2</sup></sub> from the symmetry of the orbital, respectively. Although these transitions are forbidden generally in the dipole approximation, they are allowed by mixing with oxygen p-state orbitals due to the distortion of Ti atoms from the oxygen octahedron. That is the existence of these peaks indicates that Ti atoms are distorted.

Figure 8 shows the temperature variations of the intensity of peak A in Fig. 7 (solid circle). The peak intensity of A decreases gradually as the temperature increases up to  $T_c$  and decreases discontinuously at  $T_c$  and it is almost constant at  $T > T_c$ . The peak intensity of A ( $= I_A$ ) is known to be approximately proportional to the amplitude to the Ti atom distortion as [7],

$$I_A = C e \cdot d, \quad (1)$$

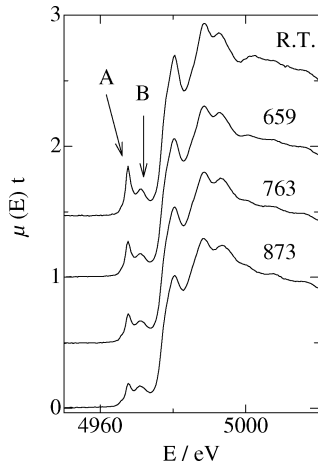


Fig. 7. X-ray absorption near edge (XANES) spectra of Ti K-edge for PbTiO<sub>3</sub> at various temperatures.

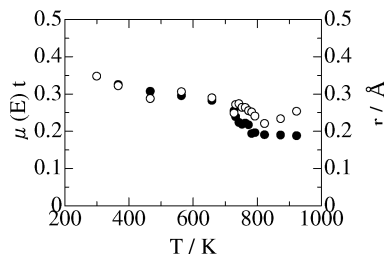


Fig. 8. Temperature variations of the intensity of peak A in XANES (Solid circle) and Ti atom distortion from the center of the oxygen octahedron (open circle).

where  $\mathbf{e}$  and  $d$  are the unit vector in the direction of the electric field of incident X-rays and the distortion of a Ti atom from the center of an oxygen octahedron, respectively.  $C$  is a proportionality constant. The behavior in Fig. 8 indicates that the distortion of Ti atoms from O octahedron decreases as temperature increases and it remains finite at  $T > T_c$ . The values of the Ti atom distortion ( $d$ ) along the  $c$ -axis with temperature evaluated from the present EXAFS by

$$d = (r_{\text{Ti-O}(3)} - r_{\text{Ti-O}(1)})/2 \quad (2)$$

are also presented (open circle) in Fig. 8. When we put the constant  $C$  to be 1.0, the curve of  $d$  vs  $T$  coincides approximately

with that of  $I_A$  vs  $T$  at room temperature.  $d$  shows the same behavior as  $I_A$  and decreases as temperature increases up to  $T_c$ . As discussed previously 0.35 Å of  $d$  is the same as the value Sicron *et al.* reported [3, 4]. However they concluded that  $d$  is almost constant at the temperature range from low temperature to  $T_c$  and decreases slightly with 30% at  $T > T_c$ . On the other hand, our result shows clear decreasing of  $d$  in the ferroelectric phase ( $T < T_c$ ).

#### 4. Conclusion

We measured Ti K-edge EXAFS for PbTiO<sub>3</sub> in the temperature range including  $T_c$ . The structural changes were discussed from the viewpoint of short-range order. Three kinds of atomic pairs, shorter Ti-O(1), medium Ti-O(2) and longer Ti-O(3) were analyzed independently. The longest Ti-O(3) is discontinuously changed at the transition. The distortion of Ti atoms evaluated from EXAFS indicates that tetragonal distortion remains above  $T_c$ . The XANES study supports the temperature dependence the Ti distortion from EXAFS. The proposed solution may not be unique and further measurements, e.g. fluorescence mode for Ti K-edge XAFS, will hopefully confirm the obtained results.

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