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XAFS Study of the Antiferroelectric Phase Transition in PbZrO₃

N. Sicron, Y. Yacoby, E.A. Stern* and F. Dogan**

Racah Institut of Physics, Hebrew University of Jerusalem, Jerusalem 91904, Israel

** Physics Department FM-15, University of Washington, Seattle, WA 98195, U.S.A.*

*** Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195, U.S.A.*

Abstract. The temperature dependence of the local structure of PbZrO₃ (PZ) was investigated using XAFS analysis. This perovskite undergoes an antiferroelectric (AFE) phase transition at about 500 K. XAFS of Pb L_{III}-edge and Zr K-edge in PZ were measured between 173 K and 824 K. The local structure was determined by fitting a parameterized theoretical XAFS to the experimental data. The distortion parameters obtained at room temperature are consistent with previous diffraction results. The Pb [1,1,0] displacement remains almost constant at all temperatures. The ZrO₆ octahedron remains distorted at all temperatures but the exact distortion above T_C cannot be determined. The oxygen AFE distortion and the [1,1,0] octahedral rotation decrease as temperature increases. At 824K the oxygen distortions are at least 50% of their 298 K values. The presence of structural distortions in the paraelectric phase of PZ indicates that like in many other perovskites these distortions are not a result of soft lattice vibrational modes and that the AFE phase transition involves the ordering of local distortions.

1. INTRODUCTION

The perovskite Lead Zirconate (PZ) undergoes an antiferroelectric (AFE) phase transition at about 500 K [1]. The distortion from the cubic paraelectric (PE) structure can be decomposed into several atomic displacements, associated with different lattice vibrational modes [2]. In PZ there are five such displacements: anti parallel [1,1,0] displacements of Pb and Zr atoms (all the vectors are in the pseudo cubic coordinate system), anti parallel [-1,-1,0] displacement of O₁ atoms (oxygen in the Pb plain), a more complicated displacement of O₂ atoms and rotation of the oxygen octahedra around the [1,1,0] axis. A rhombohedral ferroelectric (FE) intermediate phase was also reported for PZ. The temperature range and the stability of the intermediate phase are very sensitive to the presence of impurities in the crystal and to the preparation method [1].

The AFE transition in PZ was described as a *displacive* transition [2]. In the displacive model the transition is from an ordered PE phase to an ordered phase with lower symmetry. The structural distortion is caused by the softening of vibrational lattice mode (or modes). In the recent years experimental evidence, especially from XAFS have shown that local distortions exist in the PE phase of many perovskites which were previously considered as displacive. Among these are the ferroelectrics KNbO₃ [3], KNb_xTa_{1-x}O₃, [4] and PbTiO₃ [5] and the antiferrodistortive Na_xK_{1-x}TaO₃ [6]. So far no AFE transition in perovskites has been studied by XAFS. In this paper we present a study of the temperature dependence of the local distortions in PZ. We show that like in other perovskites studied previously there are local distortions in the PE phase of PZ.

2. EXPERIMENTAL CONDITIONS AND DATA ANALYSIS

PZ sample was prepared by a sol-gel process. XRD measurement verified its orthorhombic structure. Dielectric measurement showed a single phase transition at 499 K on heating and at 498 K on cooling. Pb L_{III}-edge and Zr K-edge XAFS were measured at seven different temperatures between 173 and 824 K. All data was collected at beamline X-11A at the NSLS. Full experimental details can be found elsewhere [7]. The background was removed in a procedure described in ref. 5. The useful k-range of the Zr XAFS was 3-15 Å⁻¹ at 173 K and decreased to 3-11.5 Å⁻¹ at 824 K. Because of the large Pb vibrations, the Pb XAFS quality was not as good as the Zr spectra. For Pb XAFS the useful k-range was 3-12 Å⁻¹ at 173 K and decreased to 3-10 Å⁻¹ at 824 K.

The analysis is based of fitting the Fourier transforms (FT) of theoretical calculations to the FT of experimental data in a specified range in r-space [4]. The theoretical XAFS was expressed in the form:

$$\chi(k) = \text{Im} \sum_{\eta} n_{\eta} F_{\eta}(k) \exp \left\{ i \left[\frac{B_{\eta}}{k} + kL_{\eta} + \theta_{\eta}(k) - \frac{4}{3} k^3 C_{3\eta} \right] - 2k^2 \sigma_{\eta}^2 - \frac{L_{\eta}}{\lambda_{\eta}} \right\} \quad (1)$$

Here the summation is over all different scattering paths (indexed by η), n is number of equivalent paths, k is the photoelectron's wave number, L is the scattering path length, $F(k)$ and $\theta(k)$ are the scattering amplitude and phase which were calculated by FEFF5 code [8]. B/k and L/λ are phase shifts and mean free path correction terms. σ^2 and C_3 are the second and third cumulants of the radial distribution function of the atoms in a given shell (or sub shell) relative to the probe

atom [5]. Errors in the fit parameters were estimated from the covariance matrix of the Levenberg-Marquardt non linear fit [9]. The threshold energy E_0 was set at the mid point of the absorption step. For each probe atom the B 's and λ 's were determined by fitting the data of the two lowest temperatures (173 and 298K) and then were set constant for all the data.

The Zr spectra were fitted between 1.0 and 4.2Å, using the four nearest coordination shells (O, Pb, Zr and O). The calculation included the double and triple collinear scattering of the Zr-O-Zr path. Three other double scattering paths were also included. The second moment of the rotation and the oxygen AFE distortion (or their rms values) are obtained from the affect of these distortions on the collinear scattering of the third Zr shell in the Zr XAFS [6]. Because of thermal vibrations the rms distortions are expected to be larger than the first moment of the distortion. (The first moments of distortions are obtained from their affect on the bond lengths of the first and fourth shells). Since the two oxygen distortions affect the same shells in a similar manner the oxygen distortion parameters in our parameter fit depend on each other. This could lead to errors in these parameters. Five σ^2 were used: one for each shell, except for the second Pb shell in which two σ^2 were used, one for the two near Pb atoms and one for the other six. The distortions were described with six parameters: AFE distortion of Pb and Zr, oxygen AFE distortion (it was assumed that the ratio between the O_1 and O_2 AFE distortions does not change with temperature and one parameter controlled both of them), octahedral rotation, and the rms rotation and AFE distortions. After fitting all the data with 11 parameters the σ^2 obtained were fitted to Einstein models. The refinement of the six structural parameters was done by setting the σ^2 to the values obtained in the Einstein model fit.

The Pb spectra were fitted between 1.0 and 3.7Å (1.0-4.75Å at low temperatures), using the four nearest shells (O, Zr, Pb and O) and one double scattering path, Pb-O-Zr. The third and fourth shell were not sensitive the distortions and were included mainly to avoid errors in the second Zr shell parameters. In the AFE phase of PZ there are two non equivalent Pb probe atoms and the theoretical calculations included the sum of the XAFS of the two Pb probes. Six σ^2 were used: two for the first oxygen shell, two for the second Zr shell (as in the Zr XAFS) and one for the third and fourth shells. A C_3 parameter was used for the short Pb-O bonds. The Pb displacement cannot be determined from the first oxygen shell of the Pb XAFS [7]. The Pb XAFS provides only the relative Pb-Zr [1,1,0] displacement. Following the results of Zr XAFS analysis the Zr displacement was set to 0.04Å at all temperatures and only three distortion parameters were variable. These were the Pb displacement, the oxygen AFE distortion and octahedral rotation. The refinement of the structural parameters was done by setting the σ^2 of the far Zr and the third and fourth shells to Einstein model values. The other σ^2 do not fit the Einstein model and were left variable. Typical fits are presented in fig. 1.

Figure 1: Examples of the absolute value of k^2 weighted FT of the Zr and Pb XAFS. Dashed lines - experimental data, solid lines - best fit. The vertical lines indicate the fitting range. The FT were taken from different k -ranges for different temperatures. Therefore their magnitudes are not comparable.

3. RESULTS AND DISCUSSION

The Zr and Pb [1,1,0] displacements are presented in fig. 2. The displacements at room temperature are consistent with previous results [2]. The slight increase in the Zr displacement is not significant. The magnitude of the second Pb shell in the Zr XAFS is relatively small. This causes large uncertainties in all the Pb parameters obtained from the Zr XAFS. The Pb displacements obtained from the two probes are consistent with each other. The difference between the local Pb displacement and the macroscopic average displacement obtained from XRD near T_c [1], indicates that even in the AFE phase there is partial structural disorder. The relative Pb-Zr displacement decreases only slightly at high temperatures. A similar behavior was observed in $PbTiO_3$ [5] where the relative Pb-Ti [1,0,0] displacement was constant at all temperatures.

The temperature dependence of the [1,1,0] octahedral rotation angle is presented in fig. 3. Below T_c the results of both probes are consistent with each other and with XRD results [1]. The rms rotation angle is slightly larger because of thermal vibrations. Above T_c the angles obtained from both probes are different from each other. In the Pb XAFS the rotation angle is determined mainly from the short Pb-O₂ bond length. This bond is also affected by the oxygen AFE distortion and an error in the AFE distortion parameter would lead to an error in the rotation parameter. The correlation between the oxygen distortion parameters in the Zr XAFS leads to large errors in the rms and the average rotation angles. The discrepancies between the rotation parameters might suggest that the local oxygen structure above T_c cannot be described by the low temperature

distortions. Nevertheless the perpendicular oxygen displacements decrease gradually as temperature increases but remain finite above T_c in contrast to the average distortions which vanish in the PE phase. The AFE oxygen distortion decreases by 20% from 173 K to 824 K. This distortion will not be discussed here.

We tried to fit several other structural models to the data of the PE phase in order to test the significance of our results. A cubic structure with no distortions cannot fit the Pb XAFS at all. In this case the calculated FT of the oxygen first shell is in anti phase with the experimental FT. A structure with variable Pb and Zr displacements but no oxygen distortions can fit the Pb XAFS but the fit is 10 times worse than the fit of the low temperature model. Two models were tested for the first oxygen shell in the Zr XAFS: a cubic structure with no distortions and a model with a Zr [1,1,1] displacement (in both models a C_3 parameter was included). The misfit of these models is about 7% for the cubic model and 4% for the [1,1,1] model. The misfit for the [1,1,0] model is 3%. Thus, the cubic model can be excluded for the ZrO_6 octahedron but we cannot distinguish between the [1,1,0] and [1,1,1] models. A model with Pb and Zr [1,1,1] displacements and [1,1,1] octahedral rotations can fit the data from both probes, above T_c . However, the Pb-Zr relative displacement obtained from the two probes are significantly different from each other.

Figure 2: Pb and Zr [1,1,0] displacements as a function of the temperature. The errors in the Zr displacement below T_c and in the Pb displacement obtained from the Pb XAFS are of the order of the points in the figure. The vertical dashed line indicates T_c .

Figure 3: The rotation angle of the oxygen octahedron as a function of temperature. The rotation angle in ref. 1 was deduced from the tetragonal distortion of the pseudo cubic unit cell. The vertical dashed line indicates T_c .

The results and conclusions of this study can be summarized as follows:

- 1) At room temperature the distortion parameters obtained by XAFS are consistent with the results of x-ray [1] and neutron [2] diffraction.
- 2) The Pb [1,1,0] displacement remains almost constant up to 824 K. The ZrO_6 octahedron remains distorted above T_c but its exact structure can not be determined from XAFS.
- 3) The perpendicular oxygen displacements (AFE distortion and rotations) decrease as temperature increases but do not vanish at all temperatures.
- 4) Since all local distortions in PZ remain finite more than 300 degrees above T_c the local distortions are not caused by soft modes. The transition to the AFE phase involves ordering of the local distortions.

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