

Comparison of Ti, Ta, and Sc Displacements from the Center of the Oxygen Octahedron in a Relaxor Ferroelectric System

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Introduction

Relaxor ferroelectrics exhibit a diffuse temperature dependence of various polarization - dependent properties. For instance, there is not a sudden loss of spontaneous polarization as T_C is approached, but instead a rather gradual decrease in spontaneous polarization to zero as temperature increases. An example of such a relaxor system is disordered $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ (PST) [1,2]. In this system the Sc and Ta sites can be ordered or disordered along a [100] direction by appropriate thermal treatments, as determined by intensity of x-ray diffraction (XRD) superlattice lines. The disordered material manifests relaxor behavior. Explanations for such relaxor behavior have been offered by Smolenski [3] and by Cross [4]. In Smolenskii's picture, statistical fluctuations in composition due to such disorder results in a range of T_C values associated with small regions of material. In the model of Cross, there exists a range of sizes for small scale ferroelectric regions in a relaxor, and for sufficiently small domain size relative to a characteristic temperature, thermal energies are sufficient to switch the polarization direction dynamically. The critical temperature is smaller for smaller domain sizes. Relaxor behavior can then result because a range of such small domain sizes can result in a range of such critical temperatures. These small domains may be lower symmetry structures embedded in a higher symmetry matrix. The lower symmetry regions, when arranged in random orientations, can average to appear as higher symmetry structure when observed using XRD. Whereas PST, when ordered, shows a slight rhombohedral distortion from a cubic perovskite structure, pure PbTiO_3 (PT), when ordered, shows a tetragonal distortion. The $(\text{PST})_{1-x}(\text{PT})_x$ mixed system studied by Giniewicz, et. al. is most interesting as it consists of a mixture of materials that - in the pure ferroelectric phase - are tetragonally distorting (PT) or rhombohedrally distorting (PST) [5,6]. We have investigated by x-ray absorption edge fine structure (XAFS) the local distortions about Ti, Sc, and Ta sites for x values of 0, 0.05, 0.1, 0.2, and 0.5. We have discovered that Ti atoms in the x = 0.05 composition distort *rhombohedrally* despite the fact that in pure PT the Ti atoms distort *tetragonally* from the centrosymmetric position in the oxygen octahedron.

Methods and Materials

The $(\text{PST})_{1-x}(\text{PT})_x$ ceramics were prepared by a mixed oxide method involving the use of PbO , TiO_2 , Sc_2O_3 , and Ta_2O_5 starting oxides. Each component was calcined at 900 °C for 4 hours and then at 1000 °C for 1 hour. Finally compacted specimens were fired at 1400 °C for 1 hour in sealed alumina crucibles including source powders to control lead loss. More details of sample preparation are described in the Ph.D. dissertation of Giniewicz referred to above. The samples were studied by XRD, both in the 1980 years by Giniewicz, and then

more recently at the University of Connecticut. The pyrochlore percentage was 5% for x = 0, not detected for x = .05, of order 1% or less for x = 0.1, 7% for x = 0.2, and not detected for x = 0.5. In other words, the pyrochlore contamination is not systematic with Ti concentration and does not exceed 7%. On the other hand, both the Ti K edge XAFS and the shifts in the (200) XRD peak are quite systematic with Ti concentration, and we therefore conclude that the pyrochlore phase does not significantly influence the results. The XRD data is fit well assuming a cubic structure with lattice constant systematically decreasing for x = 0 through 0.2. The structure as determined by XRD changes to tetragonal for x = 0.5 [7]. In the dissertation of Giniewicz, it was shown that the transition from cubic to tetragonal phase was abrupt.

Room temperature XAFS measurements were performed for Ti edges at the ID line of the PNC - CAT line of the Advanced Photon Source (APS), for the Sc edges at the bending magnet line of the APS, and for the Ta edges at the X-11 line of the National Synchrotron Light Source (NSLS). For the Ti K edges we used a log spiral of revolution (LSR) analyzer designed for detection of Ti K_α fluorescence. By this means the dilute Ti fluorescence could be detected clearly against the background of the concentrated Sc fluorescence [8]. The addition of a custom built annular ion chamber and a sample positioner with feedback has markedly improved the performance of this device. If the sample position was not optimized, pronounced Sc oscillations interfered with the Ti absorption edge, but these oscillations disappeared at optimum sample position.

Results

Ti K edge (XANES) data of all samples have a feature "A" located in the region corresponding to the dipole-forbidden 1s - 3d transition (Fig. 1). In Fig. 1, we also include data for pure PT and EuTiO_3 kindly furnished by B. Ravel [9]. Kraizman, et. al. have shown that this feature is a signature of off center displacements of Ti atoms [10]. A marked Ti off center displacement of in excess of 0.22 Å is observed for x = 0.05, 0.1, 0.2, and 0.5. For x = 1, the displacement is 0.31 Å and is in agreement with crystallographic data for pure PT [11]. One would also expect there to be a feature A observed for the Sc K edge if the Sc atoms were displaced from centro-symmetric positions, but no such displacement is observed (insert, Fig. 1). The extended x-ray absorption fine structure (EXAFS) Fourier transform magnitudes of the Ti K edge are shown in Fig. 2. For the x = 0.05 composition there is a pronounced splitting of the first shell FT peak corresponding to a Ti (111) displacement from the centro-symmetric position. In this case the FT shows two sets of distances; from Ti to three close oxygens and from Ti to three far oxygens. For the case of x = 0.05, fits of the data result in a magnitude of Ti displacements in agreement with the XANES. As x increases through intermediate values between 0.05 and 1, the EXAFS data becomes difficult to analyze

quantitatively, but is consistent with a gradual shift of the *average* Ti displacement from (111) to (001). On the other hand, EXAFS analysis results in no detectable shift from the centrosymmetric position for Ta or Sc sites. The Sc result is in agreement with the insert for Fig. 1. A detailed and recent description of the present investigation has been published by Frenkel, et. al. [7].

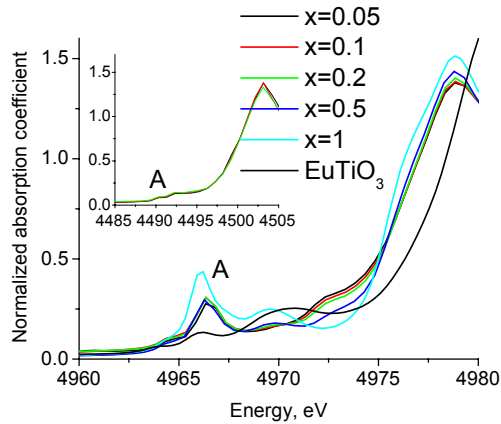


Fig. 1. XANES spectra of Ti K-edge in $(PST)_{1-x}(PT)_x$ samples. Feature A denotes the energy region of the dipole-forbidden, 1s-3d transition. The inset shows the feature-less 1s-3d transition region (A) in Sc K-edge XANES.

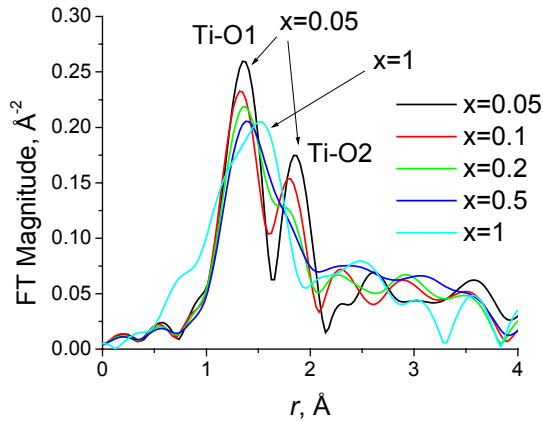


Fig. 2. The Ti K-edge EXAFS: Fourier transform magnitudes of $k\chi(k)$ in $(PST)_{1-x}(PT)_x$ samples. Shown by arrows are groups of Ti-O distances that correspond to either (111)- or (001) displacement of Ti atom from the center of TiO_6 octahedron

Discussion

The most interesting observation is the discovery for the first time of a (111) Ti displacement for Ti in a PT local environment. Pure PT exhibits a (001) Ti displacement, as observed by both EXAFS and XRD. But we find that small PT regions embedded in a rhombohedrally distorted (PST) matrix exhibit a (111) displacement. The lack of detectable Ta and Sc displacements is surprising, since the question then arises as to what is the displacive source of the ferroelectric properties of PST. However, this result is in agreement with neutron diffraction studies of PST by Dmowski, et. al. [12]. These authors do find local displacements of Pb atoms, but along the (001), not the (111) direction of the macroscopic direction of polarization. There are two interpretations we offer for the Ti atom displacements:

- (1) The Ti atom displacement gradually changes from (111) to (001) as x increases.
- (2) According to the theory of Masskand and Bersuker there is no intermediate orientation between the (111) and (001) directions [13]. This theory suggests, in correlation with our results, that the PST - PT system consists of mixed regions, some having (111) and some having (001) directions. The average displacement becomes more weighted toward (001) as x increases.

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