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## XAFS study of rhombohedral ferroelectric $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$

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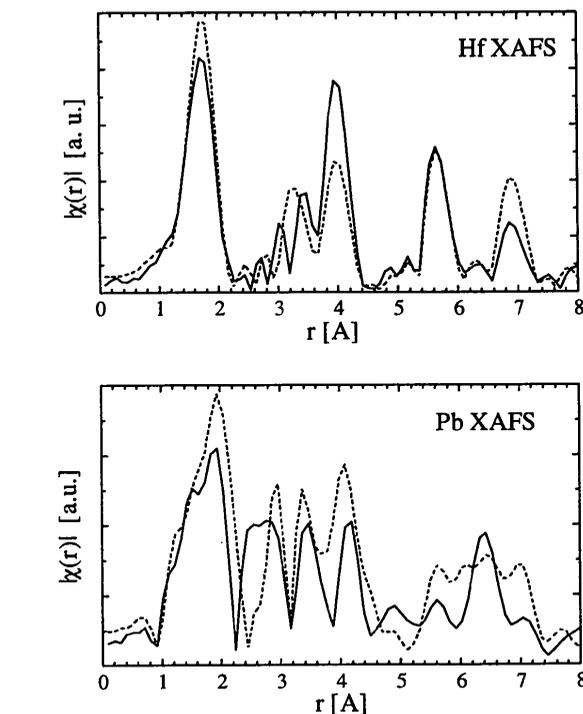
The local structure of the rhombohedral perovskite  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  was studied using Pb and Hf XAFS. XAFS data were analyzed by fitting a parameterized theoretical spectrum to the experimental data using the four nearest coordination shells. It was found that the Ti off center displacement is different from that of Hf. Furthermore, the Pb-O and Pb-Pb bonds have very large Debye Waller factors indicating that Pb and possibly O atoms are disordered about the rhombohedral positions down to 11K. Despite the structural disorder, the local structure of  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  is closer to the rhombohedral average structure measured by diffraction than to the structure of pure  $\text{PbHfO}_3$  or  $\text{PbTiO}_3$ .

**Keywords:** Structural phase transitions, Ferroelectricity, Perovskites, Lead Hafnate Titanate, XAFS

### 1. Introduction

XAFS studies of various perovskite crystals undergoing structural phase transitions have shown that although the average structure of these materials becomes cubic in the paraelectric phase the *local structure* remains distorted hundreds of degrees above  $T_C$  (Yacoby & Stern 1996, Sicron *et al.* 1997). Local distortions were also found in the cubic phase of mixed perovskites such as  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ . However, in this crystal one of the pure end materials,  $\text{KTaO}_3$ , is cubic at all temperatures and the distortions are associated with the other end material ( $\text{KNbO}_3$ ). In some perovskite systems both end materials are distorted but in different ways. For such mixed crystals the relation between local and average structure is not known.

We chose to study  $\text{PbHf}_{1-x}\text{Ti}_x\text{O}_3$  (Lead Hafnate Titanate, PHT). PHT and isostructural  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (PZT) perovskite crystals exhibit different polar phases at room temperature (RT) depending on the Ti concentration.  $\text{PbHfO}_3$  and  $\text{PbZrO}_3$  are orthorhombic and antiferroelectric (AFE). Replacing more than 5% of Hf or Zr by Ti turns the crystal into a ferroelectric (FE) with rhombohedral symmetry (Jaffe *et al.* 1955, Hall *et al.* 1964). For  $x > 0.48$  PHT and PZT (and pure  $\text{PbTiO}_3$ ) are tetragonal FE. The different symmetries reflect different directions of cation displacements and oxygen octahedral rotations (Lines & Glass 1977). Our study focused on  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$ . This crystal becomes FE rhombohedral below 480 K (space group  $R3m$ ). A second transition at about 380 K is probably associated with the rotation of oxygen octahedra which doubles the unit cell but preserves the rhombohedral symmetry (space group  $R3c$ ). No other phase transitions were reported for lower temperatures. The rhombohedral structure is characterized by several structural distortions: cation displacements along the  $[1,1,1]$  direction, octahedral rotations around the  $[1,1,1]$  axis and



**Figure 1**

Comparison between the XAFS of pure  $\text{PbHfO}_3$  (dashed line) and mixed  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  (solid line) both measured at 11 K. Top -  $k^2$  weighted FT of Hf XAFS, bottom -  $k$  weighted FT of Pb XAFS.

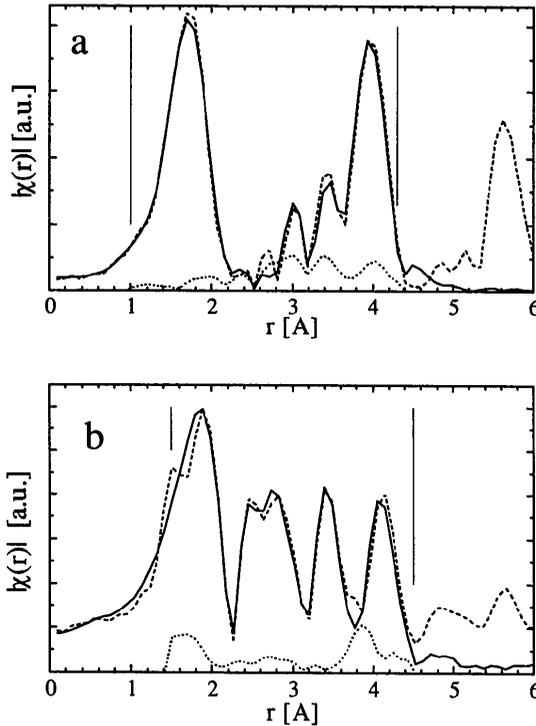
a deformation of the oxygen octahedron. This deformation stretches three O-O bonds in the  $(1,1,1)$  plane due to the  $[1,1,1]$  Hf displacement. Three O-O bonds on the opposite face of the octahedron are shortened by this deformation (Megaw & Darlington 1975). Our aim was to see if the *local distortions* in this material are consistent with the rhombohedral symmetry or whether deviations from this symmetry occur.

### 2. Sample preparation and XAFS measurements

A mixture of high purity  $\text{PbO}$ ,  $\text{HfO}_2$  and  $\text{TiO}_2$  in the correct proportions to form  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  was sintered at  $1265^\circ\text{C}$  for 5 hours in an enriched  $\text{PbO}$  atmosphere following the method of Jaffe *et al.* (1955). A weight loss of less than 0.4% indicates that very little  $\text{PbO}$  evaporated from the PHT sample during sintering. X-ray powder diffraction revealed no impurity phases in the PHT ceramics. Superlattice reflections associated with octahedral rotations were not detected because of their smallness. All diffraction lines were fitted with high accuracy assuming a rhombohedral cell yielding  $a_p = 4.121 \text{ \AA}$  and  $\alpha = 89.75^\circ$ . This is very close to  $\alpha = 89.72^\circ$  reported for  $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$  (Glazer *et al.* 1978). Dielectric measurements showed no anomalies between RT and 4 K. Pb and Hf  $L_3$ -edge XAFS were measured for  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  and for pure  $\text{PbHfO}_3$  (Sicron, unpublished). All data were measured in transmission mode between 11 K and 450 K on beamline X11A at NSLS.

### 3. XAFS Analysis and Results

The XAFS Fourier transforms (FT) of  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  are compared to those of  $\text{PbHfO}_3$  in Fig. 1. The differences between



**Figure 2**  
Fitted FT of Hf XAFS (a) and Pb XAFS (b) of  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  at 11K. Dashed lines - absolute value of experimental FT. Solid line - theoretical fit. Dotted line - absolute value of the complex difference between theoretical fit and experimental data. Vertical lines indicate fitting ranges.

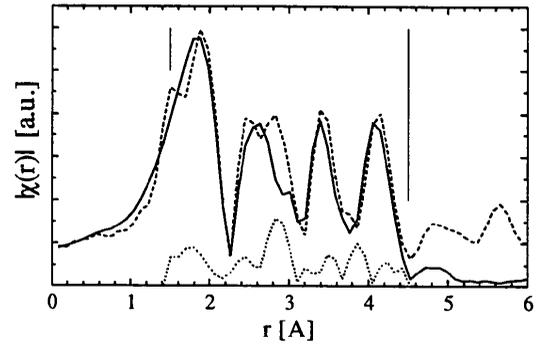
the spectra of the pure and mixed crystals are not limited to the Hf/Ti shells. Thus, the observed differences are not only because of the substitution of Hf with Ti. It is evident that as the macroscopic average structure changes from AFE to FE the local structure changes as well.

The quantitative XAFS analysis was done by fitting the FT of theoretical calculations to the FT of experimental data in a specified range in  $r$ -space (Hanske-Petitpierre *et al.* 1991). The theoretical spectrum of each probe atom included all single, double and collinear triple scattering paths of the four nearest coordination shells. The theoretical spectra were parameterized with several  $\sigma^2$  (Debye-Waller factors) and distortion parameters. In order to test the consistency of the local structure with the rhombohedral symmetry only distortions consistent with this symmetry were used. Five distortions were used: independent displacements of the Pb, Hf and Ti along the  $[1,1,1]$  axis, a rotation of the oxygen octahedron around the  $[1,1,1]$  axis and the octahedral deformation.

### 3.1 Fitting the first shell of the Hf XAFS

The Hf displacement splits the six Hf-O bonds into three short and three long ones. However, the octahedral deformation reduces this splitting. Thus, the net splitting of the oxygen shell is rather small and both distortions are correlated with each other and with the  $\sigma_{\text{Hf-O}}^2$ . To overcome this we fitted the first shell of the Hf XAFS at all temperatures ignoring distortions (i.e. six equal Hf-O bonds) and varying only  $\sigma_{\text{Hf-O}}^2$  and the Hf-O average bond length. The temperature dependence of the resulting  $\sigma^2$  was fitted with:

$$\sigma^2(T) = \sigma_{\text{th}}^2(T) + \sigma_0^2 \quad (1)$$



**Figure 3**  
Fitted FT of Pb XAFS of  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  at 11K. In this fit it was assumed that the Hf and Ti displacements are equal. Dashed lines - absolute value of experimental FT. Solid line - theoretical fit. Dotted line - absolute value of the complex difference between theoretical fit and experimental data. Vertical lines indicate fitting ranges.

Here  $\sigma_{\text{th}}^2$ , described by the Einstein model, is due to thermal vibrations (Stern & Heald, 1983). The term  $\sigma_0^2$  accounts for the broadening of the radial distribution function due to distortions missing in the structural model. This fit yielded an Einstein temperature  $T_E=585(35)$  K and  $\sigma_0^2=0.0029(5)\text{\AA}^2$ . The splitting of the Hf-O bonds due to both distortions was determined by setting  $\sigma_{\text{Hf-O}}^2$  to Einstein model values with  $T_E=585$  K and  $\sigma_0^2=0$ . The two Hf-O bond lengths, 2.13 and 2.03A, are almost identical to Zr-O distances of 2.04 and 2.13A determined by neutron diffraction in  $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$  at RT (Glazer *et al.* 1978).

### 3.2 Fitting four shells of 11 K data

The octahedral deformation could not be determined from the Hf or the Pb XAFS independently because it is correlated with the displacement of each probe. However, this deformation reduces Hf-O splitting in the Hf XAFS whereas for the Pb probe it increases the Pb-O splitting. Therefore this distortion was determined by varying its parameter until the Hf displacements obtained from both probes were consistent. The fitted FT at 11K are shown in Figs. 2(a) and 2(b). The absolute value of the difference between the fitted and the experimental FT (dotted line) provides a measure of the fit quality. In the Pb XAFS the misfit below 2A is due to a part of the background which was not removed. The reason for the misfit near 3.8A is not known but it may reflect some feature missing in our structural model. The distortions obtained from the fit of the 11 K data are compared in Table 1 to those known for  $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$  at RT. It can be seen that the cation displacements and the octahedral deformation in  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  are slightly larger than those in  $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ . The rotation angles obtained from both probes are close to rotation angle in  $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$  but the difference between the Hf and Pb XAFS results may indicate that something is missing in our structural model.

As mentioned above a separate parameter was used for the Ti displacement. We tried to fit the Pb XAFS with a model in which Ti and Hf displacements were equal. In this case the quality of the fit was significantly worse. This can be seen in Fig. 3 where there is a large misfit in the range 2.3-3.7A. Moreover, imposing the constraint  $\Delta\text{Ti}=\Delta\text{Hf}$  resulted in a large non physical  $\sigma_{\text{Pb-Ti}}^2$ . Having found that  $\Delta\text{Ti}$  is different from  $\Delta\text{Hf}$  at least in magnitude, we tried to fit models with  $\Delta\text{Ti}$  along the  $[0,0,1]$  or  $[1,1,0]$  axes. For these directions the magnitude of  $\Delta\text{Ti}$

is strongly correlated with  $\sigma_{\text{Pb-Ti}}^2$ . We found that  $\Delta\text{Ti}$  is about 0.2-0.4Å (depending on  $\sigma_{\text{Pb-Ti}}^2$ ). The fit quality and the other structural parameters were not sensitive to the direction of  $\Delta\text{Ti}$  and therefore it could not be determined conclusively.

**Table 1**

Comparison between distortions of  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  and distortions of  $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$  (Glazer *et al.* 1978).  $\Delta\text{O}$  is the oxygen displacement due to the octahedral deformation.

Distortion	$\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$ at 11 K (XAFS)	$\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$ at RT (Neutron diffraction)
$\Delta\text{Pb}$	0.48(3)Å	0.455(11)Å
$\Delta\text{Hf} / \Delta\text{Zr}$	0.21(3)Å	0.164(16)Å
$\Delta\text{O}$	0.09(3)Å	0.059(6)Å
$\omega$	7(1) $^\circ$ (Pb XAFS) 4.8(.5) $^\circ$ (Hf XAFS)	5.4(.2) $^\circ$

### 3.3 Fitting data of higher temperatures

The spectra of all other temperatures were fitted assuming an octahedral deformation as at 11 K and by varying only the four other distortions. Seven  $\sigma^2$  were used for the Pb XAFS. Because of the large Pb displacement the shortest bonds in each of the two nearest shells (O and Hf) were assigned a separate  $\sigma^2$ . The Hf XAFS was fitted using four variable  $\sigma^2$ . For the first oxygen shell we used the  $\sigma^2$  obtained previously from the Einstein model. The distortion parameters did not change significantly up to 450 K although the uncertainties increased. The  $\sigma^2$  of all bonds were fitted with Eq. 1. The Einstein temperatures and  $\sigma_0^2$  obtained from this fit are shown in Table 2. The parameters of Ti bonds and fourth shell oxygen bonds were less reliable and are not shown in Table 2.

**Table 2**

Einstein temperatures and  $\sigma_0^2$  obtained from fitting of Einstein models to the  $\sigma^2$  of the different bonds.

Bond	Pb-O (short)	Pb-O	Pb-Hf (short)	Pb-Hf	Pb-Pb
$T_E$ [K]	255(40)	215(40)	157(50)	102(25)	80 (20)
$\sigma_0^2$ [Å $^2$ ]	.0057(10)	.0086(17)	.0007(15)	.0009(10)	.0083(15)

Bond	Hf-O	Hf-Pb	Hf-Hf
$T_E$ [K]	585 (35)	120(25)	195 (20)
$\sigma_0^2$ [Å $^2$ ]	-	.0000(18)	.0026(05)

## 4. Discussion

The large  $\sigma_0^2$  of Pb-O bonds means that the local structure around the Pb probe can not be precisely described by the rhombohedral symmetry. The large  $\sigma_0^2$  of the Pb-Pb bonds suggests that part of the structural disorder is because Pb displacements are not along the [1,1,1] axis and that these displacements are not fully correlated even in neighbouring perovskite cells. The structural disorder manifested by the large  $\sigma_0^2$  means that the displacements in Table 1 are only average displacements about which the different atoms are distributed. The radius of the Pb distribution about the [1,1,1] off-center position can be estimated from the Pb-Pb  $\sigma_0^2$  to be at least 0.07Å.

The  $\sigma^2$  of the short Pb-O bonds are smaller than those of the other Pb-O bonds suggesting that the Pb distribution is broader in the directions perpendicular to the [1,1,1] axis. A similar anisotropy in the Pb distribution was observed in  $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$  (Glazer *et al.* 1978).

The disorder of the Pb displacements could be a result of anharmonicities of the Pb local potentials (e.g. due to the small

ionic radius of Pb). We also observed disorder in the Pb displacements in AFE  $\text{PbZrO}_3$  and  $\text{PbHfO}_3$  (Sicron, unpublished). However in these cases the  $\sigma_0^2$  of Pb-Pb bonds was smaller, about 0.004Å $^2$ . The Pb disorder in  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  could also be associated with the difference between Ti and Hf displacements. Because of this difference  $\text{HfO}_6$  octahedra and  $\text{TiO}_6$  octahedra are distorted in a different manner inducing strains to the oxygen octahedral frame.

The short Pb-O bond length in  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  is 2.48Å. The short Pb-O bond lengths in  $\text{PbTiO}_3$  (Sicron *et al.* 1994) and in  $\text{PbHfO}_3$  (Sicron, unpublished) are the same within 0.02Å. Although the number of nearest oxygens is different for each of these materials the shortest bond length is unchanged suggesting that the magnitude of the Pb and O displacements in any direction are determined by the short range repulsive forces between O and Pb ions.

Despite the structural disorder, our results suggest that the local structure of  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  is closer to the rhombohedral average structure than to the structure of pure  $\text{PbHfO}_3$  or  $\text{PbTiO}_3$ . This is based on the similarity of the average distortions in  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  to those in  $\text{PbZr}_{0.9}\text{Ti}_{0.1}\text{O}_3$  and on the significant differences between the XAFS of  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  and the XAFS of  $\text{PbHfO}_3$  and  $\text{PbTiO}_3$  (which was not shown in this paper).

## 5. Summary and Conclusions

We used XAFS to study the local structure of  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  and its relation to the rhombohedral average structure known from diffraction. The conclusions of our study can be summarized as follows:

1. The Ti off center displacement is different from that of Hf. The direction of the Ti displacement could not be determined from the Hf or Pb XAFS.
2. Pb and possibly O atoms are disordered about the rhombohedral positions down to 11 K.
3. The local structure of  $\text{PbHf}_{0.9}\text{Ti}_{0.1}\text{O}_3$  is closer to the rhombohedral average structure than to the AFE structure of  $\text{PbHfO}_3$  or the tetragonal FE structure of  $\text{PbTiO}_3$ .

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