

A microwave absorption study in the ferromagnetoelectric $\text{Pb}(\text{Fe}_{1-x}\text{M}_x)\text{O}_3$ ($\text{M} = \text{Ta}, \text{W}, \text{Nb}$) perovskites

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We report on the effects of dc magnetic field and temperature on the microwave absorption measurements at X-band (8.8-9.8 GHz), in powder samples of perovskites $\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PFT), $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) and $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ (PFW). At room temperature (300 K), in all these ferromagnetoelectric materials, the electron paramagnetic resonance (EPR) spectra show a single broad line associated with Fe^{3+} ions. For low temperature (77 K), these resonant absorption modes change and they can be associated with: (1) a canting of Fe^{3+} ion sublattices in the antiferromagnetic matrix and/or (2) a strong magnetic dipolar interaction between Fe^{2+} and Fe^{3+} ions. Low-Field Microwave Absorption (LFMA) is used to give further knowledge on these materials, giving an additional support to our analyses.

Keywords: Microwave absorption; electron paramagnetic resonance; magnetic transitions.

Nosotros reportamos sobre los efectos del campo magnético dc y la temperatura sobre las medidas de la absorción de microondas a banda-X (8.8-9.8 GHz), en muestras en polvo de las perovskitas $\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PFT), $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) y $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ (PFW). A temperatura ambiente (300 K), en todos estos materiales ferromagnetoelectrónicos, los espectros de resonancia paramagnética electrónica (RPE) muestran una sola línea ancha asociada con los iones de Fe^{3+} . Para baja temperatura (77 K), estos modos de absorción resonantes cambian y pueden asociarse con: (1) Un canteo de la subred de iones Fe^{3+} de la matriz antiferromagnética y/o (2) una fuerte interacción dipolar entre los iones de Fe^{2+} y Fe^{3+} . La absorción de microondas a campo bajo (AMCB) se usa para dar un mayor conocimiento sobre estos materiales, dando un soporte adicional a nuestros análisis.

Descriptores: Absorción de microondas; resonancia paramagnética electrónica; transiciones magnéticas.

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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]. In particular, the multiferroic materials in which ferroelectricity coexists with a magnetic order are called ferromagnetoelectrics [2]; representing a kind of material in which the magnetization can be induced by an electric field and electrical polarization by a magnetic field [3].

$\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PFT), $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) and $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ (PFW) are compounds of the family of Pb-based complex perovskites, with the general formula $\text{AB}'_x\text{B}''_{1-x}\text{O}_3$, which they are obtained from the simple perovskite ABO_3 by partial substitution of the B cation; where the replacement of some of the diamagnetic (d^0) B cations by transition metal (d^n) species was searched in Russia in the 1950s [4-6]. PFT, PFN and PFW are relaxor perovskites with a diffuse para-ferroelectric transition at about 240 K,

380 K and 178 K, respectively [7]; and also they have a para-antiferromagnetic transition at 170 K, 145 K and 363 K, respectively [7].

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 [8], local structural information and symmetry of paramagnetic ions incorporated in the structure [9]. This technique allows the investigation of the nature of magnetic phases in materials at different temperatures [10].

Recently, we have implemented a technique to measure the non-resonant microwave absorption around zero magnetic field [11], which has been denominated as low-field microwave absorption (LFMA). This technique has recently been used to detect the magnetic transitions in materials [10,12], and provide highly sensitive detection of magnetic order. More importantly, this technique can distinguish between different dissipative dynamics of microwave absorbing centers.

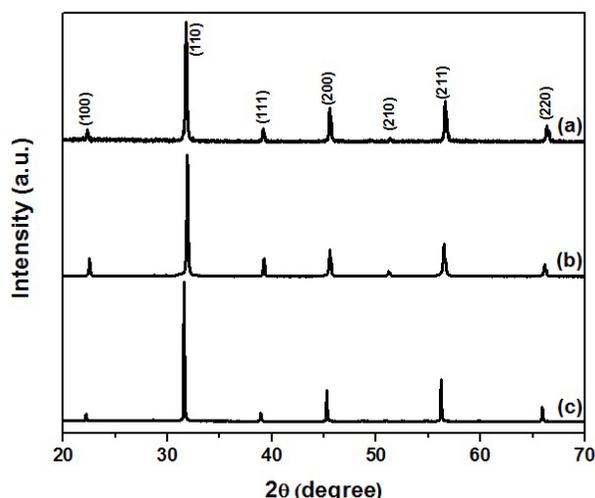


FIGURE 1. XRD pattern of the polycrystalline samples of (a) PFW, (b) PFN and (c) PFT.

2. Samples preparation and experimental techniques

The samples used in this study are prepared from different synthesis methods. The PFT powders are prepared by the wolframite precursor method [13]. The synthesis of PFW powders is prepared through columbite precursor method [14]. A coprecipitation method is developed to synthesize the PFN powders [15,16]. The complete schemes and details concerning to synthesis methods can be found elsewhere [17]. The X-ray diffraction (XRD) analysis is carried out with a Siemens D5000 diffractometer using the 1.5406 \AA Cu $K\alpha$ line to check the 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 5000 G. All EPR spectra are recorded at 300 K and 77 K. The spectrometer is modified by connecting X and Y input voltmeters that in turn are connected to a PC enabling digital data acquisition [11].

LFMA response use the same EPR spectrometer, adequately modified [11]. 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 $-1000 \text{ G} \leq H_{dc} \leq +1000 \text{ G}$; with a standard deviation of less than 0.2 G for the measured field. In the LFMA technique the sample is maintained at 300 K and 77 K during the whole measurement (~ 4 min of sweep).

3. Results and discussion

Figure 1 shows the XRD pattern of polycrystalline samples of PFW, PFN and PFT. For all these ferromagnetoelectric sam-

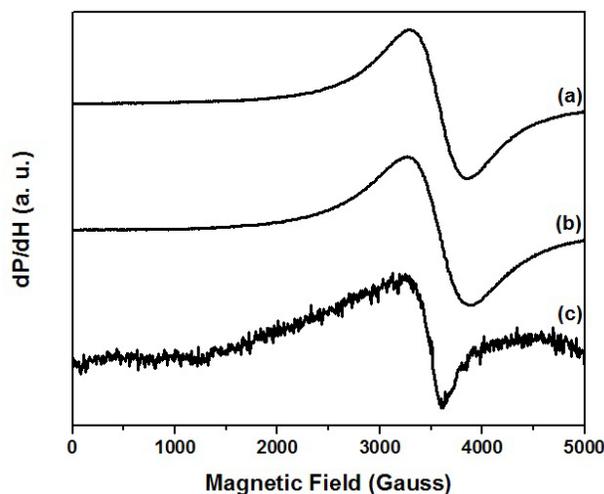


FIGURE 2. EPR spectra at 300 K of the ferromagnetoelectrics (a) PFT, (b) PFN and (c) PFW.

ples, all of the peaks of the XRD pattern are indexed as a cubic perovskite structure corresponding to space group $\text{Pm}\bar{3}\text{m}$, in a good agreement with the standard JCPDS cards (PFW 40-0374, PFN 32-0522 and PFT 89-3129); also it shows that these ferromagnetoelectric samples are free of secondary pyrochlore-type phases.

In Fig. 2, we show EPR spectra (dP/dH vs. magnetic field) recorded at room temperature (300 K) for PFT, PFN and PFW powders. It can be observed that all resonance spectra exhibit a broad symmetric Lorentzian line, due to the spin of the Fe^{3+} ions; but their peak-to-peak line width (ΔH_{pp}) and resonant magnetic field (H_r) are different among them, see Table I. At room temperature, PFT and PFN are paramagnetic, and PFW is antiferromagnetic [7]. For PFT and PFN powders, Fig. 2(a) and 2(b), the resonance signals indicates a paramagnetic nature [8,9,18], which it is suggested of the EPR parameters. The observed resonant signal in polycrystalline sample PFW, see Fig. 2(c), can be associated with a weak ferromagnetic signal (WFS); because the exchange interaction tend to narrow the absorption line and the shift in H_{res} indicates a internal field contribution. This WFS is attributed to canting of Fe^{+3} ion sublattices in the antiferromagnetic matrix [18,19].

Figure 3 shows LFMA spectra (dP/dH vs. magnetic field, around zero field) at 300 K for the polycrystalline samples of PFT, PFN and PFW.

In Fig. 3(a), for PFT powders, the LFMA spectrum exhibits a linear behavior with a positive slope and non-hyster-

TABLE I. EPR parameters of PFT, PFN and PFW powders.

	ΔH_{pp} (G) at 300 K	H_r (G) at 300 K	ΔH_{pp} (G) at 77 K	H_r (G) at 77 K
PFT	567	3587	890	3354
PFN	629	3586	1420	3151
PFW	374	3483	648	3410

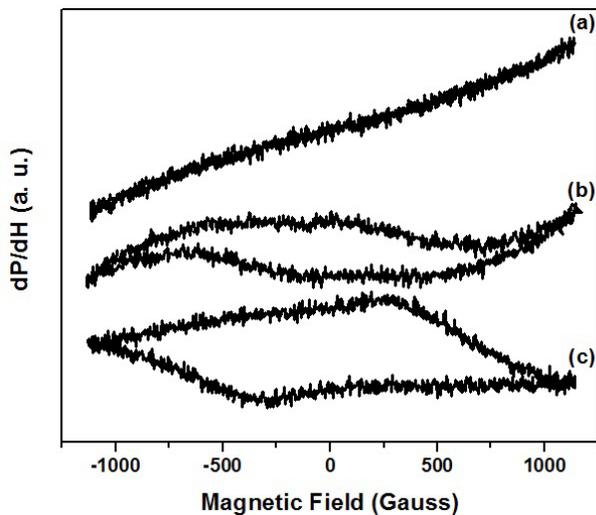


FIGURE 3. LFMA spectra at 300 K of the ferromagnetolectrics (a) PFT, (b) PFN and (c) PFW; with $H_{\text{mod}} = 0.63$ G and microwave power of 5 mW.

etic trace; *i.e.* this absorption line shows the absence of any irreversible microwave energy-absorption process in paramagnetic phase. This behavior is similar to the one observed in others ferromagnetolectric materials [12,19]. But it contrasts strongly with the LFMA spectra observed for the ferromagnetolectrics PFN and PFW, as it is shown in Fig. 3(b) and 3(c), respectively; where a clear hysteresis of these spectra appear on cycling the field. This feature has been associated with low field magnetization processes in ferromagnetic materials [10,20], suggesting the presence of a magnetic component at room temperature in these ferromagnetolectric perovskites. The differences among these LFMA spectra can be due to different absorption nature, which it is associated to absorbing centers with a different magnetic ordering; since a weak ferromagnetism is suggested from EPR measurements in PFW powders.

We turn now to results at low temperature. Figure 4 shows EPR spectra at 77 K of polycrystalline samples of PFT, PFN and PFW. For this temperature, all our ferromagnetolectric samples are antiferromagnetic [7]. In all samples, we observed the presence of WFS, where a ferromagnetic impurity in the form of a second phase with a significant concentration could explain this behavior; but the XRD spectra do not show the presence of this second phase. A more sound explanation of these features is as follows: normally, antiferromagnetic resonance is observed only at very high frequencies [21] around 100 GHz, or more, far beyond the resonance frequencies used in this experiment, hence no absorption line should be observed at X-band. The presence of a broad absorption line in the antiferromagnetic state can be interpreted in terms of a resulting magnetic moment, *i.e.* a canting between the antiparallel sublattices. Two nondegenerate resonance modes appear, one at very high frequencies (not observed in our experiments at X-band) while the other one occurs at ordinary microwave frequencies, and can be

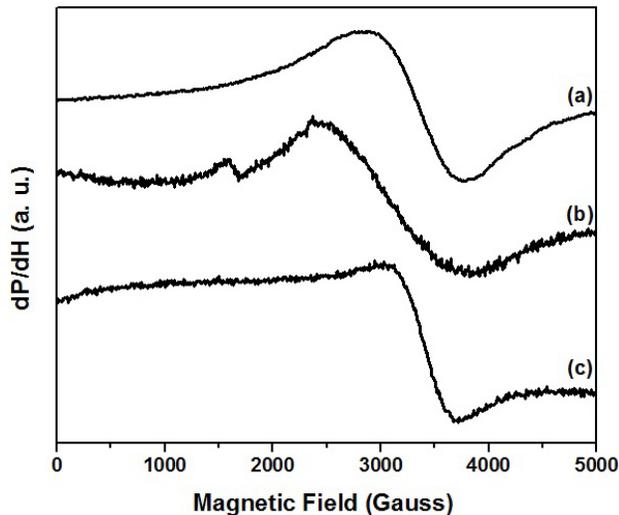


FIGURE 4. EPR spectra at 77 K of the ferromagnetolectrics (a) PFT, (b) PFN and (c) PFW.

considered similar to a ferromagnetic mode [22]. EPR parameters of the Table I agree with our interpretation.

It is necessary to mention that in Fig. 4(b), for PFN powders, we observed an additional resonant mode, due to presence of iron ions as Fe^{3+} as well as Fe^{2+} in the sample. Though Fe^{3+} and Fe^{2+} ions are both paramagnetic, only Fe^{3+} ($3d^5$, $S=5/2$) shows EPR absorption. Fe^{2+} ions are not directly involved in the EPR absorption, but their interactions with Fe^{3+} ions can influence the characteristics of the line-shape or can generate new absorption modes [9]. Then, the presence of a fraction of Fe^{2+} ions generates a strong magnetic dipolar interaction with Fe^{3+} ions [8], giving origin to this second absorption mode; however, more evidence is gathered to continuation. The existence of the interactions between Fe^{3+} and Fe^{2+} ions tend to broaden the linewidth of the main absorption mode, as can be seen in the Table I.

In Fig. 5, we show the LFMA spectra at 77 K for the polycrystalline samples of PFT, PFN and PFW.

In Fig. 5(a), for PFT powders, a linear (with a small negative slope) and non-hysteretic LFMA spectrum is observed, which is indicative of an antiferromagnetic ordering and also suggest a weak ferromagnetism at low temperature [12,19]; in good agreement with EPR measurement. Figure 5(b) and 5(c) present the LFMA spectra of the ferromagnetolectrics PFN and PFW, respectively; at this temperature, they showed also hysteresis on cycling the dc magnetic field around zero. But among these signals are exhibited a phase opposite, *i.e.* with a contrary phase between these LFMA spectra; where this opposite phase suggests a different absorption nature. Recently, we have observed that the LFMA spectra can have a phase opposite, due to absorbing centers with different magnetic ordering [10,20]. Then, this behavior can be attributed to the presence of different kinds of absorbing centers between these ferromagnetolectric materials; since the PFN powders have a strong magnetic interaction between Fe^{3+} and Fe^{2+} ions, that it is suggested by EPR analysis, leading to a change in the microwave absorption regime.

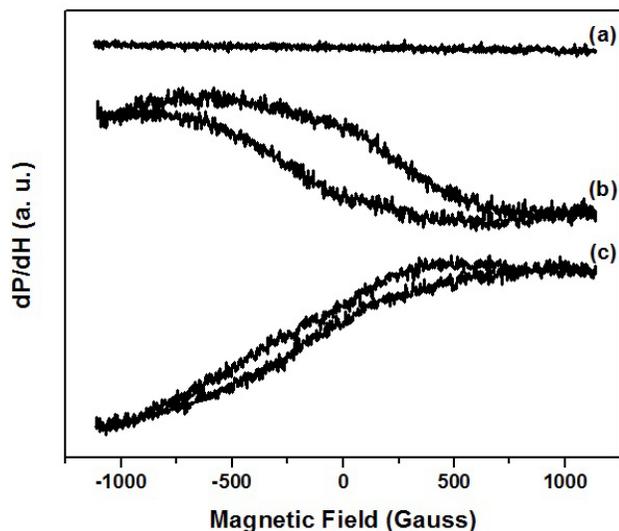


FIGURE 5. LFMA spectra at 77 K of the ferromagnetolectrics (a) PFT, (b) PFN and (c) PFW; with $H_{\text{mod}} = 0.63$ G and microwave power of 5 mW.

4. Conclusions

In this work is shown that EPR is the most powerful spectroscopic method available for obtaining local structural information and symmetry of the incorporate transition metal ion in these ferromagnetolectric perovskites. Additionally, LFMA technique provides information on the magnetic field dependence of the microwave absorption in these ferromagnetolectric materials. More important, these techniques can distinguish between different dissipative dynamics of microwave absorbing centers, and can also provide valuable information about the nature of magnetic ordering in these multiferroic materials.

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1. H. Schmid, *Ferroelectrics* **162** (1994) 317.
2. M. Fiebig, Th. Lottermoser, D. Fröhlich, A.V. Goldzev, and R.V. Pisarev, *Nature (London)* **419** (2002) 818.
3. D.N. Astrov, *Sov. Phys. JETP* **11** (1966) 708.
4. G.A. Smolenskii, A.I. Agranovskaia, S.N. Popov, and V.A. Isupov, *Sov. Phys. Tech. Phys.* **3** (1958) 1981.
5. G.A. Smolenskii, V.A. Isupov, and A.I. Agranovskaya, *Sov. Phys. Solid State* **1** (1959) 150.
6. G.A. Smolenskii, A.I. Agranovskaia, and V.A. Isupov, *Sov. Phys. Solid State* **1** (1959) 907.
7. G.A. Smolenskii, and I.E. Chupis, *Sov. Phys. USP* **25** (1982) 475.
8. G. Alvarez, R. Font, J. Portelles, O. Raymond, and R. Zamorano, *Solid State Sci.* **11** (2009) 881.
9. John A. Weil, James R. Bolton, and John E. Wertz, *Electron Spin Resonance: Elementary Theory and Practical Applications* (John Wiley & Sons, New York, 1994).
10. G. Alvarez, H. Montiel, J.F. Barron, M.P. Gutierrez, and R. Zamorano, *J. Magn. Magn. Mater.* **322** (2010) 348.
11. G. Alvarez, and R. Zamorano, *J. Alloys Compd.* **369** (2004) 231.
12. G. Alvarez, R. Font, J. Portelles, R. Zamorano, and R. Valenzuela, *J. Phys. Chem. Solids* **68** (2007) 1436.
13. J. Kulawik, and D. Szwagierczak, *Journal of the European Ceramic Society* **27** (2007) 2281.
14. Liquin Zhou, P.M. Vilarinho, J.L. Bptista, and E. Fortunato, *Journal of the European Ceramic Society* **20** (2000) 1035.
15. Jianlan Tang, Mankang Zhu, Tao Zhong, Yodong Hou, Hao Wang, and Hui Yan, *Materials Chemistry and Physics* **101** (2007) 475.
16. Yoshio Yoshikawa, and Kenji Uchino, *Journal of the American Ceramic Society* **79** (1996) 2417.
17. J. A. Peña, "Síntesis de relajantes ferroeléctricos a base de plomo", (Bachelor's thesis dissertation, Faculty of Chemistry, UNAM, Mexico, 2010).
18. G. Alvarez, R. Font, J. Portelles, R. Valenzuela, and R. Zamorano, *Physica B* **384** (2006) 322.
19. G. Alvarez, M.P. Cruz, A.C. Durán, H. Montiel, and R. Zamorano, *Solid State Commun.* **150** (2010) 1597.
20. H. Montiel, G. Alvarez, I. Betancourt, R. Zamorano, and R. Valenzuela, *Appl. Phys. Lett.* **86** (2005) 072503.
21. J.M. Rawson, A. Alberola, H. El-Mkami, and G.M. Smith, *J. Phys. Chem. Solids* **65** (2004) 727.
22. A.H. Morrish, *The Physical Principles of Magnetism* (John Wiley & Sons, New York, 1965).