XAFS Studies of Fe Doped $PbTiO_3$ Nanoparticles

Tomohiro Shibata*, Soma Chattopadhyay*, Bin Lin †, V.R. Palkar¶

*Physics Division, BCPS, Illinois Institute of Technology, Chicago, IL60616, USA
†Institute of Applied Physics and Computational Mathematics, Beijing 100088, China
¶Tata Institute of Fundamental Research, Bhabha road, Mumbai, 400005, India

Abstract. Fe K and Ti K edge XAFS studies are reported on Fe doped $PbTiO_3$ nanoparticles down to the 10 nm size. Fe forms Fe^{3+} ions and substitute for Ti^{4+} ions. For 18 nm nanoparticles, the Fe and Ti environment is found to be quite different. For $PbFe_{0.5}Ti_{0.5}O_3$, *locally* the structure remains distorted from bulk to 10 nm size although the average structure changes.

Keywords: EXAFS, XANES, ferroelectrics, magnetoelectrics, nanoparticles
PACS: 61.46.Df, 61.10.Ht

INTRODUCTION

Oxidic perovskite materials with the chemical composition ABO_3 show various important properties and their stable structure is determined by several competing parameters. In ferroelectrics (FE), mechanical and electronic structures are competing parameters; the FE structure is realized at the cost of the lattice distortion. The properties are further modified by introducing various species with controlled amount of dopants. In many ferroelectrics, d^0-ness, i.e. absence of *d* electrons in the transition metals is essential, which can be modified by being replaced by magnetic transition metals. Because of these competitions, the materials with the coexistence of magnetization and ferroelectricity are very rare.

Lead titanate ($PbTiO_3$) is a very well-known FE material and the Curie temperature is 768 K [1]. It was shown that both the Pb and Ti ions are displaced from their respective oxygen planes by 0.47 and 0.3 Å at 300 K, the ratio of lattice constants being (c/a) = 1.06 [2]. At room temperature, Ti ions are surrounded by 6 oxygen (O) atoms; 4×O at 1.97 Å, 1× O at 1.72 Å and 1×O at 2.43Å in C_{4v} symmetry. Ti^{4+} has empty *d* electron states. Fe ions have 3*d* electrons and are Fe^{2+}(d^6,S=2) and Fe^{3+}(d^5,S=5/2) in high spin states. It was shown that magnetism and ferroelectricity coexist in Fe doped $PbTiO_3$, and both spontaneous magnetization and electric polarization exist, varying in magnitude with *x*. Those materials, retaining magnetoelectric properties down to nanometer size, attract great attention for industrial applications, including nonvolatile memory devices. XAFS spectroscopy is sensitive to the short range structure. XANES, including the pre-edge, and the main edge crest, reflects the structure of the coordination cluster, but also includes second or higher shell multiple scattering. For 3*d* transition metal K edge XAFS, local structure around metals, including the metal-ligand clusters is obtained. On the other hand, EXAFS provides more quantitative information about bond lengths, Debye Waller factors (DWF), and coordination numbers.

EXPERIMENTAL

The Fe doped $PbTiO_3$ ($PbFe_xTi_{1-x}O_3$) nanoparticles (NP) for *x*=0.1-0.5, particles size down to 10 nm, were prepared by co-precipitation techniques so as to gain better control on chemical homogeneity and stoichiometry. Powder x-ray diffraction confirmed the successive change in lattice parameters and decrease of tetragonality (c/a) with x, indicating that Fe is in the lattice, yet very small portion of pyrochlore type impurity phase ($Pb_2Ti_2O_6$) is present [3].

Fe K edge XAFS were performed at the undulator beamline 10 ID and Ti K edge XAFS at the bending magnet 9 BM at the Advanced Photon Source (APS), Argonne National Laboratory. Rhodium coated harmonic rejection mirrors were used, and gas filled ion chambers were used for incident monitor. The energy calibration was done by the first inflection point of the metal foils, and Fe (7111.1 eV). For Ti K edge, and Fe K edge XAFS measurements, fluorescence signals were detected using Stern-Heald geometry. Since the absorbance (μ) of Ti and Fe are

about 0.15 of the total μ, the use of fluorescence mode is justified and the consistency with transmission mode is ensured within the noise level. For EXAFS, χ(k) were reduced using standard methods; after the background subtraction, the post-edge data are fitted with 3 to 5 spline knots. *k*-weighted $\chi(k^w \chi)$ were fitted in real space as well as *k* space using paths produced by FEFF6 as standard [4]. The data were fit using FEFFIT program with different k^w simultaneously.

RESULTS AND DISCUSSION

Fe K edge: Fig. 1 shows Fe K-edge XANES for *x*=0.1, 0.3, and 0.5 for 18 nm nanoparticles compared with the data of bulk *x*=0.5. The pre-edge peak located at 7114 eV is related to 1*s*→3*d* (quadrupolar allowed) transitions, and can also gain intensity from mixing of 3d and 4p orbitals in noncentrosymmetric environments. It has been shown that the pre-edge feature has strong correlations with Fe oxidation states and the symmetry of the coordination sphere in a series of Fe bearing minerals [5-7] and the peak energy of Fe^{3+} ions is 1.4 eV higher than Fe^{2+}, and it is 7113.5 eV for all the minerals studied. All the nano and bulk samples in the figure appear a peak at 7114 eV, thus the oxidation states are 3+. The peak width is the order of core-hole lifetime, so that the transition is to a single energy state. It seems that the local symmetry is intermediate between tetragonal and octahedral symmetry, compared with spectra in [6]. It is consistent with that Fe is substituting Ti, not interstitial sites having lower symmetry, partly because of similar ionic sizes [8] (R_{Fe}^{3+}=0.64 Å, R_{Ti}^{4+}=0.68 Å). We note that *x*=0.1 shows much more distinct XANES features than those of *x*=0.3 or *x*=0.5; smaller intensity of the pre-edge peak as well as a steeper edge step and larger crest around 7128 eV. This may indicate that the Fe-O cage is less distorted such as toward centrosymmetric D_{4h} symmetry for lightly doped *x*=0.1. FEFF8 [9] calculation simulates the decrease of the pre-edge intensity with higher symmetry, and also post-edge distinct features are due to the scattering from second and farther neighbors. *x*=0.1 XANES shows a hump at 7120 eV possibly coming from other electronic transition. On the other hand, size dependent XANES for *x*=0.5 samples show very similar pre-edge peaks and 1*s*→4*p* dipole transition features.

For EXAFS, the initial model is that Fe is substituting for Ti, with fixed coordination 6×O, 8×Pb and 6×Fe neighbors modeled by FEFF6, and bond lengths, DWFs varied. Thus the bond length distribution will be included in the DWF. We are mainly interested in the first coordination, but including higher neighbors sometimes helps obtaining reasonable fits. The multiple scattering in the focusing geometry is evaluated [10] with the angle varied. For all nano and bulk $PbFe_{0.5}Ti_{0.5}O_3$ samples, the Fe-O bond has a large DWF (Fig. 2), ranging (9-11) $\times 10^{-3}$ $Å^2$ with fixed 6 coordination. A similar quality fit is obtained with smaller coordination numbers such as 5. However, due to the limited data range and strong parameters correlation, it could not be distinguished. From the tetragonal bulk $PbTiO_3$ structure, for the Ti-O bond, a large bond length variation could be expected as σ^2=0.04 $Å^2$ with average 2.01Å. In either case, it could be interpreted that 5×O are coordinated to Fe, but 1× O could be located much farther.

A remarkable increase of the DWF was observed from *x*=0.1 to *x*=0.5 for 18 nm NP. This is consistent with the XANES results. The *x*=0.3 NP is fit with shorter bond lengths by 0.03 Å from *x*=0.1 and 0.5 NP. From EXAFS, the size dependence of DWF and bond lengths is nearly constant. Since x-ray diffraction has shown the decrease of c/a with reduction of the particles size, this may indicate that the local FeO_x coordination cage remains distorted regardless of the particle size.

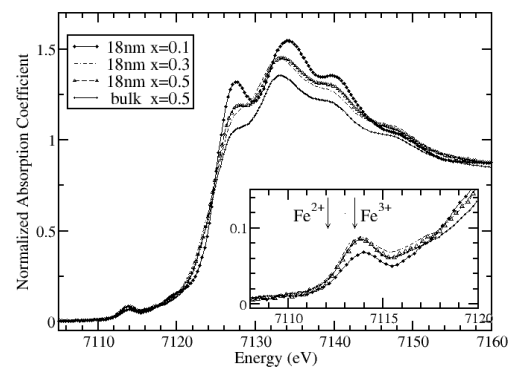

FIGURE 1. Fe K edge XANES for 18 nm $PbFe_xTi_{1-x}O_3$ nanoparticles with *x*=0.1, 0.3 and 0.5 shown with x=0.5 bulk. Inset shows the pre-edge peaks, and the Fe^{2+} and Fe^{3+} peak position is shown as arrows from [6].

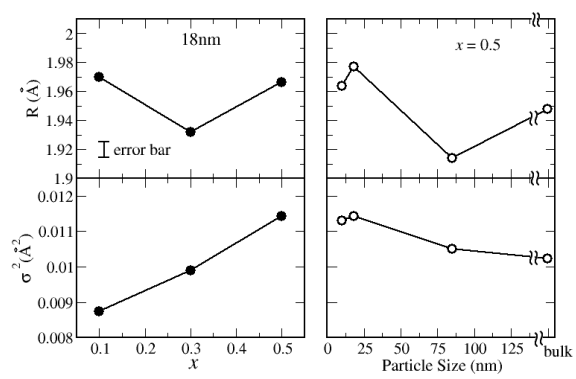

FIGURE 2. Bond lengths and DWFs for the Fe-O bonds. Fixed coordination of 6×(Fe-O). Left: 18 nm NP with several *x*. Right: Size dependence for *x*=0.5.

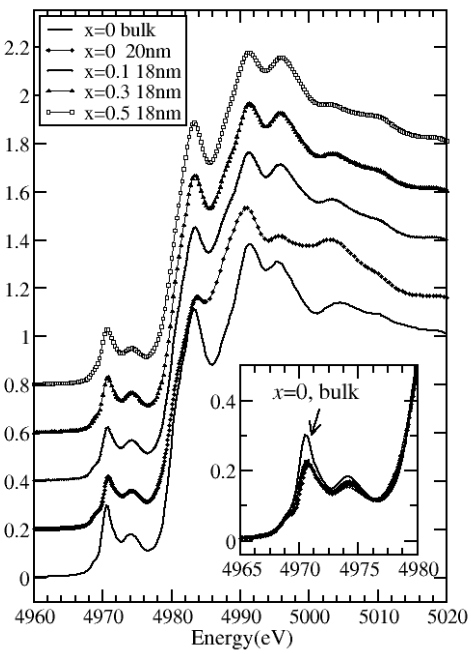

FIGURE 3. Ti K edge XANES for x=0 (20 nm), 0.1, 0.3 and 0.5 for 18 nm NP. The inset shows the pre-edge region. NP samples show much smaller pre-edge peak than the undoped bulk sample. The spectra are shifted for clarity.

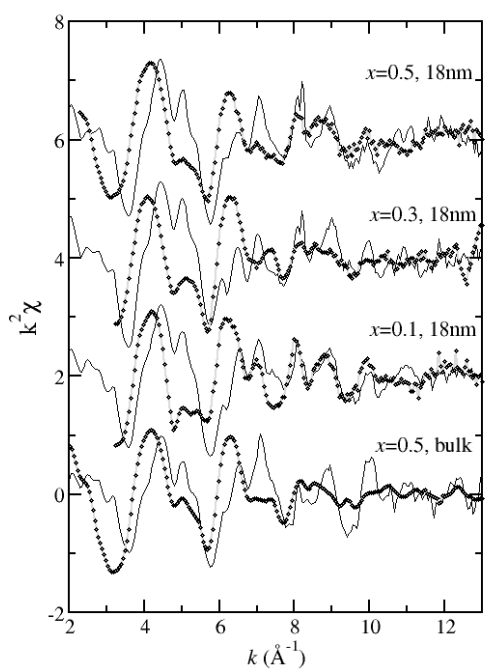

FIGURE 4. $k^2\chi$ of Fe (dot), and Ti (line) K edge are shown for 18 nm NP with several x. Quite different EXAFS oscillation was observed, indicating Fe and Ti environment, including distortion, is different.

Ti K edge: Fig. 3 shows XANES spectra for NP for several x. Similar to the Fe K edge, pre-edge peaks 4960-4976eV features are sensitive to the oxidation states and site symmetry around Ti ions [11]. Characteristic pre-edge with three peaks (one is at the lower energy side shoulder of the middle peak) is seen for all the samples. Here the x=0 bulk sample has the largest pre-edge intensity (see inset of Fig. 3) and a distinct post-edge crest (4982 eV), which decreases for NP, indicating that TiO_6 in NP is less distorted than in bulk x=0. However, for NP with Fe doping, the post-edge peak regains clear features, which suggest that the medium range order develops with doping. This is simulated with different full multiple scattering radii.

Fig. 4 shows the $k^2\ \chi$ for doped NP shown with bulk x=0.5 sample data. The dots are for Fe K edge, and line is Ti K edge data, shown without corrections. For all of these, significant difference in the spectra is seen indicating different Ti and Fe environments.

CONCLUSION

Fe and Ti K edge XAFS is found to be very useful for studying the local environment of $PbFe_xTi_{1-x}O_3$ NP. The most reasonable picture is that Fe is in the 3+ oxidation state, replacing Ti^{4+} ions. For 18-nm NP, x=0.1 NP shows relatively smaller lattice distortion than x>0.3. For NP, the Ti environments are less distorted than for bulk x=0.5. The Fe and Ti environment is significantly different for all samples.

ACKNOWLEDGMENTS

The authors acknowledge Dr. C. Segre of IIT, Dr. T. Bolin of CMC CAT. MRCAT is funded by the MRCAT host institutions. The APS is funded by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract number W-31-109-Eng-38.

REFERENCES

1. G. Shirane *et al*., *J. Phys. Soc. Jpn*, **6**, 265 (1951).
2. G. Shirane *et al*., *Acta.Crystallogr*. **9,** 131 (1956).
3. V.R. Palkar *et al., Solid State Commun*. **134**, 783 (2005).
4. S.I. Zabinsky *et al., Phys. Rev. B* **52,** 2995 (1995).
5. A.J. Berry *et al*., *Am. Mineral*. **88**, 967 (2003).
6. M. Wilke *et al., Am. Mineral*. **86**, 714 (2001).
7. M.A. Arrio *et al., Europhys. Lett*. **51**, 454 (2000).
8. V.V. Laguta *et al*., *Phys. Rev. B* **54** 12353 (1996).
9. A.L. Ankudinov *et al, Phys. Rev. B* **58**, 7665 (1998).
10. A. Frenkel *et al*., *Phys. Rev. B* **49**, 11662 (1994).
11. F. Farges *et al*., *Phys. Rev. B* **56,** 1809 (1997).