

Measurement of Ti, Ta and Sc Off-Center Displacements in Relaxor Ferroelectric PST-PT

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We probed titanium (Ti), tantalum (Ta), and scandium (Sc) environments in the (1-x)Pb(ScTa)O₃ - xPbTiO₃ relaxor ferroelectric (PST-PT), which displays variable order-disorder, relaxor, a mixed phase region, and normal ferroelectric behaviors as x is increased. The abrupt structural phase transition from rhombohedral to tetragonal is observed by x-ray diffraction at x = 0.45. According to x-ray absorption fine structure (XAFS) studies, the structure around Ta, Sc, or Ti atoms changes differently with x and there are no abrupt changes at any concentration. No displacements of Ta or Sc atoms from their oxygen octahedron centers were observed. But surprisingly, we find that Ti is displaced along the (111) direction for x = 0.05. However, it gradually changes direction from (111) to (001) as x increases. We suggest that PST-PT consists of mixed regions, some characterized by a (111) Ti displacement and others by a (001) displacement. The displacement averaged over all regions becomes more weighted toward (001) as x increases.

Relaxor ferroelectrics display a diffuse temperature dependence of their polarization-related macroscopic properties. The origin of this behavior lies in the interactions of polarized entities at the nanoscale. Relaxors typically belong to a class of “oxygen-octahedra compounds,” in which six oxygen ions surround a particular transition metal ion, such as Ti, Ta, or Sc (**Figure 1**). The unique characteristics of the relaxor ferroelectric (1-x) Pb(Sc_{1/2}Ta_{1/2})O₃ - x PbTiO₃ (PST-PT) are revealed when one traverses a variety of compositions, x. A variety of thermally “adjustable” states of structural ordering, Curie temperatures, and material properties are accessible for these materials. PST-PT is attractive for device applications, and also as a model to explore the nature of relaxor ferroelectrics.

The structure determined by x-ray diffraction (XRD) was rhombohedral for low x values, but abruptly becomes tetragonal for x = 0.45. The Ta L₃-edge XAFS data of the same samples were measured at beamline X11A. The Sc and Ti K-edges were measured at the Pacific Northwest Consortium - Collaborative Access Team beamlines at the Advanced Photon Source.



At low x values, an energy dispersive detector is required to separate Ti K_α fluorescence photons from the Sc K_α photons that dominate the fluorescence background. We used a log-spiral of revolution analyzer designed by Doug Pease and Joe Budnick, recently improved by the addition of the annular ion chamber, designed by Ed Stern. We know of no other detector setup that could

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successfully separate the dilute Ti fluorescence from the otherwise overwhelming Sc fluorescence photons without saturating the detector, and with much more intensity than any other crystal monochromator.

Ti K-edge x-ray absorption near-edge structure (XANES) data of all the samples (**Figure 2**, left) have a feature “A” located in the region corresponding to the dipole-forbidden 1s-3d transition. In order to contribute to the XANES data, the *p*-character of the final state of the photoelectron has to be added in the solid. That may occur due to, for example, hybridization between Ti 3*d* and O 2*p* orbitals that is enhanced if Ti is displaced away from the inversion symmetry center. The presence of a large peak “A” is, therefore, a signature of the off-center displacements of Ti atoms. The area under the peak can be used to quantify the off-center displacement *d* of the Ti atom ($A \propto d^2$). In the Ti K-edge XANES data of all the samples (**Figure 2**, left), the intensity of the signal in this region is much larger than in the reference cubic EuTiO_3 system. For all $x < 1$, we obtained $d \sim 0.23(2)$ Å. We found that this large Ti atom displacement is in marked contrast with Ta and Sc atom behaviors, where no measurable displacement from the oxygen octahedron centers (**Figure 1A**) was found by their EXAFS or XANES (**Figure 2**, left (inset)) analyses.

The EXAFS analysis (**Figure 2**, right) revealed that Ti atoms were displaced along the (111) cubic direction from $x = 0.05$ (**Figure 1B**). However, this displacement gradually changes direction from (111) to (001) as x increases (**Figure 1C**).

These results allow two interpretations. First, the Ti atom displacement direction changes gradually from (111) to (001) as x increases, going through the intermediate orientations. The second interpretation, supported by Maaskant and Bersuker (MB) theory, allows no intermediate orientation between the (111) and (001) directions. In the framework of the MB model, we propose that the PST-PT system consists of mixed regions, some having (111) Ti displacement and others having (001) displacement. The displacement averaged over all regions becomes more weighted toward (001) as x increases.

Our work resulted in the atomic-level scenario of the structural transformations in PST-PT. We found that the changes in the local structure could not be simply interpolated from the average structure data: The independent, element-specific measurements were required to elucidate the structure around each atomic species. Our results give the first experimental observation of the 111-displacement direction of a Ti atom in the ferroelectric perovskite system.

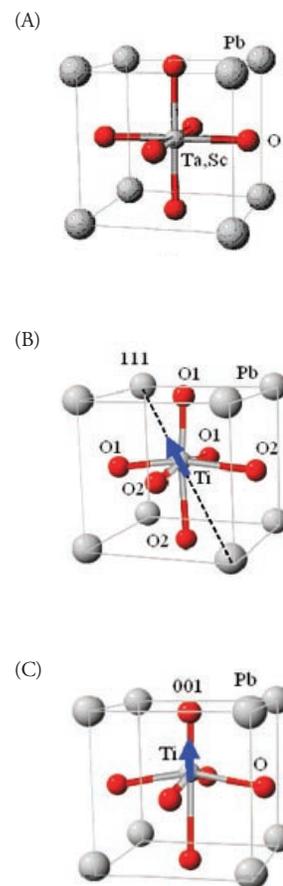
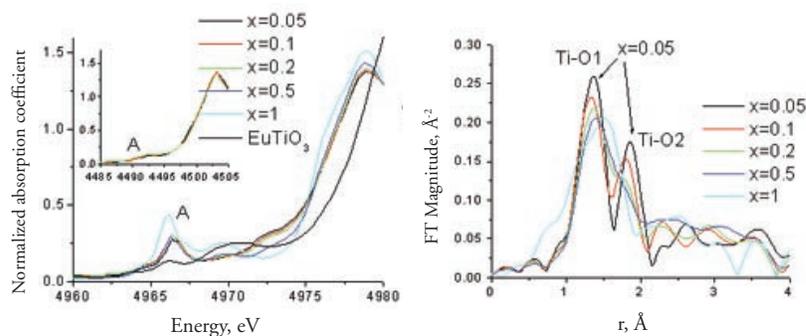


Figure 1. Perovskite pseudo-cubic ABO_3 unit cell ($A=\text{Pb}$, $B=\text{Ta}$, Sc , Ti). (A) The Ta and Sc atoms were shown to be approximately in the cell center. Arrow shows different directions of Ti atom displacements obtained by XAFS for (B) $x=0.05$ and (C) $x=1$.

Figure 2. Left: XANES spectra of Ti K-edge in $(\text{PST})_{1-x}(\text{PT})_x$ samples. Feature A denotes the energy region of the dipole-forbidden 1s-3d transition. (A) The inset shows the featureless 1s-3d transition region in Sc K-edge XANES. Right: the Ti K-edge EXAFS: Fourier transform magnitudes of $k\chi(k)$ in $(\text{PST})_{1-x}(\text{PT})_x$ samples. Shown by arrows are groups of Ti-O distances that correspond to either (111) or (001) displacement of the Ti atom from the center of the TiO_6 octahedron, depicted schematically in **Figure 1** (B) or (C), respectively.