Fe K-edge X-ray absorption spectroscopy study of Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$-PbTiO$_3$ multiferroic ceramics

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The present paper is a comprehensive study concerning Fe K-edge X-ray absorption spectroscopy (XAS) measurements, which were performed to characterize the local structure of $(1 − x)$Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$–xPbTiO$_3$ samples as a function of temperature and PbTiO$_3$ content. Results obtained by the fits of extended X-ray absorption fine structure consist with rhombohedral symmetry for Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$ composition at temperatures lower than room temperature. This result is in apparent disagreement with X-ray and neutron diffraction characterization which have been reported. This apparent disagreement is related to the fact that XAS probes the short-range order, whereas X-ray diffraction provides structural information about the average structure. Moreover, as the PbTiO$_3$ content increases, a disorder has been detected at local structure of the FeO$_6$ octahedron. Analysis of X-ray absorption near edge structure spectra did not show modifications in intensity nor energy of transitions. © *2013 American Institute of Physics*.
[http://dx.doi.org/10.1063/1.4795505]

I. INTRODUCTION

Multiferroic materials have attracted much attention in the last years due to the coexistence of magnetic and electric ordering.[1] The search for these materials is driven by the prospect of controlling charges by applied magnetic fields or spins by applied voltages, and using this ability to construct new forms of multifunctional devices.[1] It is possible due to the magnetoeletric coupling, which can be observed in multiferroic materials in the regions where magnetic and ferroelectric ordering coexists and in many cases is mediate via lattice strain.[2]

Among these materials, lead iron tungstate Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$ (PFW) is known as a perovskite-type structure in which Fe^{3+} and W^{6+} are randomly distributed at the octahedral B-site positions and presents ferroelectric and antiferromagnetic ordering. PFW has a frequency dependent permittivity with a broad maximum around 180 K, which makes difficult practical applications.[3–5] Challenges for technological applications require preferentially that the magnetic and ferroelectric ordering coexistence occurs around room temperature and a low electric conductivity, in order to enable the poling of the sample. Thus, by adding PbTiO$_3$ to PFW structure, forming the $(1−x)$Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$–xPbTiO$_3$ (PFW–PT) system, this substitution causes changes of symmetry and the range of temperature where magnetic and ferroelectric ordering coexists, depending on the PbTiO$_3$ contents.[6] Moreover, a transition from relaxor to normal ferroelectric state is induced as the PbTiO$_3$ content increases.[2]

Although the long-range structure and the electrical/magnetic properties of these compounds has been characterized in order to better understand the processes of phase transition and electrical/magnetic behavior of these compounds, as far as authors know, there are no studies concerning the local structure of PFW-PT compounds probed by X-ray absorption spectroscopy (XAS). This technique is a powerful tool to investigate local structure and provides a good likelihood of obtaining additional structural information of the materials.[7] The displacements or off center position of transition metal atoms in lattice sites of high symmetry can be determined both from extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES), which are known to be independent and very sensitive probes.[8–10] Although the information about interatomic distances given by EXAFS is usually not sufficient for constructing the whole structural model, it often provides valuable information about the structural peculiarities and allows us to verify a structural model.[8] XAS technique has been applied in the study of the structure of ferroelectric compounds and has provided information on their structure and its thermal and compositional variation.[8–10] The investigation of structural phase transitions in a large number of ferroelectric materials with perovskite structure has shown that the change in macroscopic symmetry surprisingly causes only minor modifications in the local structure of the constituent atoms, which can maintain a high degree of distortion even in samples showing a structure in average identified as "cubic" symmetry.[7,8,11,12] Our previous study concerning Fe K-edge EXAFS measurements for Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ compound allowed to better understand anomalies observed in anelastic and pyroelectric measurements, which were correlated to phase transition.[13]

Thus, the present paper concerns a study about the local order and electronic structure of PFW and PFW-PT compounds, which has been performed using X-ray absorption fine structure at the Fe K-edge at the EXAFS and XANES regions of X-ray absorption spectra.

II. EXPERIMENTAL PROCEDURE

A similar to the two-stage solid-state reaction process, first used by Swartz and Shrout to fabricate perovskite PMN, was followed in this study.[2] Experimental details about the preparation of PFW and PFW-PT samples are given elsewhere.[2,14] Ceramic samples of $Pb(Fe_{2/3}W_{1/3})O_3$ and $(1-x)$ $Pb(Fe_{2/3}W_{1/3})O_3$–$xPbTiO_3$ (PFW100xPT) compositions were prepared with $=0.00$, 0.10, 0.20, and 0.030.

EXAFS and XANES spectra at the Fe K-edge of PFW and PFW100xPT samples were collected in transmission mode as a function of the temperature using a Si(111) channel-cut monochromator on the D04B-XASF2 beamline at the LNLS (National Synchrotron Light Laboratory) facility. EXAFS spectra at the Fe K-edge were recorded for each sample between 7050 and 7900 eV using an energy step of 2 eV, whereas XANES spectra were recorded between 7020 and 7200 eV with an energy step of 0.3 eV. The extraction and fit of EXAFS spectra were performed using the Multi-Platform Applications for X-ray absorption (MAX) software package[15] and theoretical spectra were calculated using FEFF8.2 code.[16]

Quantitative structural data concerning the first coordination shell around Fe atoms were modelled by selecting the peak located between 1.0 and 2.0 Å of the modulus of Fourier transform (FT) of EXAFS spectra. Because of the great number of multiple scattering paths in region beyond 2.0 Å, only the first peak of the Fourier transform of EXAFS spectra was selected in all investigated samples. Structural information concerning Fe first coordination shell (Fe-O interactions) was then obtained by fitting the back-Fourier transform EXAFS spectra. In all fits, the number of free parameters was kept smaller than the number of independent points, which is defined as $N_{ind} = 2\Delta R\Delta K/\pi$, where ΔR is the width of the R-space filter windows and ΔK is the actual interval of the fit in the K space.[17] The reliability of the fit, determined by a quality factor (QF),[17] and interatomic distances (R) and Debye-Waller factor (σ^2) relative to the best fits are shown in Table I. In all fits, R, σ^2, and ΔE_0 were the parameters left to vary. The Fe-O neighbours number (N) was maintained fixed because it is not expected modification

and in order to maintain the number of free parameters smaller than the number of independent points.

III. RESULTS AND DISCUSSION

Figure 1(a) presents the XANES spectra at Fe K-edge of PFW sample measured at 130, 230, 270, 300, and 410 K, and of iron oxides standards samples (FeO and Fe_2O_3) measured at room temperature. Figure 1(b) shows the XANES spectra at Fe K-edge of PFW-PT samples as a function of PT content measured at 130 K in order to compare samples in ferroelectric phase.[2] The XANES spectrum of the Fe K-edge comprises peaks which have been identified as transitions between bound states: $1s$ to $3d$ (peak in the pre-edge around 7113 eV), $1s$ to $4s$ (shoulder in absorption edge), and $1s$ to $4p$ (peak after the edge).[18] The peak located in the pre-edge region, related to $1s$ to $3d$ transitions, can be attributed to electronic dipole or quadrupole transitions, which are usually up to 100 times weaker than the dipole transitions.[18] This dipole transitions to $3d$ states should be forbidden but gains intensity due to mixing with $4p$ orbitals whose dipole transitions are allowed. This mixture of $3d$-$4p$ orbital is increased
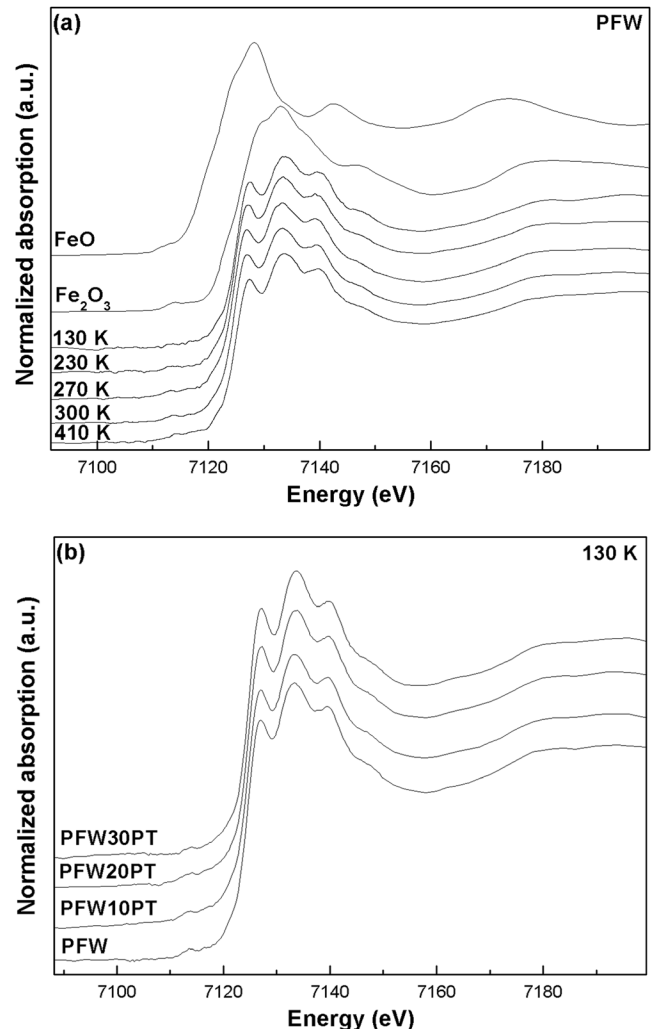
FIG. 1. XANES spectra at Fe K-edge for (a) PFW sample and Fe oxides standards as a function of temperature and (b) PFW-PT samples as a function of $PbTiO_3$ content.

TABLE I. Fe K-edge EXAFS simulated structural parameters for PFW sample at different temperatures using structural models with rhombohedral or cubic symmetries.

	Shell	N	R (Å)	σ^2 (Å2)
130 K rhombohedral	Fe-O$_I$	2	2.05(2)	0.0036(23)
	Fe-O$_{II}$	2	1.95(4)	
	Fe-O$_{III}$	2	2.13(4)	
	QF = 0.40			
230 K rhombohedral	Fe-O$_I$	2	2.04(1)	0.0011(22)
	Fe-O$_{II}$	2	1.94(2)	
	Fe-O$_{III}$	2	2.14(2)	
	QF = 0.63			
300 K Cubic	Fe-O$_I$	6	1.99(1)	0.0091(8)
	QF = 0.49			

by the coordination environment of low symmetry. As a result, quadrupole transitions are important for centrosymmetric sites, resulting in pre-edge peaks less prominent, while in other cases (no center of inversion) dipolar electronic transitions are responsible for a greater intensity in this region of the spectrum.[18] Thus, transitions to the tetrahedrally coordinated Fe are more intense than transitions in Fe in octahedral coordination.[18]

As can be seen in Figures 1(a) and 1(b), no changes are observed on the XANES spectra of PFW and PFW-PT samples with the increasing of temperature or the PT content.

As pointed out earlier, the short-range structural data provided by EXAFS offer an element-specific insight, giving quantitative information about the number, position, and identity of atoms surrounding the absorbing element as well as structural disorder within the coordination spheres. Figure 2 shows the modulus of Fourier transform of PFW sample extracted from Fe K-edge EXAFS spectra ($\chi(k)$) collected at different temperatures.

In order to obtain qualitative information from experimental EXAFS spectra, theoretical EXAFS spectra were calculated considering the reported crystalline structures of PFW structure.[19] In a study of PFW compound using neutron diffraction measurements between 10 and 700 K, Ivanov *et al.* determined that the symmetry remains cubic with a *Pm-3m* space group in the whole temperature range measured. Mitoseriu *et al.* also identify a cubic symmetry for PFW at 85 K, but reported a possible separation of peaks between 160° and 163° due to a rhombohedral phase with *R3m* space group.[20] However, these authors argue that the difference between the two types of symmetries of PFW, the cubic and the rhombohedral, could not be clearly detected by X-ray diffraction measurements due to limitations of their experimental accuracy.[20] Thus, theoretical EXAFS spectra were calculated using FEFF8.2 code[16] considering structural models with a cubic (*Pm-3m* space group) or a rhombohedral (*R3m* space group) symmetries. As the increase of PT content induces a cubic to tetragonal structural phase transition in PFW-PT compounds,[20] a tetragonal symmetry (*P4mm* space group) was also taken into account.
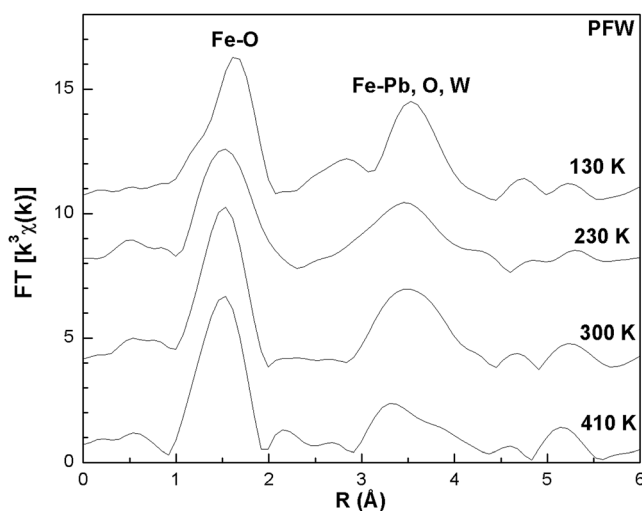
According to these structural models, the more intense peak, between 1.0 and 2.0 Å in the FTs of PFW sample, corresponds to single scattering interaction between the first six O atoms and the Fe atoms. The single scattering interactions relative to Fe-Pb, Fe-W, and Fe-O (beyond the first neighbours at FeO_6) paths correspond the peaks and shoulders observed between 2.0 and 5.0 Å. This region also includes multiple scattering paths such as Fe-O-O, Fe-O-Fe-O, Fe-Pb-O, Fe-W-O, Fe-Fe-O, Fe-O-W-O, and Fe-O-O-O interactions. The intensity relative to this region decreases with increasing temperature, due to the increase of the Debye-Waller factor as the temperature increases. Due to the complexity of the multiple scattering paths and the noise level, we could not perform the fitting of the peaks between 2.0 and 5.0 Å.

The first peak of the Fourier transform curves corresponding to the PFW samples (Figure 2) was then back Fourier transformed in order to obtain the experimental EXAFS spectra corresponding only to the first Fe-O coordination shell. The experimental and theoretical EXAFS spectra regarding only the first coordination shell of PFW samples are shown in Figure 3. As can be seen in Figure 3, the best fits were those using the rhombohedral symmetry at 130 K and 230 K and cubic symmetry at room temperature. The fitting results in Table I show that as the temperature increases from 130 to 230 K, there are no changes on the values of Fe-O interatomic distances. Moreover, in this temperature range, the Debye-Waller factor does not show differences within the margin of error, only increasing considerably its value on the case of the cubic symmetry.

Thus, the analysis of EXAFS spectra shows that local structure of PFW compound at 230 K and lower temperatures is compatible with rhombohedral symmetry. This result is in apparent disagreement with previous studies, which reported a local cubic symmetry for PFW samples, even at temperatures below the temperature of maximum permittivity.[19,20] However, this result is in accord with our previous EXAFS results at W L_{III}-edge whose fits showed agreement with local rhombohedral symmetry for WO_6 octahedron at lower temperatures.[21]

FIG. 2. Modulus of Fourier transform of $k^3\chi(k)$ EXAFS spectra for PFW sample as a function of temperature.
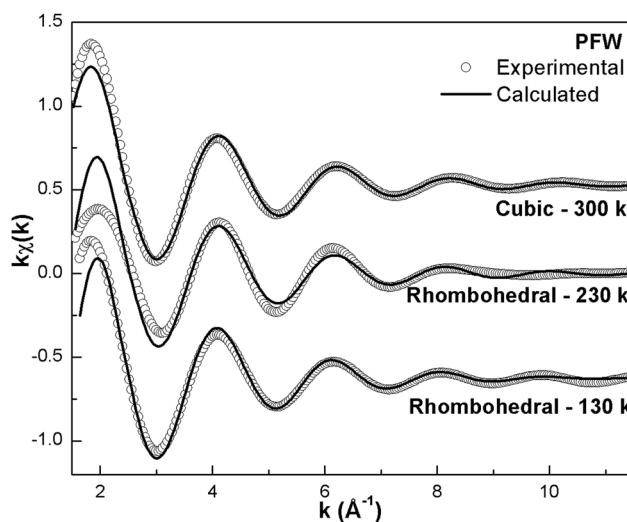

FIG. 3. Fitting and back-Fourier-filtered experimental signal of the Fe-O first shells for PFW sample at 130 K, 230 K, and 300 K.

A difference in the local symmetry obtained by different characterization techniques was also observed by other authors. Sicron *et al.* also report the observation of results consistent with a cubic symmetry through X-ray diffraction technique and a local tetragonal symmetry by XAS technique when they studied the $PbTiO_3$ compound.[22] Teslic and Egami[23,24] also have reported a similar discrepancy when they studied the local atomic structure of $PbZr_{1-x}Ti_xO_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb_{1-x}La_xZr_yTi_{1-y}O_3$ systems through X-ray diffraction and neutron scattering measurements. Their structural studies yielded evidence of slight local deviations from crystallographic lattice periodicity and local chemical ordering.

The apparent discrepancy between the results of these two techniques can be explained in terms of the level of disorder that these techniques can detect. In X-ray absorption spectroscopy, the physical process involved in the absorption occurs in the order of 10^{-15} s,[22] which is smaller than the time scale of the changes in the system, enabling to observe dynamic and fast disorder processes.[22] Regarding the technique of X-ray diffraction, the impossibility of observing the distortion at the local level is related to the structural model used in the refinements, a periodic pattern in which local distortions are not considered.[11] As a result, the XAS technique allows a better visualization of local distortions than X-ray diffraction technique. Summarizing, the discrepancy is basically due to the fact that X-ray absorption spectroscopy probed the short-range order, whereas X-ray diffraction provides structural information about the average structure.[11]

Moreover, it was expected that the symmetry of PFW structure is not completely cubic. Our previous study concerning electrical properties of this compound showed ferroelectric hysteresis loops at 80, 100, 160, and 200 K.[14] If the symmetry were completely cubic, the structure would correspond to the paraelectric phase instead of a ferroelectric one. Therefore, the observation of the ferroelectric hysteresis loops would not be expected.

The moduli of Fourier transform EXAFS spectra of PFW-PT samples measured at 130 K are shown in Figure 4. As can be seen in this figure, a decrease in the intensity of the first peak relative to the Fe-O interactions is observed w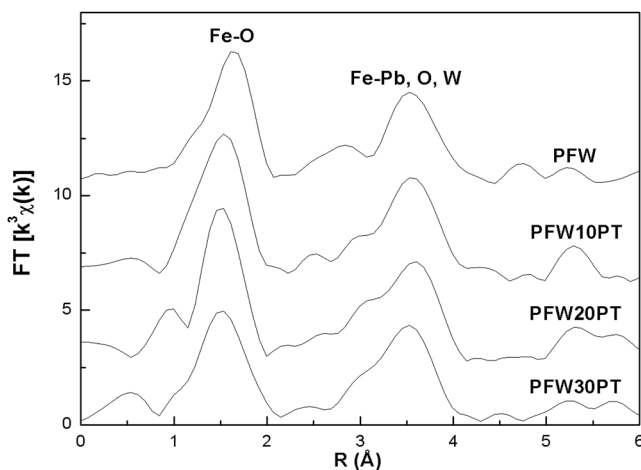ith the addition of the $PbTiO_3$ composition. A decrease in the intensity of the Fourier transform first peak can be related to an increase of the Debye-Waller factor, which means an increase in the structural disorder in first neighbors or a decrease in the neighbor's number around Fe atoms. In order to obtain quantitative structural data related to the first peak relative to the Fe-O interactions, a back Fourier transform of the first peak was undertaken and EXAFS spectra related only to the first peak (Fe-O interactions) were obtained.

The structural models used during the fitting procedure of the back Fourier transform EXAFS spectra were cubic symmetry (*Pm-3m* space group), rhombohedral symmetry (*R3m* space group), and tetragonal symmetry (*P4mm* space group). Figure 5 shows the interatomic distances and Debye-Waller factors relative to the best fits for each sample at 130 K. In these fits, the values of QF ranged from 0.19 to 0.40, indicating good reliability for the obtained results.

As discussed earlier, the fits of the EXAFS spectra of PFW composition at 130 and 230 K are compatible with rhombohedral local symmetry around Fe atoms. As illustrated in Figure 5, the fitting of the EXAFS spectra of PFW10PT sample measured at 130 K is also compatible with local rhombohedral symmetry. Interatomic distances and Debye-Waller factor do not show differences when compared to the structural data of PFW sample. With the increasing of $PbTiO_3$ content, the local structure around Fe atoms becomes more consistent with a tetragonal local symmetry. In Figure 5, the interatomic distances for PFW20PT and PFW30PT are shown and only FeO_I and FeO_{II} interactions can be assigned. In this symmetry, the neighbourhood of the Fe atoms is formed by one shell with two O atoms (FeO_I) and another with four O atoms (FeO_{II}) whereas the FeO_6 octahedra is formed by three shells of two O atoms each one around Fe in rhombohedral symmetry.

The observation of a local tetragonal symmetry for the PFW20PT and PFW30PT samples is in agreement with results obtained by X-ray diffraction that has been reported for this composition.[20] Regarding the Debye-Waller factor, it is observed an increasing as the amount of $PbTiO_3$ increases, which explains the decrease on the Fourier transform magnitude in Figure 4. This result indicates a higher degree of disorder at FeO_6 octahedron due to the addition of $PbTiO_3$ to

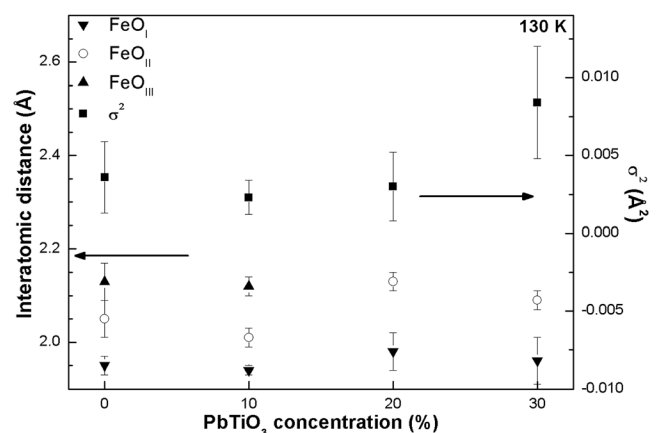FIG. 4. Modulus of Fourier transform of $k^3\chi(k)$ EXAFS spectra for PFW-PT samples as a function of $PbTiO_3$ content at 130 K.

FIG. 5. Interatomic distances and Debye-Waller factor for PFW-PT samples at 130 K. The convention to assign the FeO_I to $_{III}$ changed, compared to Table I.

PFW structure. In terms of dielectric permittivity characterization, our previous study showed a transition from a relaxor to a normal ferroelectric state induced with the increasing of $PbTiO_3$ content.[2]

IV. CONCLUSIONS

Fe K-edge XAS measurements were performed to characterize the local structure of PFW-PT samples as a function of temperature and $PbTiO_3$ content. Analysis of XANES spectra did not show modifications in intensity or energy of transitions. Results obtained by the fitting EXAFS spectra revealed rhombohedral symmetry at lower temperatures (below room temperature) for PFW composition. This result is in apparent disagreement with X-ray and neutron diffraction characterization, which have been reported cubic symmetry. This disagreement is due to the fact that X-ray absorption spectroscopy probed the short-range order, whereas X-ray diffraction provides structural information about the average structure. Furthermore, our previous study concerning electrical properties of this compound showed ferroelectric hysteresis loops at lower temperatures, which would not be expected since the completely cubic structure corresponds to the paraelectric phase instead of a ferroelectric one. Therefore, the observation of the ferroelectric hysteresis loops would not be expected. Moreover, as the $PbTiO_3$ content increases, a disorder has been detected at local structure of FeO_3 octahedron.

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