Evidence of magnetodielectric coupling in multiferroic Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ ceramics from ferroelectric measurements and electron paramagnetic resonance

Reynaldo Font,[1,2] Guillermo Alvarez,[3] Oscar Raymond,[2,a)] Jorge Portelles,[1,2] and Jesús M. Siqueiros[2]

[1]*Facultad de Física, Universidad de la Habana, San Lázaro y L, Vedado, La Habana 10400, Cuba*
[2]*Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Km. 107, Carretera Tijuana Ensenada, Ensenada, Baja California 22860, Mexico*
[3]*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Universitario S/N, Cd. Universitaria, Del. Coyoacán, Distrito Federal 04510, Mexico*

Magnetodielectric coupling effects of single phase multiferroic Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ ceramics have been studied using standard ferroelectric measurements and electron paramagnetic resonance (EPR). Changes in the electrical polarization behavior were observed in the paramagnetic to weakly magnetized antiferromagnetic transition near 103 K associated with a rhombohedral to monoclinic symmetry reduction. The analysis of changes in the EPR spectral parameters confirms the transition from paramagnetic to weakly magnetized antiferromagnetic and reveals noticeable anomalies in the high temperature region near the ferroelectric-paraelectric transition (383 K), which are correlated with the tetragonal-to-cubic symmetry change and the characteristic diffuse phase transition of this material. © 2008 American Institute of Physics. [DOI: 10.1063/1.3006433]

Multiferroics are single-component or composite materials exhibiting two or more ferroic features such as ferro- or antiferromagnetism, ferroelectricity, or ferroelasticity/shape-memory effects, which are of great scientific and technological interest.[1–5] In the past few years, single phase compounds with perovskite structure as lead iron niobate [Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$, PFN in reduced notation], in which electric and magnetic order coexist, have been widely investigated.[1–12] PFN is a ferroelectric and antiferromagnetic compound having high dielectric constant where Pb^{2+} in site *A* and Nb^{5+} in site *B″* favor electrical order and Fe^{3+} in the *B′* site gives rise to a magnetic moment that generates magnetic order. From previous studies, PFN exhibits either rhombohedral or monoclinic structure at room temperature (RT), a ferroelectric-paraelectric phase transition around 383 K (110 °C) (characterized by a tetragonal-cubic transition), an antiferromagnetic-paramagnetic transition characterized by a Néel temperature (T_N) between 122 and 145 K, and weak ferromagnetism below 10 K; moreover, the temperature-frequency response has also been reported by different authors.[6–12] However, clear evidence of the coupling between the electric and magnetic ordering has not been reported yet for PFN. Here, the magnetodielectric couplings on PFN ceramics have been investigated near the electric and magnetic phase transitions using standard ferroelectric tests and the electron paramagnetic resonance (EPR) technique.

A detailed description of the fabrication process of the sample investigated here and the experimental procedures used for the crystallographic, compositional, and surface morphological studies and the temperature-frequency response characterization were reported in previous work.[9–11] Ferroelectric properties including full and remanent hystereses were measured using a Precision Ferroelectric Tester system by Radiant Technologies, Inc. (in a virtual ground mode). EPR resonance measurements were performed with a JEOL JESRES3X spectrometer operating at the *X*-band (8.8–9.8 GHz) with 100 kHz modulation on the applied dc magnetic field, which could be varied from 0 to 8000 G. EPR spectra were recorded while cooling the sample in the 500–77 K temperature range.[13]

Representative RT *P-E* loops, consistent with soft ferroelectric behavior, are shown in Fig. 1(a) for a PFN sample with the values of $P_{\max}=11$ μC/cm^2 for the maximum polarization, $P_r=4$ μC/cm^2 for the remanent polarization, and

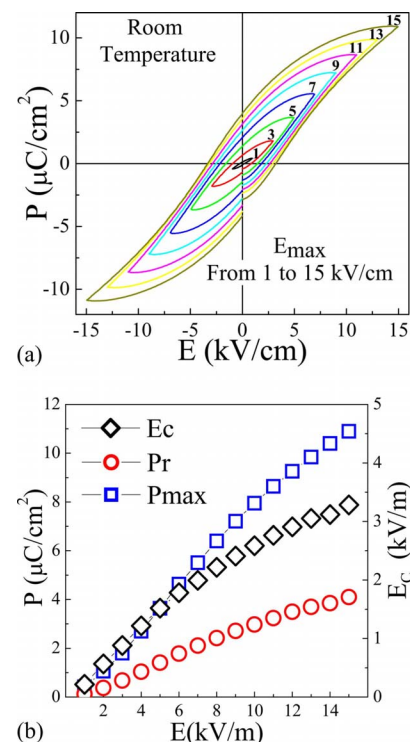FIG. 1. (Color online) (a) RT *P-E* loops for selected $E_{\max}$ values. (b) $E_{\max}$ dependence of the $P_{\max}$, P_r, and E_C parameters from full hysteresis.

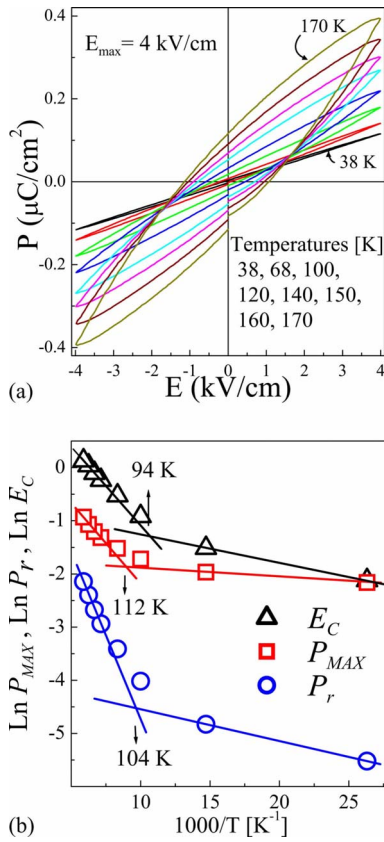a)Author to whom correspondence should be addressed. Electronic mail: raymond@cnyn.unam.mx.

FIG. 2. (Color online) (a) Low temperature *P*-*E* loops, (b) Arrhenius plots of P_{max}, and P_r values obtained from full hysteresis loops at low temperatures.

TABLE I. Activation energy values E_{act} [in meV] calculated from Arrhenius plots of the hysteresis parameters measured at temperatures between 38 and 170 K.

Parameter	T_{SC} (K)	E_{act}	
		$T < T_{SC}$	$T > T_{SC}$
P_{max}	112	2	26
P_r	104	5	54
E_C	94	5	25

out using Rietveld refinement method on neutron and x-ray diffraction data for powders in this low temperature region.[16,17] Here, changes in the electrical polarization behavior can be promoted by the transition from an ordered and less ferroelectric monoclinic structure [at $T < T_{SC}$), where the Fe^{3+} ions at the *B*-site form a weak ferromagnetic array (described below)] to a *B*-site disordered and highly ferroelectric rhombohedral structure (at $T > T_{SC}$), where an antiferromagnetic order is established. Moreover, these slope changes are in correspondence with the dielectric anomaly observed from measurements of dielectric constant and dielectric loss near 140 K, assumed as evidence of the magnetoelectric coupling by Gao *et al.*[6] in PFN ceramic samples and by Yang *et al.*[8] in PFN crystals, where coincidence with theoretical predictions was found.

EPR is a powerful technique to investigate the coupling between the electric and magnetic ordering in a single phase multiferroic material.[18,19] Figure 3(a) shows the EPR spectra—the derivative of the microwave power absorption with respect to the static field, *dP*/*dH*—recorded in the 77–300 K temperature range (the results in the 300–500 K range are not exhibited for clarity). We observe a single broad symmetric Lorentzian line along the entire temperature range due to the spin of the Fe^{3+} ions. When the temperature is decreased below 147 K, a weak absorption line has been observed [see inset of Fig. 3(a)].

The EPR spectra were fitted into the two-component Lorentzian equation accounting for the contributions from the clockwise and anticlockwise rotating components of the microwave magnetic field.[20,21] The temperature dependency of the EPR parameters—the peak to peak linewidth ΔH_{pp}, the integrated intensity I_{EPR}, and the *g-factor*—obtained from these fitting processes is plotted in Fig. 3(b). From the ΔH_{pp} behavior, it can be seen that the linewidth increases when the temperature is lowered from 300 to 147 K, which is found to be common in antiferromagnetic materials. On the other hand, I_{EPR} increases continuously with the decrease in temperature having a maximum at 183 K and followed by a rapid decrease down to 137 K; then, for $T < 137$ K a slow decrease is observed. Moreover, the *g-factor* first shows a slight decrease in the 300–183 K range. For temperatures below 183 K, however, it increases its value exhibiting a sharp peak with a maximum at 147 K. This remarkable sharp increase in the *g-factor* can be due to magnetic fluctuations in the establishment of the long-range order that precedes the transition to the antiferromagnetic order at T_N. Thus, the changes in ΔH_{pp}, I_{EPR}, and *g-factor* in the EPR spectra for PFN powders around 145 K are interpreted as a manifestation of a paramagnetic-antiferromagnetic transition. However, the weak absorption line observed at 137 K in correspondence with the increase in ΔH_{pp} and *g-factor* values for

$E_C = 3.2$ kV/cm for the coercive field for a maximum applied electric field of 15 kV/cm. Values of P_{max}, P_r, and E_C as functions of maximum electric field are plotted in Fig. 1(b), illustrating a nonlinear behavior, and that saturation was not achieved.

To investigate the direct coupling between the electric and magnetic ordering, measurements of polarization versus electric field were realized at cryogenic temperatures using a 20 K closed cycle refrigerator system with a temperature uncertainty of ±5 K. Hysteresis loops measured with a field value of $E_{max} = 4$ kV/cm [higher than the maximum E_C observed in Fig. 1(b) at RT] at different temperatures are shown in Fig. 2(a). A change in the loop shape from *quasi*linear to hysteretic behavior is observed. Moreover, plots of the P_{max}, P_r, and E_C parameters as function of temperature exhibit nonlinear behavior. Taking into account that the polarization mechanisms are thermally activated, the values of P_{max}, P_r, and E_C are assumed to follow an Arrhenius-like behavior.

Figure 2(b) shows the plots of ln P_{max}, ln P_r, and ln E_C versus $1/T$. Interesting changes in slope near 103 K are observed for all parameters. The activation energy (E_{act}) values obtained below and above each slope-change temperature T_{SC} [see Fig. 2(b)] are shown in Table I. The small values of the E_{act} in meV are attributed to hopping of electrons associated with thermally induced spin-state transitions which, in other circumstances, would be perturbed when an electric field is applied.[14,15] The differences between the E_{act} values below and above T_{SC} in Table I can be explained by the occurrence of a symmetry change depending on the degree of ordering of Fe^{3+} and Nb^{5+} ions over *B*-sites in good agreement with the previous reports on structural studies carried
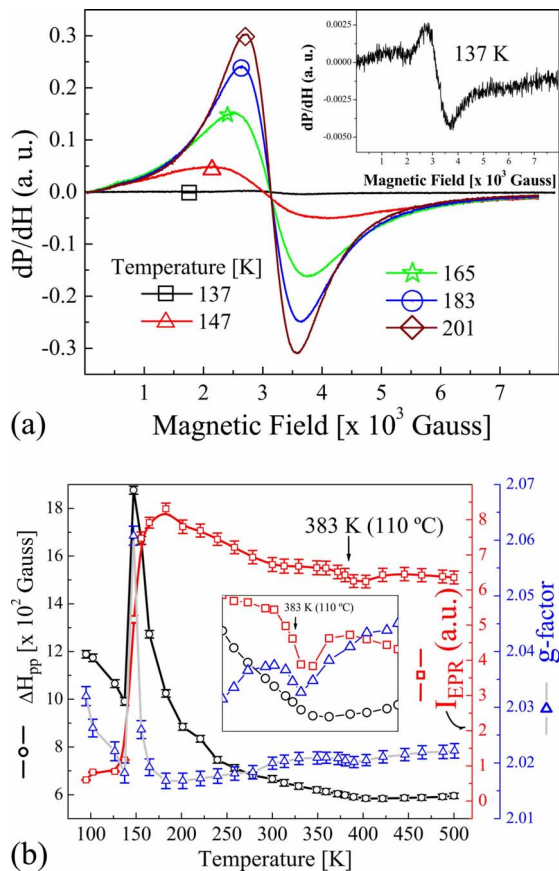
FIG. 3. (Color online) (a) EPR spectra of PFN for selected temperatures; the inset shows an extended scale EPR spectrum at 137 K. (b) Temperature dependence of the peak-to-peak linewidth $\Delta H_{p.p.}$, the integral intensity I_{EPR}, and the *g-factor*; the inset shows a zoom of the behavior of $\Delta H_{p.p.}$, I_{EPR}, and the *g-factor* in the 300 to 500 K range illustrating the anomalies near 383 K. Lines connecting points are only a guide for the eyes.

$T < 137$ K is a weak ferromagnetic signal that can be interpreted in terms of a resulting magnetic moment, probably due to canting between the antiparallel sublattices in the antiferromagnetic matrix. Recent publications of Yan *et al.*[7] and Yang *et al.*[8] reported the existence of a weak ferromagnetic moment in PFN thin films at $T = 5$ K and in PFN crystals below the Néel temperature (~ 143 K), respectively.

Additionally, in the high temperature range, noticeable anomalies were observed for the EPR parameters near the ferroelectric-paraelectric transition at 383 K (110 °C) [see Fig. 3(b)]. Starting at RT, ΔH_{pp} decreases continuously up to 403 K. In this temperature region, the paramagnetic absorption decreases when temperature increases due to the paramagnetic nature of this material. For $T > 403$ K, ΔH_{pp} shows a slight increase that can be associated with the tetragonal-to-cubic structural change, which creates variations in the vicinity of the Fe^{3+} ions, resulting in a reorganization of the spin-spin and spin-magnetic field interactions. From the temperature dependence of I_{EPR}, which in the paramagnetic phase is directly proportional to the static spin susceptibility, the minimum observed in the 390–403 K temperature range is associated with the ferroelectric-paraelectric phase transition in such manner that the electrical reordering leads to a redistribution of the electron spins, which, in turn, produces a change in the magnetic moments in concomitance with the variation in the Fe–O–Fe angle that defines these magnetic interactions. Regarding the *g-factor* behavior, our experiments give *g* values greater than that of a

free electron (equal to 2.0023) along the entire temperature range. The *g-factor* shows a net increase in the 300–500 K range but reaching a minimum around 390 K ($g_{min} = 2.0201$). We associate this behavior with the diffuse character of the ferroelectric-paraelectric transition,[9] where polar micro- or nanoregions with different Curie temperatures and where the coupling of the local polarizations and magnetizations in superparamagnetic polar nanoclusters in the paraelectric and ferroelectric phases take place.

In summary, we investigate the magnetodielectric behavior of the PFN ceramic. Changes in the electrical polarization behavior were observed during the occurrence of a paramagnetic to weakly magnetized antiferromagnetic transition near 103 K associated with a symmetry reduction from rhombohedral to monoclinic structure. EPR spectra confirm this transition at temperatures lower than 137 K. Changes in the EPR spectra in the high temperature region near the ferroelectric-paraelectric transition are correlated with the tetragonal-to-cubic symmetry change and interpreted in terms of the characteristic diffuse phase transition of this material. Such interactions between the electric and magnetic order are taken as evidence of magnetodielectric coupling in this multiferroic compound.

[1] R. Ramesh and N. A. Spaldin, Nature Mater. **6**, 21 (2007).
[2] J. F. Scott, Nature Mater. **6**, 256 (2007).
[3] M. Gajek, M. Bibes, S. Fusil, K. Bouzehouane, J. Fontcuberta, A. Barthelemy, and A. Fert, Nature Mater. **6**, 296 (2007).
[4] W. Eerenstein, M. Wiora, J. L. Prieto, J. F. Scott, and N. D. Mathur, Nature Mater. **6**, 348 (2007).
[5] Y. H. Chu, L. W. Martin, M. B. Holcomb, and R. Ramesh, Mater. Today **10**, 16 (2007).
[6] X. S. Gao, X. Y. Chen, J. Yin, J. Wu, Z. G. Liu, and M. Wang, J. Mater. Sci. **35**, 5421 (2000).
[7] L. Yan, J. Li, C. Suchicital, and D. Viehland, Appl. Phys. Lett. **89**, 132913 (2006).
[8] Y. Yang, J. M. Liu, H. B. Huang, W. Q. Zou, P. Bao, and Z. G. Liu, Phys. Rev. B **70**, 132101 (2004).
[9] O. Raymond, R. Font, N. Suárez-Almodovar, J. Portelles, and J. M. Siqueiros, J. Appl. Phys. **97**, 084107 (2005).
[10] O. Raymond, R. Font, N. Suárez-Almodovar, J. Portelles, and J. M. Siqueiros, J. Appl. Phys. **97**, 084108 (2005).
[11] O. Raymond, R. Font, N. Suárez-Almodovar, J. Portelles, and J. M. Siqueiros, J. Appl. Phys. **99**, 124101 (2006).
[12] D. Varshney, R. N. P. Choudhary, and R. S. Katiyar, Appl. Phys. Lett. **89**, 172901 (2006).
[13] G. Alvarez and R. J. Zamorano, J. Alloys Compd. **369**, 231 (2004).
[14] S. R. English, J. Wu, and C. Leighton, Phys. Rev. B **65**, 220407 (2002).
[15] T. H. O'Dell, in *The Electrodynamics of Magneto-Electric Media*, Selected Topics in Solid State Physics Vol. XI, edited by E. P. Wohlfarth (North-Holland, Amsterdam/American Elsevier, New York, 1970).
[16] N. Lampis, P. Sciau, and A. G. Lehmann, J. Phys.: Condens. Matter **11**, 3489 (1999).
[17] S. A. Ivanov, R. Tellgren, H. Rundlof, N. W. Thomas, and S. Ananta, J. Phys.: Condens. Matter **12**, 2393 (2000).
[18] G. E. Pake, in *Paramagnetic Resonance*, edited by W. A. Benjamin (INC, New York, 1962).
[19] T. Okamura, Y. Torizuka, and Y. Kojima, Phys. Rev. **82**, 285 (1951).
[20] J. P. Joshi, R. Gupta, A. K. Sood, S. V. Bhat, A. R. Raju, and C. N. R. Rao, Phys. Rev. B **65**, 024410 (2001).
[21] H. Montiel, G. Alvarez, I. Betancourt, R. Zamorano, and R. Valenzuela, Physica B (Amsterdam) **384**, 297 (2006).