Journal of Alloys and Compounds 508 (2010) 471–474

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Detection of the magnetic and electric transitions by electron paramagnetic resonance and low-field microwave absorption in the magnetoelectric $Pb(Fe_{0.5}Ta_{0.5})O_3$

G. Alvarez [a,*], H. Montiel [b], J.A. Peña [c], M.A. Castellanos [c], R. Zamorano [a]

[a] *Departamento de Física, ESFM-IPN, U.P. Adolfo López Mateos Edificio 9, Av. Instituto Politécnico Nacional S/N, San Pedro Zacatenco, México DF 07738, Mexico*
[b] *Departamento de Tecnociencias, Centro de Ciencias Aplicadas y Desarrollo Tecnológico de la Universidad Nacional Autónoma de México, Apartado Postal 70-360, México DF 04510, Mexico*
[c] *Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, México DF 04510, Mexico*

ARTICLE INFO

Article history:
Received 6 February 2010
Received in revised form 21 August 2010
Accepted 24 August 2010
Available online 19 September 2010

Keywords:
Perovskite
Multiferroic
Magnetoelectric
Resonant and non-resonant microwave absorption

ABSTRACT

An electron paramagnetic resonance (EPR) study of $Pb(Fe_{0.5}Ta_{0.5})O_3$ powder samples in perovskite-type structure at X-band (8.8–9.8 GHz), in the 120–300 K temperature range, is presented. For all the temperatures, the EPR spectra show a single broad line attributable to Fe^{3+} ions. The onset of the ferro-paraelectric and antiferro-paramagnetic transitions has been determined from the temperature dependence of parameters deduced from the EPR spectra: the peak-to-peak linewidth (ΔH_{pp}), the resonance field (H_{res}) and the integrated intensity (I_{EPR}). Low-field microwave absorption (LFMA) is used to give further knowledge on this material; where this technique also gives evidence of the magnetic and electric orders.

1. Introduction

The term multiferroic is associated with phenomena in which at least two of the three properties ferroelectricity, ferromagnetism, and ferroelasticity occur in the same material [1,2]. In particular, the multiferroic materials in which ferroelectricity coexists with a magnetic order are called magnetoelectrics [3]; representing a kind of material in which the magnetization can be induced by an electric field and electrical polarization by a magnetic field [4,5]. These materials have received much attention in recent years because of the possibility of new device applications envisaged from a strong coupling between these parameters [6].

In particular, lead iron tantalate $Pb(Fe_{0.5}Ta_{0.5})O_3$ (PFT) is among the first perovskite-type ferroelectrics (ABO_3) synthesized in Russia in the 1950s [7]; where magnetic Fe^{3+} ($3d^5$, $S = 5/2$) and non-magnetic Ta^{5+} ($5d^0$, $S = 0$) share the B site of the simple perovskite structure. Additionally, Pb^{2+} in A site and Ta^{5+} in B site favor the electric order, due to lattice distortion; and Fe^{3+} provides the magnetic moment of the magnetic order. These are the bases of coexistence for ferroelectric–antiferromagnetic orders in this magnetoelectric material.

PFT is a relaxor ferroelectric with a diffuse transition at about 243 K [8], and with an antiferromagnetic transition in the range from 133 to 180 K [9,10]. In this material, a scarce evidence of the magnetoelectric effect (a coupling between the ferroelectric and magnetic orders) has been reported; where another manifestation of this effect is associated with changes in the magnetic properties, due to onset of the electric transition or by the application of an electric field.

In general, for magnetoelectric materials, the change in the electrical ordering caused by the ferro-paraelectric phase transition or by an external electric field leads to a redistribution of the electron spin; and this produces a change in the magnetic moments, and therefore a variation in magnetic properties [11].

On the other hand, the electron paramagnetic resonance (EPR) is the most powerful spectroscopic method available to unambiguously determine the valence state of paramagnetic ions [12], local structural information and symmetry of paramagnetic ions incorporated in the structure [13,14]. This technique allows the investigation of the nature of magnetic phases in materials at different temperatures [12,15].

Recently, we have implemented a technique to measure the non-resonant microwave absorption around zero magnetic field [16], which has been denominated as low-field microwave absorption (LFMA). This technique has recently been used to detect the magnetic transition in materials [12,15,17], and provide highly

---

* Corresponding author. Tel.: +52 5557296000.
E-mail address: memodin@yahoo.com (G. Alvarez).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.08.095

sensitive detection of magnetic order. More importantly, this technique can distinguish between different dissipative dynamics of microwave absorbing centers.

To our knowledge, however, studies of magnetoelectric PFT with EPR and LFMA techniques are scarce. For this reason, we study the changes in the EPR line shape of PFT powders in this paper; these changes are quantified by means of the following parameters: the peak-to-peak linewidth (ΔH_{pp}), the resonant field (H_{res}) and the integrated intensity (I_{EPR}) as a function of temperature, through ferro-paraelectric and antiferro-paramagnetic transitions. LFMA technique is used to give further knowledge on this material, where this technique also gives evidence of the magnetic and electric orders.

2. Samples preparation and experimental details

The samples of PFT were prepared by the wolframite precursor method [18]. The PFT powders are synthesized from commercially available oxides. In this method, stoichiometric Fe_2O_3 (99% purity) and Ta_2O_5 (99.99% purity) are mixed by ball milling for 8 h followed by calcination in air at 1000 °C for 4 h, to obtain the $FeTaO_4$ precursor. The last product was mixed with $Pb(NO_3)_2$ and then calcined at 1000 °C for 1 h. This method enhances the efficiency of the formation of the desired phase and it confines the creation of detrimental pyrochlore-type phases. The X-ray diffraction (XRD) analysis is carried out with a Siemens D5000 diffractometer using the 1.5406 Å Cu Kα line to check phase purity; XRD measurements are made at 300 K.

EPR measurements are performed with a JEOL JES-RES 3X spectrometer operating at X-band (8.8–9.8 GHz) with 100 kHz of modulation on the applied dc magnetic field (H_{dc}). H_{dc} could be varied from 0 to 6000 G. EPR spectra are recorded while cooling the sample in the 120–300 K temperature range. The spectrometer is modified by connecting X and Y input voltmeters that in turn are connected to a PC enabling digital data acquisition [16].

LFMA response uses the same EPR spectrometer, adequately modified [16]. These measurements are performed using a Jeol ES-ZCS2 zero-cross sweep unit that digitally compensates any remanence in the electromagnet, allowing the measurements to be carried out by cycling H_{dc} about their zero value, continuously of $-1000\,G \leq H_{dc} \leq +1000\,G$; with a standard deviation of less than 0.2 G for the measured field. In the LFMA technique the sample is zero-field cooled to the desired temperature, and then it is maintained at a fixed temperature with a maximum deviation of ±1 K during the whole LFMA measurement (~4 min of sweep).

3. Results and discussion

Fig. 1 shows the XRD pattern of polycrystalline PFT sample. All observed reflection lines are indexed as a perovskite-type structure corresponding to space group *Pm*3*m*; and it shows that PFT is free of secondary pyrochlore-type phases.

In Fig. 2, we show EPR spectra (d*P*/d*H* vs. magnetic field) recorded in the 120–300 K temperature range. It can be observed that resonance spectra exhibit a single broad symmetric Lorentzian line along the entire temperature range, due to the spin of the Fe^{3+} ions. The derivative of microwave power absorption with respect to the static field (d*P*/d*H*) is fitted into the two-component Lorentzian equation accounting for the contributions from the clockwise and anticlockwise rotating components of the microwave magnetic field [19,20], as follows:

$$\frac{dP}{dH} \propto \frac{d}{dH}\left(\frac{\Delta H_{pp}}{(H_{dc}-H_{res})^2+\Delta H_{pp}^2}+\frac{\Delta H_{pp}}{(H_{dc}+H_{res})^2+\Delta H_{pp}^2}\right) \quad (1)$$

where H_{dc} is the applied magnetic field. The temperature dependences of the EPR parameters obtained from these fits are plotted in Fig. 3.

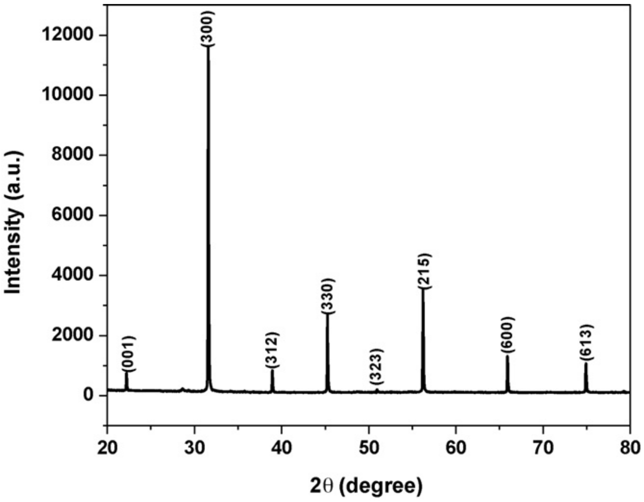

Fig. 1. XRD pattern of the polycrystalline sample of lead iron tantalate $Pb(Fe_{0.5}Ta_{0.5})O_3$.

Fig. 3(a) shows the temperature dependence of ΔH_{pp} for PFT powders. ΔH_{pp} increases slightly as temperature decreases from 300 to 170 K. As temperature continues to decrease, $T < 170$ K, ΔH_{pp} increases continuously, but this time with a higher change rate. In Fig. 3(b), we show the behavior of the H_{res} vs. temperature. H_{res} increases continuously with the temperature decrease, exhibiting a maximum at 170 K, and followed by a fast decrease until 120 K.

For 170–300 K temperature region the material is paramagnetic [9,10], and microwave absorption increases with the decrease in temperature [13,14]; and it would explain the behavior of ΔH_{pp} and H_{res} in this temperature interval. On the other hand, the sud-

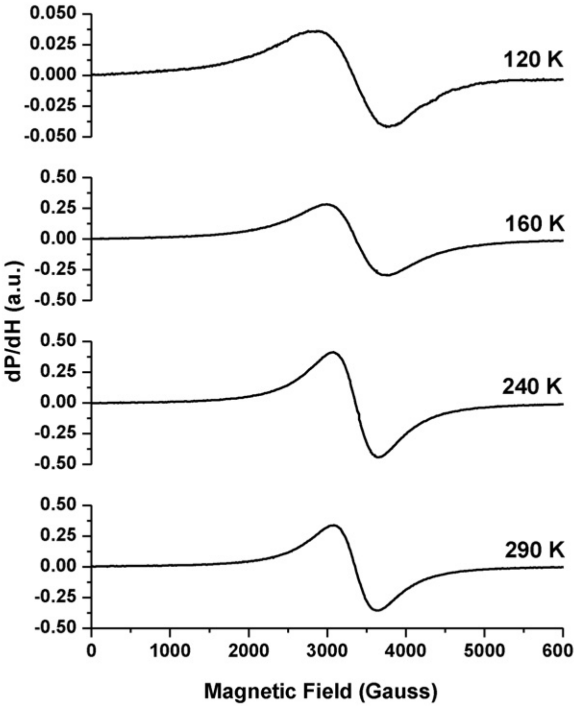

Fig. 2. EPR spectra of the magnetoelectric $Pb(Fe_{0.5}Ta_{0.5})O_3$ for selected temperatures.

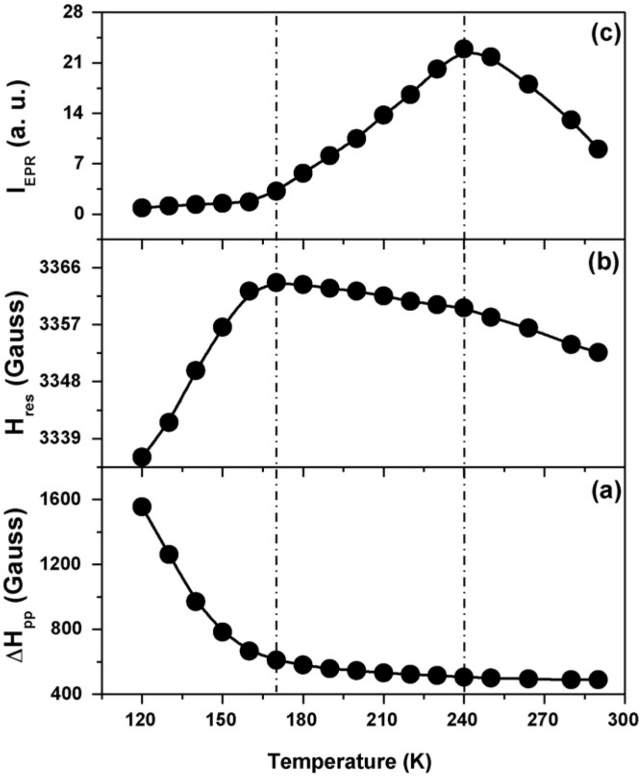

Fig. 3. Temperature dependence of (a) the peak-to-peak linewidth – ΔH_{pp}, (b) the resonant field – H_{res} and (c) the integral intensity – I_{EPR}. Solid lines are guides for the eye only.

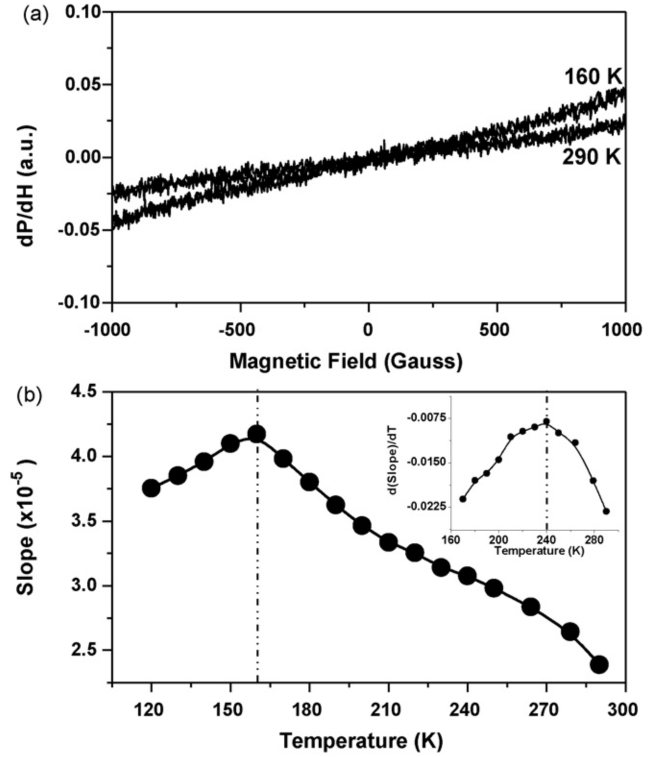

Fig. 4. (a) LFMA spectra for 290 and 160 K, with H_{mod} = 0.63 G and microwave power of 1 mW. (b) The temperature dependence of the absorption line slope for temperature interval of 120–290 K. The inset of (b) shows the temperature dependence of d(*Slope*)/d*T* in the 160–290 K temperature range. The curves connecting points are only guides for the eye.

den shift in H_{res} and the broadening in ΔH_{pp}, as the temperature is lowered ($T < 170$ K), can be due at three possible explanations. The first possibility is that a ferromagnetic impurity in the form of a second phase, with a Curie point close to 170 K and a significant concentration, could explain this behavior; but the XRD spectrum does not show the presence of a second phase. The other possibility can be understood as a manifestation of the existence of a strong magnetic dipolar interaction between Fe^{3+} and Fe^{2+} ions, where oxygen atoms deficiency would generate a state of mixed valency; however, this behavior would reveal the presence of short-range magnetic correlations [12], but this process would not explain the decrement sudden in H_{res} at low temperature. The more sound explanation of this behavior can be attributed to a long-range antiferromagnetic order at T_N = 170 K, as result of the linear superexchange interaction between Fe ions.

The temperature dependence of I_{EPR}, which in the paramagnetic phase is directly proportional to the static spin susceptibility [13,14], is shown in Fig. 3(c). Starting from 300 K, I_{EPR} increases continuously with the temperature decrease, exhibiting a maximum at T_{max} = 240 K; this behavior indicates the paramagnetic nature of this signal [13,14]. After T_{max}, when the temperature continues to decrease, I_{EPR} diminishes; where an inflection point at T_N = 170 K is clearly observed. We associate the maximum, T_{max}, with the onset of the ferro-paraelectric phase transition and which is accompanied with a structural change [8]. This structural change leads to a redistribution of the Fe^{3+} ions, and it generates a reorganization of all the magnetic interactions; affording the variation of the Fe–O–Fe angle that defines these interactions. The Curie temperature (T_{max}) obtained by the technique EPR is in a good agreement with the reported values [8]. For low temperature, the decrease in I_{EPR} can be associated with the decrement of the quantity of absorbing paramagnetic centers, due to the process of antiparallel spin alignment and which is associated with the antiferromagnetic order. The change in slope at T_N, as is shown in Fig. 3(c), can be associated with the onset of antiferro-paramagnetic transition, in a good correspondence with plots of H_{res} and ΔH_{pp}.

We turn now to LFMA results. Fig. 4(a) shows LFMA spectra (d*P*/d*H* vs. magnetic field, around zero field) for selected temperatures. The curves exhibit a linear behavior with a positive slope and non-hysteretic traces. The positive slope implies that this non-resonant microwave absorption is a minimum around zero magnetic field and that it increases with applied magnetic field; in other words, this is a magnetic field-dependent absorption. LFMA lines show the absence of any irreversible microwave energy-absorption process in the ordered and disordered phases. This behavior contrasts strongly with the one shown by high-T_c superconductors [16], ferrimagnetic [15] and ferromagnetic [17,21] materials.

The LFMA line can be described by the experimental correlation:

$$\frac{dP}{dH} = S(T)H \tag{2}$$

where $S(T)$ is the slope of the absorption line and that it depends only on temperature.

Fig. 4(b) shows the behavior of the slope of the LFMA line in the 90–290 K temperature range. The slope increases monotonically when the temperature decreases from 290 K, reaching a maximum value at 160 K. This increasing behavior is characteristic of a paramagnetic phase [12,22], in good agreement with the EPR results. Additionally, a change in slope at 240 K is observed, this inflection point is more apparent in the plot d(*Slope*)/d*T* vs. *T* and it is shown as a maximum at 240 K; see the inset of Fig. 4(b). This change indicates the presence of an additional absorption process, which we propose as originated by the ferro-paraelectric phase transition; where the ferroelectric transition originate a change in the relative orientation of magnetic moments due to structural change, affecting the superexchange interactions between Fe ions, and it generate a change in the dynamics of microwave absorption.

As the temperature is decreased further, $T < 160\,\text{K}$, the slope slowly decreases and another magnetic process sets-in which we propose as originated by long-range magnetic correlations; in this region the quantity of absorbing centers diminishes due to the process of antiparallel spin alignment. The whole profile of the slope of the LFMA line depends on the thermal dependence of the spin dynamics prior to their antiparallel alignment at $T < 160\,\text{K}$; and its intensity follows the variation in the number of absorption centers, which in turn is controlled by the establishment of the antiferromagnetic order at low temperature.

4. Conclusions

The changes in the parameters ΔH_{pp}, H_{res} and I_{EPR} in the EPR spectra for the magnetoelectric PFT at $T_C = 240\,\text{K}$ and $T_N = 170\,\text{K}$, are interpreted as a ferro-paraelectric and antiferro-paramagnetic transitions, respectively. These transitions promote a spin redistribution of Fe^{3+} ions, which creates changes in dynamics of microwave absorption.

For all temperatures, LFMA spectra showed straight lines with positive slope and non-hysteretic traces. The spectral changes for the plot of the slope vs. temperature also give evidence of magnetic and electric orderings, with a very high detection sensibility.

Acknowledgments

G. Alvarez acknowledges research support in the laboratory of magnetic mensurations and biophysics of ESFM-IPN-Mexico. Support from project PAPIIT-UNAM No. IN116608-3 is gratefully acknowledged.

References

[1] C.-W. Nan, M.I. Bichurin, S. Dong, D. Viehland, G. Srinivasan, J. Appl. Phys. 103 (2008) 031101.
[2] C.N.R. Rao, C.R. Serrao, J. Mater. Chem. 17 (2007) 4931–4938.
[3] M. Fiebig, Th. Lottermoser, D. Fröhlic, A.V. Goldzev, R.V. Pisarev, Nature 419 (2002) 818–820.
[4] Y.-H. Chu, L.W. Martin, M.B. Holcomb, R. Ramesh, Mater. Today 10 (2007) 16–23.
[5] A.K. Zvezdin, A.M. Kadomtseva, S.S. Krotov, A.P. Pyatakov, Yu.F. Popov, G.P. Vorob'ev, J. Magn. Magn. Mater. 300 (2006) 224–228.
[6] J.F. Scott, Nat. Mater. 6 (2007) 256–257.
[7] G.A. Smolenskii, A.I. Agranovskaia, V.A. Isupov, Sov. Phys. Solid State 1 (1959) 907–911.
[8] W.Z. Zhu, A. Kholkin, P.Q. Mantas, J.L. Baptista, J. Eur. Ceram. Soc. 20 (2000) 2029–2034.
[9] A. Falqui, N. Lampis, A. Geddo-Lehmann, G. Pinna, J. Phys. Chem. B 109 (2005) 22967–22970.
[10] N. Lampis, C. Franchini, G. Satta, A.G. Lehmann, S. Massidad, Phys. Rev. B 69 (2004) 064412.
[11] R. Font, G. Alvarez, O. Raymond, J. Portelles, J.M. Siqueiros, Appl. Phys. Lett. 93 (2008) 172902.
[12] G. Alvarez, R. Font, J. Portelles, O. Raymond, R. Zamorano, Solid State Sci. 11 (2009) 881–884.
[13] J.A. Weil, J.R. Bolton, J.E. Wertz, Electron Spin Resonance: Elementary Theory and Practical Applications, John Wiley & Sons Inc., New York, 1994.
[14] J.R. Pilbrow, Transition Ion Electron Paramagnetic Resonance, Clarendon Press, Oxford, 1990.
[15] G. Alvarez, H. Montiel, J.F. Barron, M.P. Gutierrez, R. Zamorano, J. Magn. Magn. Mater. 322 (2010) 348–352.
[16] G. Alvarez, R. Zamorano, J. Alloys Compd. 369 (2004) 231–234.
[17] M.P. Gutiérrez, G. Alvarez, H. Montiel, R. Zamorano, R. Valenzuela, J. Magn. Magn. Mater. 316 (2007) e738–e740.
[18] J. Kulawik, D. Szwagierczak, J. Eur. Ceram. Soc. 27 (2007) 2281–2286.
[19] J.P. Joshi, R. Gupta, A.K. Sood, S.V. Bhat, A.R. Raju, C.N.R. Rao, Phys. Rev. B 65 (2002) 024410.
[20] H. Montiel, G. Alvarez, I. Betancourt, R. Zamorano, R. Valenzuela, Physica B 384 (2006) 297–299.
[21] H. Montiel, G. Alvarez, I. Betancourt, R. Zamorano, R. Valenzuela, Appl. Phys. Lett. 86 (2005) 072503.
[22] G. Alvarez, R. Font, J. Portelles, R. Zamorano, R. Valenzuela, J. Phys. Chem. Solids 68 (2007) 1436–1442.