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Local structure around Fe ions on multiferroic Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ ceramics probed by x-ray absorption spectroscopy

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Local structure around Fe ions on Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ ceramics was probed by x-ray absorption spectroscopy in order to settle the controversies about its structure. It is observed that the shell structure around Fe atoms exhibits a monoclinic local symmetry at 130 and 230 K, tetragonal local symmetry at room temperature, and cubic local symmetry at 410 K. Independently of the coordination, temperature, or symmetry, Fe-O mean bond-length does not vary significantly.

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In recent years, multiferroic materials have attracted much attention viewing to explore and understand details about the coexistence of magnetic and electric ordering. 1 The search for these materials is driven by the prospect of controlling charges applying magnetic fields and spins applying electric fields and use this ability to construct new forms of multifunctional devices. 1 Among the multiferroic materials, PbFe$_{1/2}$Nb$_{1/2}$O$_3$ (PFN) is a Pb-based perovskite which exhibits high dielectric constant, diffuse ferroelectric phase transition, and low sintering temperature, making this material an attractive candidate for applications such as multilayer ceramic, capacitors, and other electronic devices. 2 PFN presents a ferroelectric phase transition with Curie temperature $T_C \approx 380$ K and G-type antiferromagnetic ordering below the Néel temperature ($T_N \approx 140–170$ K). 2

Although multiferroic properties have been well characterized, there exist controversies about the structure of PFN as a function of the temperature. In a study concerning synchrotron x-ray diffraction for powder and single crystals of PFN, Bonny et al. have been reported a monoclinic ferroelectric structure at 293 K, which undergoes a structural transition at 355 K (for single crystals) to another ferroelectric phase with tetragonal symmetry, which would be stable up to 376 K, temperature in which occurs a phase transition to a paraelectric structure with cubic symmetry. 3 These results are consistent with the study of Lampis et al., 4 who performed neutron and x-ray diffraction experiments in PFN powders obtained by grinding single crystals, although these authors have shown a monoclinic distortion ("pseudo-rhombohedral" structure) in the ferroelectric phase with measurements performed at 80, 250, and 363 K. On the other hand, it has been pointed out that the structure of PFN ceramic samples corresponds to a rhombohedral symmetry. 5 In agreement with this result, Ivanov et al. refined the structure from neutron diffraction measurements as a rhombohedral symmetry at 10 and 300 K. 6 However, more recently, it has been published that PFN exhibits monoclinic structure with $Cm$ space group from 12 K up to room temperature. 2

Since x-ray absorption spectroscopy (XAS) is highly sensitive to local symmetry change, this technique is an interesting method to analyze the complex structure of multiferroic PFN with compositional and structural disorder. The short-range structural data provided by EXAFS offers an element-specific insight, giving information about the number, position, identity, and structural disorder of atoms surrounding the absorbing element within the coordination spheres. As far as we know, there are no studies available in the literature concerning the local structure of PFN composition wherein XAS technique has been applied.

Thus, polycrystalline PFN sample was prepared following the columbite route and characterized with XAS technique. The experimental details of synthesis and sintering of PFN sample are given elsewhere. 7 In order to confirm the nominal composition, energy-dispersive x-ray spectroscopy (EDX) measurements were performed. The average atomic percentages for Pb, Fe, and Nb obtained are 1.0, 0.50, and 0.50, which is the nominal composition. Microstructural characterization was carried out in a scanning electron microscopy (SEM) (Jeol/S800LV). SEM images were performed on a fractured surface and is shown in Fig. 1. The average grain size is around 3–4 μm.

The iron K-edge XAS data were collected at the Fe K-edge (7112 eV) in transmission mode as a function of the temperature using a Si(111) channel-cut monochromator using the D04B-XASF2 beam line at the LNLS (National Synchrotron Light Laboratory). Extended x-ray absorption

![FIG. 1. SEM micrograph for PFN sample.](image-url)
fine structure (EXAFS) spectra at the Fe K-edge were recorded for each sample between 7050 and 7900 eV using energy steps of 2 eV. The extraction of EXAFS spectra was performed using the multi-platform applications for x-ray absorption (MAX) software package, and theoretical spectra were calculated using FEFF8.2 code.

Fig. 2 shows the corresponding Fourier transform moduli (FT) of EXAFS oscillations obtained at Fe K-edge of PFN ceramics measured at different temperatures. It can be observed a more intense peak between 1.0 and 2.0 Å does not show a significant modification as a function of the temperature. As Fe atoms is in a octahedral symmetry, the peak between 1.0 and 2.0 Å corresponds to single scattering interaction between Fe and the six O atoms, forming the coordination shell. The single scattering interactions relative to Fe-Pb, Fe-Nb, and Fe-O (beyond the FeO₆ coordination shell) paths correspond to the peaks and shoulders lying between 2.0 and 5.0 Å in Fig. 2. This region also includes multiple scattering paths such as Fe-O-O, Fe-O-Fe-O, Fe-Pb-O, Fe-Nb-O, Fe-Fe-O, Fe-O-Nb-O, and Fe-O-O-O interactions.

In order to obtain quantitative structural data concerning the coordination shell, the neighbourhood of Fe atoms was modelled by the analysis of the back-Fourier transform EXAFS spectra of the peak between 1.0 and 2.0 Å. Because of the large number of possible multiple scattering paths, back-Fourier filtered spectra relative to peaks beyond 2.0 were not fitted. In all fits, the number of free parameters was kept smaller than the number of independent points defined as N_{ind} = 2ΔRΔK/π, where ΔR is the width of the R-space filter windows and ΔK is the actual interval of the fit in the K space. The reliability of the fit was determined by a quality factor (QF). Interatomic distances (R) and Debye-Waller factor (σ²) are shown in Table I. In all fits R, σ², and absorption edge shift (ΔE₀) were the parameters left to vary, and as it is not expected modification in the number of neighbours (N), this parameter was fixed during the fitting procedure.

As discussed above, there are controversies about the structure of the PFN ferroelectric phase, which was assigned as monoclinic and rhombohedral symmetries. The back Fourier transform EXAFS spectrum of PFN at 130 K was fitted using the theoretical phase and amplitude functions calculated using FEFF8.2 code, considering two different structures phases: one obtained from a monoclinic structure with a Cm space group and the other with a rhombohedral structure with a R₃m space group. The fitting results are presented in Table I while experimental and fitted spectra of both situations are shown in Fig. 3. On the monoclinic local structure model, the neighbourhood of Fe atoms is formed by four shells of O atoms: two with one O atom and two with two O atoms, whereas in the rhombohedral local structure model, Fe atoms are surrounded by three shells of O atoms with two atoms in each one. As can be

**Table I.** Fe K-edge EXAFS simulation results for PFN sample at different temperatures assuming structural models with monoclinic, rhombohedral, and tetragonal symmetries.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Structure</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>QF</th>
</tr>
</thead>
<tbody>
<tr>
<td>130 K</td>
<td>Monoclinic</td>
<td>Fe-O1</td>
<td>1</td>
<td>1.99(8)</td>
<td>0.0070(11)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O2</td>
<td>2</td>
<td>1.98(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O3</td>
<td>2</td>
<td>1.97(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O4</td>
<td>1</td>
<td>2.17(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>130 K</td>
<td>Rhombohedral</td>
<td>Fe-O1</td>
<td>2</td>
<td>1.97(1)</td>
<td>0.0009(10)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O2</td>
<td>2</td>
<td>2.64(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O3</td>
<td>2</td>
<td>2.82(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>297 K</td>
<td>Monoclinic</td>
<td>Fe-O1</td>
<td>1</td>
<td>1.89(9)</td>
<td>0.0076(9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O2</td>
<td>2</td>
<td>2.00(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O3</td>
<td>2</td>
<td>2.01(23)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O4</td>
<td>1</td>
<td>2.05(40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tetragonal</td>
<td>Fe-O1</td>
<td>2</td>
<td>2.00(6)</td>
<td>0.0087(12)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O2</td>
<td>4</td>
<td>2.00(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cubic</td>
<td>Fe-O1</td>
<td>6</td>
<td>2.03(4)</td>
<td>0.0047(13)</td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 2.** Fe K-edge Fourier transform modulus for PFN at 130, 230, 297, and 410 K.

**FIG. 3.** Fitting and back-Fourier-filtered experimental spectrum at 130 K.
seen in Fig. 3, the best fitted was attained when the monoclinic crystallographic model was used. The large difference between QF values for the two models also confirms that the rhombohedral symmetry is not compatible with the local structure around Fe atoms on the PFN sample measured at 130 K.

The fitting of the EXAFS spectra extracted from the peak positioned between 1.0 and 2.0 Å at FT of PFN sample measured at 230 K (not shown in this letter) was also performed and showed a better agreement when a monoclinic local symmetry was assumed.

Due to a phase transition process reported at 355 K (in single crystals) from monoclinic to tetragonal symmetry, the fitting of EXAFS spectrum of PFN sample at room temperature was performed considering two crystallographic models with these symmetries. The model with tetragonal symmetry with the $P4_{1}mm$ space group consists of two shells for the neighbourhood of Fe atoms: one with two O atoms and other one with four O atoms. EXAFS spectra measured at room temperature and at 410 K are compared to their fitted spectra in Fig. 4. As can be observed in Table I, even with similar values for interatomic distances, QF values indicate that the local structure for PFN sample at room temperature exhibits tetragonal symmetry. However, our anelastic measurements of PFN sample showed anomalies around room temperature which has been interpreted as a ferroelectric-ferroelectric phase transition. Moreover, pyroelectric measurements showed around 315 K a peak in pyroelectric current, which can be associated with a polarization reorientation characteristic of a symmetry change in a ferroelectric-ferroelectric phase transition. Therefore, our anelastic, pyroelectric, and EXAFS measurements indicate that the monoclinic to tetragonal phase transition of PFN occurs at lower temperature than it is reported by x-ray diffraction characterization.

Shifts in the temperature of phase transition, specially the temperature for AFM ordering, for similar PFN samples can be associated with fluctuation in composition, impurities, different average grain sizes. However, our EDX measurements have shown a very close value of nominal composition. Moreover, the average grain size determined in this study is similar to the PFN ceramics analysed in several studies. Furthermore, our dielectric measurements revealed a temperature of ferroelectric-paraelectric transition equal to 379 K, also in agreement to studies developed using different techniques and methods of synthesis.

The apparent discrepancy between x-ray diffraction and XAS results 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. This time is less than the time scale of the changes in the system, enabling to observe dynamic and fast disorder processes. 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. 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.

The tetragonal crystallographic model was also used in the fit for the spectrum at 410 K, besides a model with cubic symmetry and $Pm-3m$ space group. This temperature is 30 K above the Curie temperature, and the cubic symmetry fits better the local structure of PFN sample as well as the structure at long distance refined with x-ray and neutron diffraction.

In summary, the local structure of PFN as a function of temperature was characterized using XAS technique. It was observed that the shell structure around Fe atoms exhibits a monoclinic local symmetry at 130 and 230 K, tetragonal local symmetry at room temperature, and cubic local symmetry at 410 K. Independently of the coordination, temperature, or symmetry, interatomic distances between Fe and O atoms do not vary significantly, indicating a small distortion of FeO$_6$ octahedron at phase transitions.

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FIG. 4. Fitting and back-Fourier-filtered experimental spectra at room temperature and 410 K.

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