

# Fe valence fluctuations and magnetoelastic coupling in Pb-based multiferroics perovskites

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Lead-based multiferroics perovskites with nominal compositions  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  and  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  were synthesized following a two-stage method. Magnetic properties were investigated and correlated to anelastic properties, measured by the conventional pulse-echo method. The discussions are focused in the region around 250 K, where magnetoelastoe-

lastic instabilities have been observed. X-ray absorption near-edge structure (XANES) study further indicates that the edge position varies with temperature revealing a fluctuation on the valence of iron ions with the temperature, which can be related to a variation in anelastic and magnetic properties.

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**1 Introduction** Multiferroic materials have attracted much recent attention due to the strong coupling between their electric and magnetic degrees of freedom, potentially enabling control of the polarization with an external magnetic field or control of the magnetization with an applied electric field. This is of great interest from a fundamental perspective, as well as for potential applications in magnetoelectric and magneto-optical devices. In these systems, the interplay and competitions between spins, dopant charge carriers, the degree of freedom of orbital, and lattice symmetry lead to a variety of couplings and phase transitions [1].

Compounds such as  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (lead iron niobate – PFN) and  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  (lead iron tungstate – PFW) have recently been the subject of intense study because of their multiferroics properties [2–5]. Lead iron tungstate  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  (PFW) is known as a material with a perovskite-type structure in which  $\text{Fe}^{3+}$  and  $\text{W}^{6+}$  are randomly distributed at the octahedral B-site positions and presents a relaxor ferroelectric and antiferromagnetic ordering. The ferroelectric Curie temperature,  $T_C$ , was reported to occur between 150 and 200 K. PFN, in turn, undergoes a normal ferroelectric phase transition around

380 K and an antiferromagnetic phase transition at 145 K [6, 7]. However, in both compounds, a set of magnetoelastoelectric “anomalies” were observed around 250 K [3, 8, 9]. Some controversies and inconsistent interpretations were proposed to describe these anomalies, in such a way that their origins still remain unclear.

In this sense, synchrotron-based X-ray absorption spectroscopy is a very useful tool to investigate the local structure and electronic properties of these compounds and it can therefore be used as a tool to follow structural and electronic changes during an ongoing thermal process.

In this study, lead-based multiferroics perovskites with PFN and PFW compositions were synthesized by a two-stage method. Magnetic properties were investigated and correlated with anelastic properties, measured by the conventional pulse-echo method. These materials were also characterized using an X-ray absorption spectroscopy technique in terms of the X-ray absorption near-edge structure (XANES) region of the X-ray absorption spectra. This technique was used to investigate the bulk electronic structure to get information about the local symmetry and the valence of incorporated iron ions.

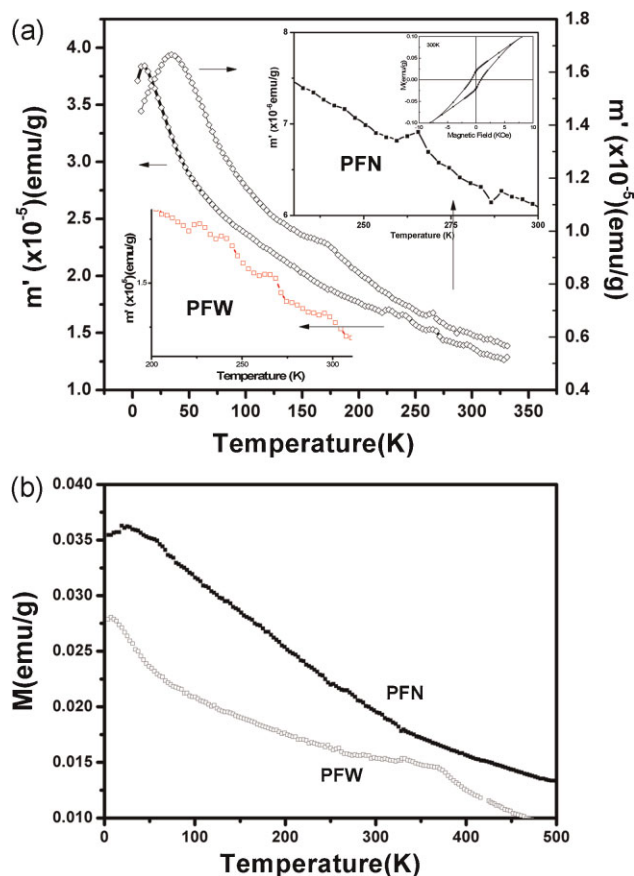
**2 Experimental procedure** High-quality polycrystalline PFN and PFW samples were prepared by using a B-site precursor route and densified by conventional sintering. PFW,  $\text{Fe}_2\text{O}_3$ , and  $\text{WO}_3$  powders were milled for 2 h, and then preheated at  $950^\circ\text{C}$  for 3 h to form  $\text{Fe}_2\text{WO}_6$ . Afterward,  $\text{PbO}$  was mixed with the  $\text{Fe}_2\text{WO}_6$ , to form  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ –PFW [10]. The mixture was initially calcined at  $800^\circ\text{C}$  for 3 h, reground, pressed in pellets and finally sintered at  $830^\circ\text{C}$  for 5 h. In a similar procedure for PFN, the  $\text{FeNbO}_4$  and  $\text{PbO}$  powders were stoichiometrically mixed and calcined at 1073 K to form lead iron niobate (PFN). PFN samples were sintered at 1273 K for 5 h, in controlled oxygen atmosphere. In both cases, the temperature ramps were controlled at  $5^\circ\text{C}/\text{min}$  for heating and  $2^\circ\text{C}/\text{min}$  for cooling.

The temperature dependence of the magnetization  $M(T)$  and magnetic moment  $m'(T)$  were measured using a commercial SQUID magnetometer or a PPMS in the range of temperatures 4–600 K. The samples were cooled to 4 K in the absence of a magnetic field (ZFC) and subsequently heated applying magnetic fields (200 Oe DC and to 10 Oe AC at 1 kHz).

The ceramic bodies for ultrasonic measurements were shaped in parallelepiped form with dimensions of  $7.3\text{ mm} \times 6\text{ mm} \times 6\text{ mm}$ . Two opposite faces ( $6\text{ mm} \times 6\text{ mm}$ ) were polished to a parallelism of about  $10^{-4}$  rad. Gold was sputtered on the sample in order to have an earth electrical contact for the measurements. The ultrasonic velocity was measured using the conventional pulse-echo method. This method allows detection of small variations of the phase velocity with high accuracy by determining the transit time of the ultrasonic pulse ( $t$ ) in a round trip. If  $l$  is the length of the sample, the ultrasound velocity is given by  $v = 2l/t$ . The transit time was determined through the cross-correlation technique, monitoring two selected RF echoes. All presented ultrasonic data were obtained at 10 MHz.

The iron K-edge X-ray absorption spectra (XAS) were collected at the LNLS (National Synchrotron Light Laboratory) using the D04B-XAS2 beamline. The LNLS storage ring was operated at 1.36 GeV and 100–160 mA. Sample pellets, obtained after sintering, were grounded for XAS measurements. XAS data were collected at the Fe K-edge (7112 eV) in transmission mode as a function of temperature using a Si(111) channel-cut monochromator. Ionization chambers were used to detect the incident and the transmitted flux. X-ray absorption near-edge structure (XANES) spectra at the Fe K-edge were recorded between 7050 and 7200 eV using an energy step of 0.3 eV. To provide a good energy reproducibility during the XANES data collection, the energy calibration of the monochromator was checked during the collection of the sample data using a Fe metal foil. The normalization of XANES spectra were performed using the Multi-Platform Applications for X-ray absorption (MAX) software package [11].

**3 Results and discussions** The temperature dependence of the magnetization  $M(T)$  (DC) of PFW and PFN



**Figure 1** (online color at: [www.pss-a.com](http://www.pss-a.com)) (a) Temperature dependence of the magnetic moment  $m'(T)$  (AC measurements) for  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  and  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics. Insert: zoom in the region between 200–300 K magnetic hysteresis loop at 300 K for PFN. (b) Temperature dependence of the magnetic moment  $M(T)$  (DC measurements) for  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  and  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ .

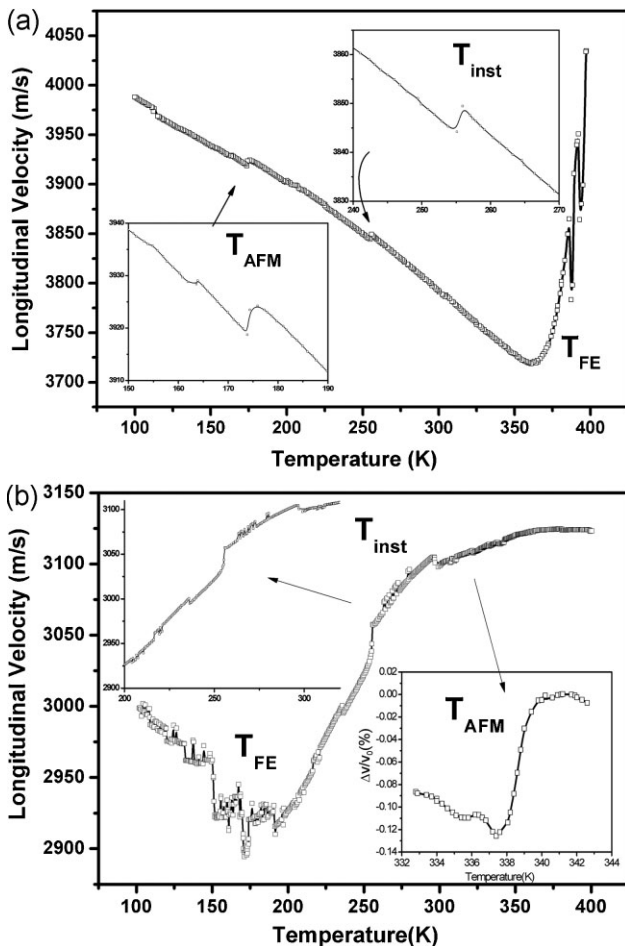
ceramics is presented in Fig. 1. It is noticeable that by cooling the magnetization curve shows an inflexion, around  $T_{N1} \sim 340\text{ K}$ , for PFW, which corresponds to the paramagnetic (PM)–antiferromagnetic (AFM) phase transition, which is attributed to a strong superexchange of  $\text{Fe}^{3+}$ –O– $\text{Fe}^{3+}$  interactions in the disordered regions in a G-type magnetic structure (with a Fe–Fe distance of  $3.9828\text{ \AA}$ ) [11]. Otherwise, a weak superexchange of  $\text{Fe}^{3+}$ –O–W–O– $\text{Fe}^{3+}$  interaction, caused by local short-range order in the B site, is responsible for the magnetic anomaly at lower temperatures (around  $T_{N2} \sim 15\text{ K}$ ), in the Fe/W ordered regions [12]. Similar behavior was observed for PFN samples: an antiferromagnetic state, established at  $T_{N1} \sim 170\text{ K}$ , which, analogous to PFW, is attributed to a strong superexchange of  $\text{Fe}^{3+}$ –O– $\text{Fe}^{3+}$  interaction in the B-site disordered regions, and a weak superexchange (around  $T_{N2} \sim 30\text{ K}$ ) of  $\text{Fe}^{3+}$ –O–Nb–O– $\text{Fe}^{3+}$  interaction caused by local short-range order at the B site in the Fe/Nb ordered nanoregion were identified.

In Fig. 1a, in the magnetic moment  $m'$ , it is possible to identify the temperatures where both magnetic orderings are established, for both samples. Additionally, as highlighted in

the inserts (at the upper side for PFN and lower for PFW), at temperatures around 250 K, it is possible to also distinguish a series of anomalies in the  $M$  and  $m'$  curves, indicating a region of magnetic instability, denominated as  $T_{inst}$  region in following.

However, it must be emphasized that this is assuming that PFN magnetic ordering is only present below 170 K. This indicates the presence of some kind of magnetic ordering at high temperature, as proposed by Blinc et al. [3] and Majumder et al. [13], confirmed by the magnetic hysteresis loop at 300 K (insert Fig. 1a). Due to the different behavior of both perovskites with respect to their multiferroics proprieties and despite the fact that both are antiferromagnetics, PFW is a relaxor ferroelectric below 180 K and PFN is a normal ferroelectric up to 380 K. Hence, the anomalies seem not be related to the ferroelectric phase. In the same way, PFN display AFM ordering below to 170 K, while PFW is AFM below 340 K.

The temperature dependence of the ultrasonic velocity for the investigated PFW and PFN samples is shown in Fig. 2. It can be seen in Fig. 2b that for PFW the longitudinal ultrasonic velocity shows a broad minimum associated to a



**Figure 2** Longitudinal ultrasonic velocity as a function of the temperature in as fired (a) PFN and (b) PFW ceramic.

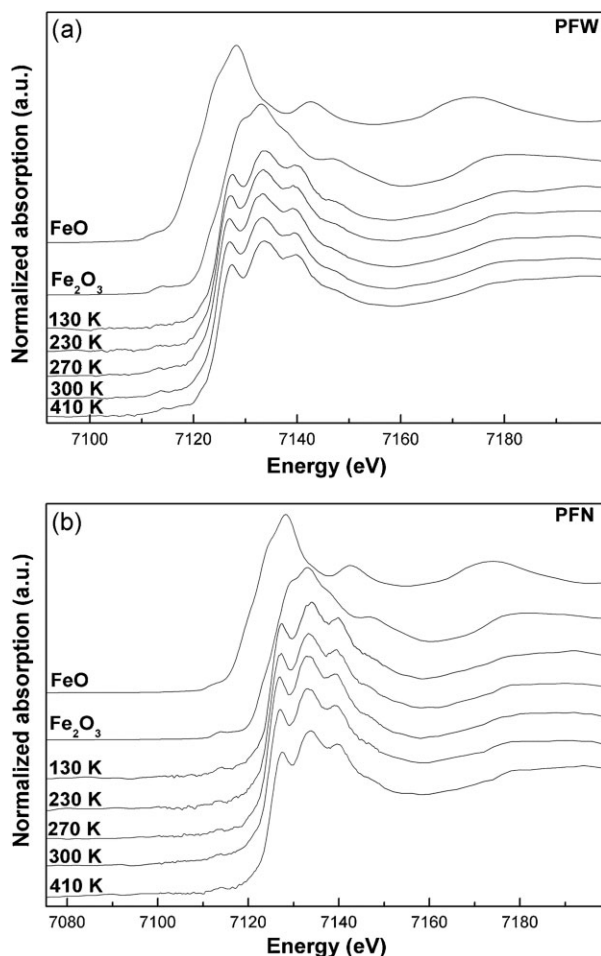
diffuse FE transition around 180 K (relaxor like in the dielectric response [10]) and also a local minimum (around 340 K) corresponding to the PM–AFM transition. Additionally, between 200 and 300 K, corresponding to the temperature range where anomalies were found in magnetic measurements, a series of similar velocity instabilities can be identified. These results indicate that these instabilities involve a spin lattice coupling. A qualitatively similar anelastic response can be observed for PFN in the same range of temperature (Fig. 2a). In addition to the elastic softening around 362 K, associated with the paraelectric–ferroelectric phase transition, the anomaly observed around 170 K is related to the antiferromagnetic ordering (transition).

At temperatures around 250 K it can be observed for both materials (PFW and PFN), the presence of fluctuations in the temperature dependence of the ultrasonic velocities, in correspondence with the above-mentioned magnetic instabilities.

Blinc et al. [3] suggested the existence of a non-equilibrium state in lead iron niobate (PFN) to explain the differences observed between the static FC and ZFC magnetic susceptibilities in the same range of temperature region. On the contrary, Ivanov et al. [9] reported for PFW between  $T_C$  and  $T_N$ , a nonlinear behavior of the temperature dependence of the Fe/W–O interatomic distance, which was attributed to the electrostrictive properties at temperatures above the relaxor phase transition. However, it is remarkable that PFN presents ferroelectric order instead of magnetic order, as the PFW, in the temperature range between 200 and 300 K. Although both samples are multiferroic below approximately the same temperature (170–180 K), the orders at 250 K are different, so that the instabilities cannot be related to the existence of ferroelectric or antiferromagnetic ordering. Therefore, new results are necessary to describe the mechanism responsible for the observed instabilities.

With the aim of obtaining an alternative insight to investigate the origin of the anomalies, observed around 250 K, in order to determine the Fe oxidation state, XANES spectra at Fe K-edge was measured in PFW and PFN samples as a function of temperature.

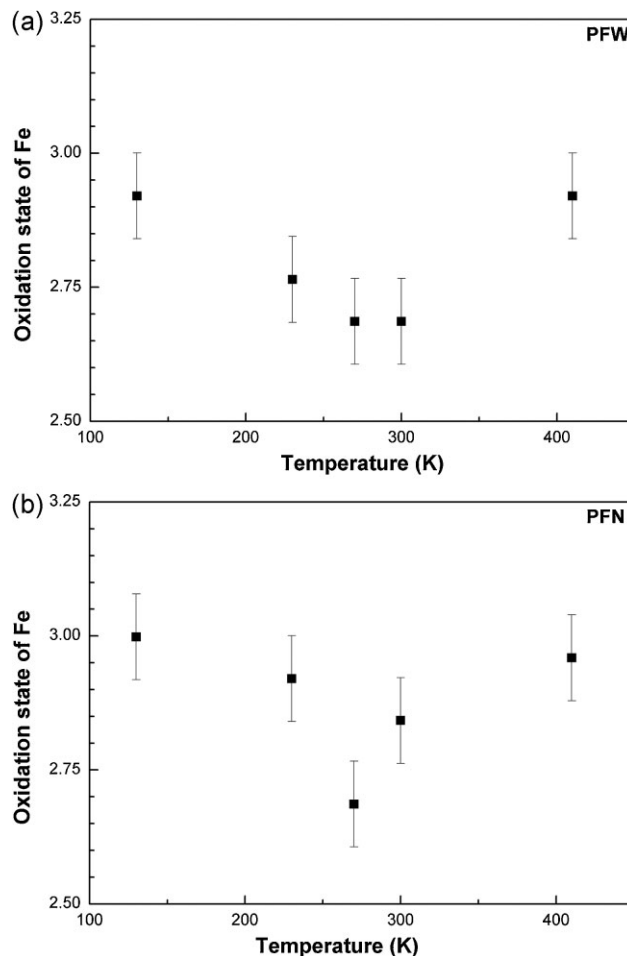
Figure 3a and b present the Fe K-edge XANES spectra of PFW and PFN, respectively collected at 130, 230, 270, 300, and 410 K. In these figures, the XANES spectra for iron oxides standard samples (FeO and Fe<sub>2</sub>O<sub>3</sub>) collected at room temperature are also presented as a reference for different Fe ion valences. As can be seen, no changes in the peak amplitude or energy of the transitions are observed for PFW and PFN samples with increasing temperature. The energy of the edge for PFW and PFN spectra has values closer to those of the Fe<sub>2</sub>O<sub>3</sub> spectrum indicating that the Fe oxidation state for PFW and PFN samples assumes predominantly a value of 3+, which agrees with an octahedral occupation in ABO<sub>3</sub> perovskite. In order to determine the values of Fe oxidation state as a function of temperature, a comparative analysis of the edge position between the PFW and PFN samples and the Fe oxides standards was performed. The actual edge positions were determined in a procedure similar to that



**Figure 3** XANES spectra at Fe K-edge for FeO and Fe<sub>2</sub>O<sub>3</sub> compounds at room temperature and for (a) PFW and (b) PFN samples as a function of temperature.

described by Capehart et al. [14] and Sham [15] The absorption was integrated up to the energy at which the absorption coefficient of the normalized function reached 1 for the first time. The energy position at which this integral reaches 80% of this value has been fixed as the corresponding edge position. This method was used in order to eliminate the white line contribution in most of the total integrated absorption spectra.

Following this procedure, the energy of the absorption edges of XANES spectra was determined for FeO and Fe<sub>2</sub>O<sub>3</sub> compounds. Then a line that describes the oxidation state as a function of edge energy was determined, since the Fe valence in FeO and Fe<sub>2</sub>O<sub>3</sub> (2+ and 3+, respectively) are well known. Thus, from the values of the energy of the absorption edge for the PFW and PFN samples, at each temperature, the Fe oxidation state was determined. The values of the Fe oxidation state as a function of temperature for PFW and PFN are shown in Fig. 4a and b, respectively. As can be observed in Fig. 4a, the Fe oxidation state in PFW is equal to  $2.92 \pm 0.15$  at 410 K. As the temperature decreases, this value decreases to  $2.69 \pm 0.15$  at 300 and 270 K. After



**Figure 4** Fe oxidation state for (a) PFW and (b) PFN ceramic samples as a function of the temperature determined from XANES spectra.

reaching this minimum, the oxidation state of Fe increases to  $2.76 \pm 0.15$  at 230 K and  $2.92 \pm 0.15$  at 130 K. For the PFN sample, the Fe oxidation state as a function of temperature is shown in Fig. 4b. The Fe oxidation state is equal to  $2.96 \pm 0.15$  at 410 K decreases to  $2.84 \pm 0.15$  at 300 K and to  $2.69 \pm 0.15$  at 270 K. After reaching this minimum it then increases to  $2.92 \pm 0.15$  at 130 K and to  $3.00 \pm 0.15$  at 130 K.

It can be concluded from these results that there exists a fluctuation in the valence of iron cations, for both lead perovskite samples, in the same temperature range as the instabilities that have been detected by magnetic and anelastic measurements.

It is widely recognized that geometrical frustration produces a variety of nontrivial exotic phenomena in correlated electron systems with different amount of Fe<sup>2+</sup> and Fe<sup>3+</sup> coexisting at the same site in the lattice [16]. Considering the “mixed” iron valence obtained in turn of 250 K (Fe<sup>2.6+</sup> for 260 K approximately), Fe<sup>2+</sup> and Fe<sup>3+</sup> are considered as having an excess and a deficiency of half an electron, respectively. The coulombic preference for pairing of “oppositely” signed charges is considered to cause a

degeneracy in the lowest energy level for the charge configuration in the lattice, similarly to the triangular antiferromagnetic Ising spins [17]. Thus, PFW and PFN can be considered as presenting “charge-frustrated” electronic structure at these temperatures that would be responsible for the observed magnetic and elastic anomalies. These results may also be ascribed to either the change in spin moment or in the lattice modification, both of which are caused by the fluctuation from  $\text{Fe}^{3+}$  ( $5.9\mu_{\text{B}}$ ) to  $\text{Fe}^{2+}$  ( $4.9\mu_{\text{B}}$ ) ions, which have different magnetic properties and different ionic radio. Otherwise, the anomalies detected around 250 K in elastic measurements may also be caused by some kind of structural instability distortions caused by these charge fluctuations. In the same form, since iron is a magnetic ion and is directly involved with magnetic exchanges, this fluctuation influences the magnetic properties. On the other hand, the magnetostrictive contribution (spin–lattice coupling) is reflected in the instabilities in magnetic curves, instead of a direct influence in the exchange.

**4 Conclusions** In summary, a series of magnetic and elastic anomalies in multiferroic PFN and PFW ceramics were investigated through magnetic, anelastic, and XANES measurements. The experimental data revealed that the observed magneto-electroelastic instabilities, around 250 K, in both lead-based perovskites, are associated with valence fluctuations of the iron ions, configuring a charge-frustrated electronic structure.

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