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Magnetoelectric intrinsic coupling in PFW based perovskites

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Abstract Magnetic, electric and mechanical properties can be strongly coupled in multiferroic materials. However, only few models were developed to describe electro-magnetomechanical coupling effects on them. We report the influence of the strain induced phase transitions on the enhancement of the magnetoelectric intrinsic properties in multiferroic Pb[(Fe_{2/3}W_{1/3})_{(1-x})Ti_x]O₃ (x=0.17,0.20) ceramics. We argue that when both ferroelectric and antiferromagnetic transitions temperatures are closer together, the magnetoelectric intrinsic and extrinsic responses increase. Colossal magnetoelectric intrinsic response was found for Pb(Fe_{2/3}W_{1/3})_{0.83}Ti0.17O₃.

Keywords Magnetoelectric · Multiferroic · Ferroelectric · Ceramics

1 Introduction

Magnetoelectric (ME) coupling in a material can be either extrinsic (obtained by applying fields, in composites materials) or intrinsic (spontaneous, in single phase materials) [1-3]. Multiferroic single phase materials present an intrinsic

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(spontaneous) ME effects due to the interaction of strong internal electric and magnetic fields. One of the alternatives to investigate this intrinsic phenomenon is, for example, to measure changes in the electric permittivity or in the electric polarization near the temperature of the magnetic phase transition or changes in the magnetization in the region of ferroelectric phase transition. However, as a first observation, it can be a demanding task: it is well known that extrinsic contributions, such as parasite capacitances formed at the interface between the samples and the electrodes or at the grain boundaries, often account for the apparent colossal electric permittivity reported for many dielectric materials [4, 5].

A second observation, is that there is only one well known multiferroic that exhibits both ferroelectric and antiferromagnetic phase transitions above room temperature, BiFeO₃, but its ME coupling is already too small for practical applications. The scarcity of materials that are magnetic ferroelectrics is related to the competition between the conventional mechanism of ferroelectric cation off-centering, which requires empty *d*-orbitals, and the formation of magnetic moments which requires partially filled d-orbitals [5-8]. A concomitance of magnetism and ferroelectricity has to rely on more subtle microscopic coupling mechanisms, driven by spin-orbit coupling in the form of Dzyaloshinskii-Moriya interactions [8] or exchangestriction [9], generally obtained in materials with complex structure and low ordering temperatures as, for example, TbMnO₃ and other spin-induced ferroelectrics that exhibit relatively large ME coupling [1, 10, 11].

An option is to look for materials with a large ME coupling going to mixed solid solutions, combining materials that present magnetic and/or ferroelectric ordering at high temperatures. Among them, arise $Pb(Fe_{2/3}W_{1/3})O_3 -PbTiO_3$ (PFW-PT) as modified $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) systems [12, 13]. PFW is one of the classical relaxors with lower sintering temperature (about 830 °C). However, the lower Curie temperature T_{FE} at 180 K is a disadvantage. The lattice structure, the dielectric and magnetic properties of the pure PFW can be easily changed by adding PbTiO₃ (PT) composition. PT is a typical ferroelectric with a sharp maximum of dielectric constant at 763 K. It is possible to move the Curie and Neél temperature and to modify the relaxation behavior by choosing an appropriate amount of PT in the system [14]. A continuous spectrum of structural and physical properties, from dielectrics, ferroelectric, atomic and magnetic were obtained for the PFW–PT systems with various PT content [15–22]. In most approaches the effect of an applied external field and the effect of the proximity between the temperatures of the phase transitions have never been shown.

In this work, viewing from a fundamental aspect, the electric permittivity was measured in Pb(Fe_{2/3}W_{1/3})_{(1-x})Ti_xO₃ (x= 0.17,0.20, denominated as PFW-17PT and PFW-20PT, respectively) ceramic samples looking for its temperature dependence around the para-antiferromagnetic transition temperature (T_{AFM}), in which a G-type antiferromagnetic structure and the multiferroic state are established [23, 24]. The governing equations for the magnetoelectroelastically coupled systems will be presented. An interpretation of the changes observed in the dielectric and elastic coefficients in the antiferromagnetic phase transition is proposed.

2 Experimental procedure

High quality polycrystalline PFW-PT samples were prepared by using a B-site precursor route and densified by conventional sintering. For PFW, Fe₂O₃ and WO₃ powders were milled for 2 h, and then preheated at 950 °C for 3 h to form Fe₂WO₆. Afterward, PbO was mixed to the Fe₂WO₆, to form PFW. The mixture was initially calcined at 800 °C for 3 h, regrounded, pressed in pellets and finally sintered at 830 °C for 5 h. More synthesis and processing details can be found elsewhere [12, 13].

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

For dielectric measurements, the ceramic samples were shaped in a disc form, with approximately 12 mm in diameter and 0.75 mm in height. The same samples were used for pyroelectric measurements. For ferroelectric measurements, P(E), virgen samples were polished down to 0.3 mm in height. After that, they were annealed at 850 K for 0.5 h to release mechanical stresses introduced during the polishing. Gold electrodes were sputtered onto the sample surfaces. Dielectric characterization was made as a function of the temperature (15 K-750 K, rate 2 K/min) and frequency (100 Hz-10 MHz) using a HP4194A impedance gain/phase analyzer

interfaced with a computer (amplitude of ac voltage 0.5 V) and an ADP cryogenic system.

During the Pyroelectric measurements, the sample was cooled down to 10 K under an DC electric field of 0.5 kV/ cm, then the current flow from the sample was recorded upon heating (3 K/min) without the electric field and the spontaneous polarization was estimated by the integral of the current from the sample.

Pyroelectric characterization, based in the Byer-Roundy technique [25], was performed on the gold sputtered ceramics. The pyroelectric current was measured using a KEITHLEY 617 electrometer coupled in a computer assisted system that included an APD cryogenic system. Different poling conditions (time, electric field, temperature) were tested to optimize the pyroelectric response. The samples were cooled under electric field (0.5 kV/cm), with a rate of 3 K/min down to 10 K. Next, the electric field was removed, the samples were short-circuited for 5 min to eliminate accumulated charges during the poling process and the pyroelectric current was measured under a heating rate of 3 K/min. From the values of temperature rate, of the pyroelectric current and the area of the sample, the pyroelectric coefficient was calculated and integrated in function of the temperature for obtained the polarization [26].

Hysteresis loops were measured in a typical Sawyer-Tower configuration applying a sinusoidal electric field and frequency of 10 Hz on the samples. In this case, samples were placed in an APD cryogenic system for measurements below room temperature.

The ceramic bodies for ultrasonic measurements were shaped in parallelepiped form with $7.3 \times 6 \times 6$ mm. Two opposite faces $(6 \times 6 \text{ mm})$ were polished to a parallelism of about 10^{-4} rad. Gold was sputtered on the sample surface in order to have a direct ground electrical contact with the sample holder. Phase velocity was measured with high accuracy with a pulse echo method 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 cross correlation technique, monitoring two selected RF echoes. X cut quartz transducer was used for longitudinal ultrasonic excitation, respectively. Nonaq stopcock grease was used to bind the transducers to the sample surface. All the presented data were obtained at 10 MHz. The experimental setup consists essentially of a MATEC generator/receptor connected to a digital oscilloscope. Low temperatures where reached by using a cryogenic system and FERP50 temperature controller. The experiment was automatized and the temperature was swept at rate of 0.10 K/min (for both warming-up and cooling down processes). From the longitudinal velocity (v) measurements and density (ρ), the elastic modulus c was calculated using the relationship

$$\rho v^2(T) = c(T) \tag{1}$$

3 Results

The characterization of the system $Pb(Fe_{2/3}W_{1/3})O_3-PbTiO_3$ (PFW–PT) from its physical, structural and electrical proprieties have been reported in other works [12, 13, 16]. From these results, it was concluded that all samples resulted in single phase, highly densified (>98 % of the theoretical density), grain size around 3–5 µm and with relatively high electrical resistivity, which allowed us to perform the dielectric, elastic, pyroelectric and magnetic characterizations.

3.1 Magnetic and ferroelectric results

Two types of magnetic ordering have been observed from the temperature dependence of magnetization (Fig. 1(a)) which arise from different magnetic interactions. The low temperature magnetic ordering corresponds to a weak ferromagnetic to antiferromagnetic transitions which occurs at low Neél temperature, T_{N2} =10 K and 17 K for PFW-17PT and PFW-20PT, respectively. The high temperature ordering is referred to an



Fig. 1 Magnetic momentum m'(T) (ac measurement) and ferroelectric hysteresis loop for $Pb(Fe_{2/3}W_{1/3})_{0.80}Ti_{0.20}O_3$ (200 K) and $Pb(Fe_{2/3}W_{1/3})_{0.83}Ti_{0.17}O_3$ (170 K) ceramics

antiferromagnetic to paramagnetic transition at Neél temperature, T_N =179 K and 161 K for PFW-17PT and PFW-20PT, respectively. There are two factors that affect mainly the T_N magnetic transition in the PFW-PT system: the dilution of the magnetic ion Fe³⁺ by the addition of the non magnetic component PT that, consequently, changes the distances of adjacent Fe³⁺ ions, which change the magnetic exchange. The magnetic interactions that give rise to the observed magnetization might be ascribed as follows: in the Fe/W ordered region, a weak superexchange of Fe³⁺-O-W-O-Fe³⁺ interaction type is responsible for the magnetic anomaly at lowtemperatures (T_{N2}). At high temperatures (T_N), a stronger superexchange of Fe³⁺-O-Fe³⁺ pathway interaction is responsible for the magnetic ordering [23, 24].

Nevertheless, different values for T_N have been also observed for the same PT content in PFW, depending on the samples characteristics: ceramics or single crystal or between ceramics processed in different conditions [23, 24].

Figure 1(b) shows P-E loops for the PFW-PT ceramics measured at low temperatures, selected around 50 K below ferroelectric ordering temperature, in both cases. Due to the conductivity of the samples, it was not possible to apply even higher fields looking for saturation of the loop. The remanent polarization P_r and coercive field E_c of PFW–xPT ceramics, x=0.17 and 0.20, determined from the saturated hysteresis loops, are 18 μ C/cm² and 8.6 kV/mm (at 170 K) and 2.7 μ C/cm² and 14 kV/mm (at 200 K), respectively. The values for the pure PFW sample are 0.12 μ C/cm² and 6.5 kV/mm. The high value of P_r for both samples with respect to the pure PFW ceramics is attributed to the enhancement of the ferroelectric order due to the addition of ferroelectric ion Ti⁺⁴ into the system [16].

3.2 Dielectric results and effect of an external electric field on the antiferromagnetic phase transition

In antiferromagnets, the order parameter has been defined as L, $L=M_1-M_2$ the AFM vector, M_1 and M_2 the specific magnetization for each AFM sublattice , P is the electric polarization and S the strain. The thermodynamic potential F in these cases can be written in the form [17]:

$$F = \frac{1}{2}cS^{2} + \frac{1}{2}a_{2}P^{2} + \frac{1}{4}a_{4}P^{4} + \frac{1}{2}b_{2}L^{2} + \frac{1}{4}b_{4}L^{4} + Q^{M}SL^{2} + Q^{E}P^{2}S \pm EP$$
(2)

1

Here, a_2 , a_4 , b_2 and b_4 are constants related to the electric and magnetic susceptibilities. The first term describe the elastic energy, second and third the electric energy and fourth and fifth the magnetic energy. The "coupling energy" is composed by two types of couplings: $F_c(S,L)$, $F_c(S,P)$. For the magnetoelastic coupling term $F_c(S,L)$, the coupling term associated with the strain S_i can be written in terms of increasing powers of the strain or magnetization, represented by the sixth term in Eq. (2) (Q^M) . The electroelastic coupling between elastic and electrical parameters is given by Q^E . The ME exchange interaction term can be found by imposing an equilibrium deformation state, $(\frac{\partial F}{\partial S}) = 0$. Substituting the imposed equilibrium condition for the spontaneous strain in Eq. (2) results a contribution to the magnetoelectric energy in the form of

$$F_c(M,P) = \eta L^2 P^2,\tag{3}$$

where η is a combination of the elastic (*c*), electric (*a*), magnetic (*b*), electro-elastic (Q^E) and magneto-elastic (Q^M) coefficients and is a measure of the intrinsic magnetoelectroelastic interaction, mediated via strain, in the absence of any external field. In this way, the free energy can be rewritten as:

$$\mathbf{F} = a_2 P^{2+} \frac{a_4}{2} P^4 + b_2 L^2 + b_4 L^4 + \eta P^2 L^2.$$
(4)

If intrinsic ME effect is present ($\eta \neq 0$), the dielectric susceptibility below the temperature of magnetic ordering, in the absence of external electric fields, will differ from the values that would be obtained by extrapolation, following the temperature dependence observed in the paramagnetic phase. This difference, which we denote as $\Delta \varepsilon$, depends to the square

150

200

250

(x10³) **50**

40

100

$$\Delta \varepsilon \approx \eta L^2(T) \quad (T < T_{AFM}) \tag{5}$$

when $T < T_{AFM} < T_{FE}$. The sign of $\Delta \varepsilon$ in (5), positive or negative, depends on the sign of the intrinsic ME interaction constant η .

Figure 2 shows the real (ϵ) and the imaginary (ϵ) parts of the electric permittivity as a function of the temperature and frequency obtained during the cooling at rate of 2 K/min. The results for a frequency of 100 kHz clearly reveal the presence of a broad dielectric peak occurring around T_{FE}~238 K for the sample with 17%PT (b) and around 253 K for 20%PT (a) and anomalies around 173 K and 153 K, respectively, more visible in Figure 2c and d. The dielectric peak of the sample with 17 % of PT presents a weak signature of a relaxor-like dielectric dispersion (the peak temperature increases with the measuring frequency), while at higher temperatures the observed increase with the temperature in the electric permittivity has been associated to conductive contributions [23]. The sample with 20% of PT shows normal FE behavior. It was better studied previously [15].

Remarkable in these results is that, even without applied bias electric field, there is a variation of the dielectric

2500



2000

 $(x10^{3})$

300

Fig. 2 Dielectric permittivity in the region of the PM-AFM transition temperature for **a** $Pb(Fe_{2/3}W_{1/3})_{0.80}Ti_{0.20}O_3$ and **b** $Pb(Fe_{2/3}W_{1/3})_{0.83}Ti_{0.17}O_3$ ceramics as a function of the temperature and under different bias electric fields **c** (0.3 KV/mm to 17%PT) or **d** (0.5 KV/mm for 20%PT) (at 100 KHz)

permittivity of about $\Delta \varepsilon \cong \frac{\varepsilon_{paramagnetic} - \varepsilon_{AFM}}{\varepsilon_{paramagnetic}} \approx 3\%$ and -1.7%, just 10 K below the temperature of the magnetic ordering, for samples with 17% PT and 20% PT, respectively. $\varepsilon_{paramagnetic}$ corresponds to the estimated electric permittivity if the magnetic ordering did not have occurred.

From Eq. 5, it can be concluded that the break in dielectric permittivity observed just below T_N , is due to the intrinsic ME coupling (η), proportional to the magnetic order parameter, and $\Delta \varepsilon \approx \varepsilon_{AFM} - \varepsilon_{PM} \approx \eta L^2(T) > 0$ in the case of PFW-17PT ceramics, and negative (<0) in the case of 20 % of PT. This behavior is not common in ceramic and even in single crystals, occurring only in multiferroic with improper ferroelectricity [8, 11].

Figures 2(c) and (d) also show the effect of a DC bias electric field superposed to the measuring field (applied at 400 K). It can be observed that T_N and $\Delta \varepsilon$ increase with respect to the zero field measurement. The "new" temperature of break, here called $T_N \ _E$, is marked in the figures.

Under an external electric field the ferroelectric polarization can be reoriented. Then, by assuming that the all three parameters (FE, AFM and elastic) are mutually coupled, as it was described in the Eqs. (2–4), these results show that this poling process modifies not only the ferroelectric domain configuration, but also the antiferromagnetic anomalies near the Néel temperature are strongly enhanced as well. Our results show that an additional term must be taken into account either explicitly or implicitly in the free energy of magnetoelectric multiferroic materials for a realistic description of these experimental results. Therefore, the obtained $\Delta \varepsilon$ (E) is not only due to the intrinsic contribution described by the last term of Eq. (4), that results in the Eq. (5), being necessary to include an extra contribution to the free energy equation. In this case Eq. (5) must contain an additional electric field dependent term (δ), corresponding to an extrinsic contribution:

$$\Delta \varepsilon \approx \eta L^2(T) + \delta (Q^E, E). \quad (T < T_{AFM})$$
(6)

Then, by considering the elastic strain, cross terms involving the product of strain, magnetic and electric fields will naturally appear in order to describe the magnetoelectric coupling, resulting in an "effective ME coefficient". Figure 3 presents the influence of a bias electric field in the investigated samples.

The temperature shifts in the magnetic transition temperature due to the external electric field (~ -40 K for PFW-17PT and~11 K in PFW-20PT), is also consequence of the ME interaction. Mitsek and Smolenskii [23, 24] demonstrated by thermodynamical analysis of Eq. 2 that, in multiferroic materials having $T_N < T_{FE}$, the shift in the magnetic transition temperature ΔT_{FM} should be proportional to the electric field strength. The change of T_N under the bias external electric field E is proportional to the magnetoelectric coupling coefficient and is given by [27]

$$\frac{\partial T_N}{\partial E} = -\frac{\partial \varphi}{\partial P^2} \left(\frac{\partial \varphi}{\partial T}\right)^{-1} P \chi_E \tag{7}$$

Fig. 3 a Dielectric permittivity of PFW-17PT ceramics as a function of the temperature under different bias electric fields a 0 V/mm b $0.3 \text{ kV/mm. c} 0.6 \text{ kV/mm d} T_N$ dependence as a function of a bias electric field for PFW-17PT and PFW-20PT ceramics. e Relative change of the low field dielectric permittivity at 10 K below the PM-AFM transition temperature (at 100 kHz)



where $\phi = \phi(T,P^2)$ is the coefficient of L² in the thermodynamic potential (considering applied electric fields in the free energy). Therefore, this implies that the variation in T_N depends on the applied electric field strength and on the "effective" ferroelectromagnetoelastic coefficient η . A negative shift in T_N implies a positive intrinsic magnetoelectric coupling while a positive shift corresponds to a negative magnetoelectric coupling.

The nearly linear field dependence decrease observed in the Neél temperatures, shown in Fig. 3(c), is then consistent with a positive magnetoelectric coupling for PFW-17PT and a negative for PFW-20PT when compared to the intrinsic case (without bias field), characterizes a colossal magnetoelectric coupling in PFW-17PT. ME is usually called "colossal" or "giant" when the change of an electric (magnetic) property, due to magnetic (electric) field influence is of order of ten or more per cent [28]. Generally "colossal ME" occurs in the ferroelectromagnets with improper FE transition, where electric polarization is induced by magnetic ordering [29] that leads to a significant response of the polarization by changing the magnetic state. This increase is shown in Fig. 3(a) and (d) as a function of the bias electric field. It can be seen that $\Delta \varepsilon$, around 10 K below the antiferromagnetic phase transition, increases up to 25 % for PFW-17PT as the electric field is increased up to 0.6 KV/mm but only 2.6 % (in absolute values, 0.5 KV/mm) for the PFW-20PT sample. We can infer that a DC bias electric field increases the variation of the electric permittivity $\Delta \varepsilon$ at the magnetic ordering temperature and, consequently, increases the extrinsic ME coupling. Comparing both samples, it is possible conclude that the extrinsic ME coupling increases as the T_{FE} and T_{AFM} ordering temperatures are closer.

3.3 Anelastic properties

The symmetry and lattice dynamics, as stated in the introduction, also play an important role in the spin-orbit coupling and in the manifestation of ferroelectric polarization. Therefore, one of the key issues is to detect and characterize structural distortions or lattice instabilities in the material, so that the coupling between magnetic, electric and lattice degrees of freedom could be better described. As a sensitive tool, ultrasonic technique has been proven to be particularly successful in studying systems with electron–phonon coupling, spinphonon coupling, and phase transition [29–33]. In this case, let's rewritte the free energy as:

$$dF = TdS + HdL + EdP, (8)$$

with

$$T = T(S, L, P) = \frac{\partial F}{\partial S}\Big|_{L, P} \quad E = E(S, L, P) = \frac{\partial F}{\partial P}\Big|_{L, S} \quad H = H(S, L, P) = \frac{\partial F}{\partial L}\Big|_{S, P}$$
(9)

Minimizing the Landau energy with respect to the strain, results a spontaneous strain, which is used to derive the elastic constant c_{ij} . A model to describe the elastic changes in a structural FE phase transition region was proposed by Rehwald²¹, ²² regarding the softening $\Delta c = c^{NO} - c^{O}$ (O-ordered phase, NO- disordered), where the elastic coefficient can be obtained from $c_{nm} = \frac{\partial^2 F}{\partial S_m S_n}$. As an analogy, this model was successfully used to describe elastic changes observed in magnetic phase transitions [33, 34].

Considering a single phase multiferroic material presenting ferroelectric (FE) and antiferromagnetic (AFM) phase transitions following a similar treatment, the difference $\Delta c = c^{NO} - c^{O}$ can be calculated by:

$$\frac{\partial^{2} F}{\partial S_{kj}^{2}} - \frac{\partial^{2} F}{\partial S_{kj}^{2}}\Big|_{P,L} = -\frac{\partial^{2} F}{\partial P_{m} S_{kj}}\Big|_{M} \frac{\partial^{2} F}{\partial P_{m} S_{kj}}\Big|_{M} \frac{\partial P_{m}}{\partial E_{n}}\Big|_{M} \\ -\frac{\partial^{2} F}{\partial P_{m} S_{kj}}\Big|_{M} \frac{\partial^{2} F}{\partial P_{m} L_{l}}\Big|_{S} \frac{\partial L_{l}}{\partial S_{kj}}\Big|_{P} \frac{\partial P_{m}}{\partial E_{n}}\Big|_{L} -\frac{\partial^{2} F}{\partial L_{k} S_{kj}}\Big|_{P} \frac{\partial^{2} F}{\partial L_{l} S_{kj}}\Big|_{P} \frac{\partial L_{l}}{\partial H_{s}}\Big|_{L} \\ -\frac{\partial P_{m}}{\partial S_{kj}}\Big|_{L} \frac{\partial^{2} F}{\partial P_{m} L_{l}}\Big|_{S} \frac{\partial L_{l}}{\partial H_{s}}\Big|_{L} \frac{\partial^{2} F}{\partial L_{l} S_{kj}}\Big|_{L}$$
(10)

In Eq. (10) the first term corresponds to the softening of the elastic modulus due to a spontaneous magnetic order establishment, while the second one arises from the establishment of a ferroelectric order. For single phase multiferroics two cases can be taking into account:

- The ferroelectric order is established at temperatures above that of the magnetic ordering $(T_{FE}>T_{AFM})$.
- The magnetic order is established at temperatures higher than that of ferroelectric ordering (T_{AFM}>T_{FE}).

In this work, the intrinsic ME coupling is established at AFM phase transitions ($T_{FE}>T_{AFM}$). Therefore, the total softening Δc of the elastic modulus, at T_N , results from the intrinsic electroelastic coupling (first term in Eq.(12)) and due to the establishment of a spontaneous magnetic ordering, which is coupled to the polarization via lattice strain (second term in Eq. (12)):

$$\Delta \boldsymbol{c} = -\boldsymbol{Q}^{\boldsymbol{E}} \boldsymbol{\chi}_{\boldsymbol{e}}^{-1} \boldsymbol{Q}^{\boldsymbol{E}} + \boldsymbol{Q}^{\boldsymbol{M}} \boldsymbol{\chi}_{\boldsymbol{m}}^{-1} \boldsymbol{\eta} \boldsymbol{q}^{\boldsymbol{E}} \quad (\mathbf{T}_{\mathrm{FE}} > \mathbf{T}_{\mathrm{AFM}}) \quad (12)$$

Here, $\chi_e = \frac{\partial^2 F}{\partial \mathbf{p}_k \mathbf{p}_l}$ and $\chi_m = \frac{\partial^2 F}{\partial \mathbf{L}_k \mathbf{L}_l}$ are the electrical and magnetic susceptibilities, respectively, and q^E is a electrostrictive term.

The temperature dependence of the elastic modulus c and the ultrasonic attenuation are shown in Fig. 4. In fact, in Fig. 4 it is possible to distinguish two anomalies, at the temperature of the FE and at AFM phase transitions. Clearly, the stiffness c values at T_N change weakly, if at all, in contrast with the strong effects observed on the ferroelectric transition. In the case of the



Fig. 4 Temperature dependence of the elastic constant c_{11} and attenuation for the samples with **a** Pb(Fe_{2/3}W_{1/3})_{0.80}Ti_{0.20}O₃ and **b** Pb(Fe_{2/3}W_{1/3})_{0.83}Ti_{0.17}O₃. Insert: critical contribution to the ultrasonic velocity anomaly around T_N

FE contribution, it is a "pure" contribution, since there is no expected ME contribution. Therefore, it is only caused by an electroelastic interaction, given by the first term in $(11)(Q^E\chi_e^{-1}Q^E)$. At lower temperatures, magnetoelastic interactions appear at T_N . In the absence of external applied fields, the source of magnetoelectric energy is the macroscopic electro-magneto-elastic interaction which appears as a result of the fact that changes in the dimensions of the crystals lead to a change not only in magnetic but also in electric state.

Figure 4 contains the relative change in elastic constant (c_{11}) in the PM-AFM region for PFW-17PT and 20PT. The temperature dependence (like a step) suggests a linear strain coupling (always quadratic in the magnetization) [29]. Moreover, the variation in this region is 0.3 % for the sample with 17 % of PT, i.e., larger by at least two orders than that usually achieved in the literature for such kind of transition [33–37]. This suggests the existence of an additional coupling already at these temperatures (magnetoelectric coupling would be expected only below 180 K, where both orders were established). For samples 20 % of PT, the variation is only 0.07 %, proving this additional and not expected coupling, especially for samples where the ferroelectric and antiferromagnetic transitions are close.

3.4 Pyroelectric

When the temperature of the ferroelectric ceramics is changed, the polarization Ps/Pr changes, so that an excess of free charge appears on one of the polar faces of the ceramics and gives rise to a current flow. In ferroelectric ceramic the pyroelectric effect is observed only after a preliminary poling. The total pyroelectric effect can be determined by measuring of the voltage, current or charge. In this work the method relying on the measurement of the pyroelectric current was chosen.

When the sample is heated with a constant rate, the total pyroelectric current as a result of the primary and secondary effect is induced and is given by the formula:

$$i(\theta) = A \frac{dP}{d\theta} \frac{d\theta}{dt}$$
(13)

where A is the surface area of the sample, $\frac{dP}{d\theta}$ the pyroelectric coefficient and $\frac{d\theta}{dt}$ the heating rate.

The most complete expression of the pyroelectric coefficient for a solid possessing fully coupled piezoelectric, piezomagnetic, pyroelectric, and pyromagnetic effects is deduced considering

$$D = T(S, L, \theta) \quad S = S(T, \theta) \quad L = L(S, \theta)$$
(14)



Fig. 5 Pyroelectric current and spontaneous polarization as a function of the temperature for Pb($Fe_{2/3}W_{1/3}$)_{0.80}Ti_{0.20}O₃ and Pb($Fe_{2/3}W_{1/3}$)_{0.83}Ti_{0.17}O₃ ceramics

where here θ is the temperature.

We can prove that

$$\frac{\partial D}{\partial \theta} = \frac{\partial D}{\partial T} \frac{\partial T}{\partial S} \frac{\partial S}{\partial \theta} + \frac{\partial D}{\partial L} \frac{\partial L}{\partial S} \frac{\partial S}{\partial \theta} + \frac{\partial L}{\partial \theta} \frac{\partial D}{\partial L}$$
(15)

$$p = p_{int} + q^E c\alpha + \eta q^M \alpha + \eta m \tag{16}$$

where α is the linear expansion coefficient and *m* the pyromagnetic coefficient.

Figure 5 shows the obtained temperature dependence of the electric polarization. A series of large decreases of polarization occurs as the temperature increases: For PFW-17PT samples, at 235 K, at the ferroelectric phase transition ($\Delta P_{FE}=26 \ \mu C/cm^2$) and around 143 K ($\Delta P_{AFM}=24 \ \mu C/cm^2$), which is the magnetic transition temperature and in the case of PFW-20PT, $\Delta P_{FE}=21 \ \mu C/cm^2$ and $\Delta P_{AFM}=16 \ \mu C/cm^2$. This shows that PFW-PT samples have an electric polarization at magnetic AFM temperature, indicating the coupling between both order parameters.

In the case of PFW-PT ceramics, we can exclude the pyromagnetic term, due symmetry considerations [37–40]. Again, like in anelastic case, we have additional to the intrinsic pyroelectric term, a term due the coupling between electric and elastic part and a term associated to a magnetostriction and magnetoelectric intrinsic effect, at the temperature of magnetic phase transition. This term is responsible for the second contribution to polarization at T_N .

4 Conclusions

In summary, the presence of the strain at AFM phase transitions, where the multiferroic state is established, confirmed directly by the anelastic measurements, showed an additional contribution to Δc at T_N, which is associated with the intrinsic magnetoelectric coupling. These changes reflected also in the electric permittivity and in the polarization of the material. A big strain induced when both antiferromagnetic and ferroelectric phase transition are close to each other, maximizes both magnetoelastic and electroelastic couplings and enhances the magnetoelectric intrinsic coupling.

Under an electric field the ferroelectric polarization is reoriented. If the three order parameters (FE, AFM and elastic) are mutually coupled, this poling process modifies not only the ferroelectric domain orientation, but the antiferromagnetic as well, changing the value of the total coupling through electrostrictive effect. The experimental results of this work indicate that PFW-17PT presents "colossal" ME effect, even for electric fields as small as 0.15 kV/mm (considering the criteria indicated in [17]). However, a remarkable feature in this case is that the "colossal" ME effect response occurs in a proper intrinsic multiferroic. This is not the case for the sample with 20 of PT, where a wide range of temperature separates the FE and AFM transitions. This demonstrate that bringing the magnetic and ferroelectric ordering temperatures closer together induces higher ME coupling.

The analysis of all data, based on the Landau-Devonshire thermodynamic formalism, indicates that the ME effects is a contribution of intrinsic ME coupling, with elastic contribution, and a field dependent term. The changes in AFM phase transitions observed in PFW-PT are considered a result of a renormalization of the FE constants by the magnetoelectric interaction. Thermodynamically and experimentally, it has been demonstrated that the strain plays a fundamental roll in the magnetoelectric intrinsic coupling. The experimental results show that a variation in the electric permittivity and in the elastic constant, both near T_N, can be understood in terms of an intrinsic magneto-electro-elastic coupling. Under the action of a DC bias electric field the variation of the electric permittivity $\Delta \epsilon$ increases at the magnetic ordering temperature and, consequently, the extrinsic ME coupling increases. Both intrinsic and extrinsic ME coupling increase as the $T_{\rm FE}$ and TAFM ordering temperatures are closer.

This confirms the ability of control of magnetic proprieties with an applied electric field.

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