Ti K-edge XANES and Pb L_{III}-edge EXAFS studies of PbZr_{0.40}Ti_{0.60}O_{3} ferroelectric material

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Abstract. The structure of PbZr_{0.40}Ti_{0.60}O_{3} crystalline ferroelectric material was studied by powder X-ray diffraction (XRD), X-ray absorption near-edge structure (XANES) at Ti K-edge and Extended X-ray Absorption Fine Structure (EXAFS) at Pb L_{III}-edge. The XRD Rietveld refinement shows a tetragonal crystal structure. The resulting crystal model was used to calculate both theoretical XAFS spectra. The mismatch between experimental and calculated XAFS spectra is interpreted as a consequence of the random distribution of Ti and Zr. The resulting disorder effect is averaged in the long-range structure probed by XRD whereas the XAFS techniques probe the local order of each site.

1. Introduction

Lead zirconate titanate (PbZr_{1-x}Ti_{x}O_{3}) is an alloy of lead titanate (PbTiO_{3}) and lead zirconate (PbZrO_{3}) which presents a perovskite structure (ABO_{3}). This system has been studied due to its interesting piezoelectric, pyroelectric, ferroelectric and dielectric properties [1]. Because of these characteristics, PbZr_{1-x}Ti_{x}O_{3} (PZT) system has been used in a great number of applications in many areas, such as hydrophones, thermal imaging, nonvolatile memories, surface acoustic wave generators, capacitors and gas sensors [1].

The PZT system exhibits a cubic structure at higher temperatures and three different structures at room temperature depending on the composition: tetragonal, orthorhombic or rhombohedral. According to the proposed phase diagram [2], at the titanium-rich side all compositions present tetragonal structure with $P4mm$ symmetry. On the other hand depending on the composition and the temperature, two rhombohedral phases, $R3m$ and $R3c$, are known to occur in Zr-rich PZT ceramics.

Most XAFS works of the PZT system involve Zr-rich compositions [3]. On the other hand, there are few works available in the literature about the short-range order structure of Ti-rich compositions [4, 5]. The most complete studies of Ti rich PZT compounds [5] are essentially devoted to the XAFS study of amorphous compounds and thin films prepared by sol-gel methods. On the contrary, the aim of the present study is to characterize the local structure of the tetragonal ferroelectric PbZr_{0.40}Ti_{0.60}O_{3} system, prepared by ball milling and calcination, using XAFS at Ti K-edge and Pb L_{III}-edge and to compare these local structures with those obtained by powder XRD refinement.
2. Experimental

PZT ceramic sample was prepared by the conventional mixed oxide method. The oxides, PbO, ZrO$_2$ and TiO$_2$, weighed according to stoichiometry, were mixed by ball milling and calcined at 850 °C for 4 h. The sintering process was performed at 1100 °C for 2 h in a rich Pb atmosphere to avoid losses in stoichiometry.

X-ray powder diffraction patterns were measured at room temperature on a Rigaku Denki powder diffractometer with geometry $\theta$-2$\theta$, a rotating anode X-ray source (Cu-K$_\alpha$ radiation, $\lambda = 1.542$ Å), and a scintillation detector. The measurements were carried out using a current of 100 mA and tension of 50 kV. The data were collected with a step size of 0.02°. The count time was 5 s per step. The refinement of the structure was carried out using the Rietveld method and the program used was the General Structure Analysis System (GSAS) [6].

The titanium K-edge and the lead L$_{III}$-edge X-ray absorption spectra were collected at LNLS (Brazilian National Synchrotron Light Laboratory) facility on the D04B-XAS2 beamline. The storage ring was operated at 1.36 GeV and 100-160 mA. X-ray absorption spectra were collected at the Ti K-edge (4966 eV) and the Pb L$_{III}$-edge (13055 eV) in transmission mode at room temperature using a Si(111) channel-cut monochromator. Normalized XANES and EXAFS spectra were obtained by the Multipatform Applications for XAFS code (MAX) [7]. Theoretical XANES and EXAFS spectra were calculated with the ab initio FEFF8.4 code [8]. Random distributions of Zr and Ti atoms were generated by CRYSTALFFREV, the FEFF input file generator of MAX [7].

3. Results and discussion

Figure 1 shows the XRD pattern of PZT sample at room temperature. According to the literature, this XRD pattern corresponds to a tetragonal structure with a $P4mm$ space group [9]. This type of structure was used as the initial model to perform Rietveld refinement. The calculated XRD pattern and the difference between experimental and calculated diffractograms are shown in Figure 1. The model used in this refinement fits well the XRD pattern with the following refinement statistics: $wR_p = 0.1033$, $R_p = 0.073$, $\chi^2 = 2.758$ and $R(F^2) = 0.0487$. The calculated values of cell parameters $a$ and $c$ are equal to 4.0041(8) Å and 4.1460(5) Å respectively and the fractional coordinates are shown in Table 1.

Figure 1. Experimental and calculated XRD patterns of the PZT. The difference between the two patterns and the Bragg positions are presented below the diffractograms.

Figure 2 shows the experimental and calculated XANES spectra at Ti K-edge (a) and Pb L$_{III}$-edge (b). In Fig. 2a, the pre-edge feature labeled as A is due to quadrupolar transitions of $t_{2g}$-type molecular orbitals located in the absorption atom (Ti) [10]. The transitions named as B are caused by hybridization of p- and d-symmetry states at the Ti atom under the influence of the neighboring oxygen atoms that takes place if the inversion symmetry is broken relative to the absorbing atom instantaneous position [10]. The pre-edge feature labeled C is attributed to Ti 1s electron transition to the unoccupied 3d states of the neighboring Ti atoms and the transition named as D occurs if there are 4d atoms in the vicinity of the absorbing Ti atom, for instance, Zr atoms in the PZT solid solution [10].
The transitions labeled E, F, G, H and I beyond the absorption edge are related to electronic transitions and atomic structure of second and third neighbors of Ti within distances up to 8 Å [10].

Table 1. Fractional coordinates for PZT sample.

| atom     | fractional coordinates | x       | y       | z       |
|----------|------------------------|---------|---------|---------|
| Pb       | 0.027(0) 0.027(0) 0.001(1) |         |         |         |
| Ti       | 0.500(0) 0.500(0) 0.545(0) |         |         |         |
| Zr       | 0.500(0) 0.500(0) 0.545(0) |         |         |         |
| O(1)     | 0.500(0) 0.500(0) 0.101(2) |         |         |         |
| O(2)     | 0.500(0) 0.000(0) 0.618(2) |         |         |         |

The theoretical FEFF8.4 (Full Multiple Scattering Self-Consistant Energy) XANES spectrum in Fig. 2a was calculated in terms of a 6 Å and 68 atoms cluster, centered on the Ti site, derived from the XRD parameters obtained through the Rietveld refinement. This spectrum reproduces reasonably the XANES structure present in the experimental spectrum. All the transitions exhibit a displacement in energy by a few electron volts and the transitions labeled as E and G present a lower intensity than the in experimental spectrum. Moreover, the pre-edge features labeled as C and D in the experimental spectrum do not appear in the theory.

In the experimental Pb L$_{III}$-edge XANES spectrum showed in Fig. 2b, the absorption features after the edge are related to the internal transitions between the 2p and the empty nd states in Pb$^{2+}$ ions [11]. In order to calculate this spectrum theoretically, a cluster with a size up to 6 Å and 61 atoms around the Pb absorber was created using the XRD refinement results. As can be seen in Fig 2b, the calculated spectrum exhibits some discrepancies with the experimental one. The transitions present a displacement of few electron volts in energy positions and the first transition after the edge do not fit.

![Figure 2. Experimental and calculated XANES spectra in Ti K-edge (a) and Pb L$_{III}$-edge (b).](image)

Figure 3a shows the experimental and calculated EXAFS spectra of Pb L$_{III}$-edge of PZT. The FEFF multiple scattering expansion model was also based on the Rietveld refined structure, without any distances fitting. The only fitted parameter was a global Debye-Waller of 0.009 Å$^2$. The corresponding Fourier transforms moduli are presented in Figure 3b. The two first peaks present reasonable agreement. According to the theoretical model, the first peak is related to the first Pb-O neighbors and the second peak corresponds to the second Pb-O and first Pb-Ti/Zr neighbors. The shoulder between 3 and 4 Å in the calculated curve, which is not observed in the experimental curve, is also related to Pb-Ti/Zr neighbors, first Pb-Pb neighbors and contributions of multiple-scattering paths (Pb-Ti-O, Pb-O-O and Pb-Zr-O).

Although the XRD Rietveld refinement fits correctly the powder diffraction data, the crystallographic model used to create the XANES and EXAFS theoretical spectra appears inappropriate to describe the short-range order structure in PZT. These discrepancies between XRD
and XAS results is basically due to the random distribution of Ti and Zr sites which are averaged in the crystal structure probed by XRD.

**Figure 3.** Experimental and calculated $k \chi(k)$ of Pb L$_{III}$-edge EXAFS (a) and the corresponding moduli of the Fourier transforms (b).

### 4. Conclusions

The crystal structure of PbZr$_{0.40}$Ti$_{0.60}$O$_3$ probed by powder XRD provides crystallographic information to the calculation of the XAFS spectra. The resulting theoretical XAFS spectra do not match completely the experimental data, neither at the Ti K-edge nor at the Pb L$_{III}$-edge. This apparent discrepancy between local and crystallographic structures is another example of disorder effect on the averaged crystal structures refined on the Bragg reflexions of dopped and partially substituted materials. This work represents the first XAFS results of a complete study of La and Ba dopped PZT crystalline ferroelectric materials where crystal and local structures at Pb, Zr and Ti edges are probed both by powder XRD and XAFS.

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