

Electron paramagnetic resonance study of the ferroelectromagnet $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ through ferro-paraelectric transition

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Abstract

An electron paramagnetic resonance (EPR) study of ferroelectromagnet $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) powders is presented. The EPR spectra show a single broad line in the 300–500 K temperature range, attributable to Fe^{3+} ions. The onset of the ferro-paraelectric transition was determined from the temperature dependence of three main parameters deduced from the EPR spectra: *g*-factor, peak-to-peak linewidth and integrated intensity. These parameters indicate a behavior in agreement with a diffuse phase transition.

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1. Introduction

Lead iron niobate $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) was discovered by Smolenskii in 1958 [1]; it is a ferroelectric material with perovskite structure (ABO_3). It is currently of interest as a component in commercial electroceramic materials due to their high dielectric constant and low sintering temperatures.

At room temperature, the PFN is ferroelectric with Pb^{+2} in A site and Nb^{+5} in B site favoring the electric order. Its spontaneous polarization associated with ferroelectricity is caused by lattice distortion. The Fe^{+3} located in octahedral B sites provide the magnetic moment of the magnetic order. These are the basis of coexistence for ferroelectric–ferromagnetic orders in this ferroelectromagnet material.

The phase transition from ferroelectric phase with rhombohedral structure to paraelectric phase with cubic structure was observed for this material at temperatures close to 380 K [1–3].

At temperatures below 145 K, this system shows an antiferromagnetic order [2–4].

Previous evidence of coupling between the ferroelectric and magnetic orders has been reported [3–5]. This coupling can result in the so-called magnetoelectric effect, where the magnetic properties of the ferroelectromagnet may be altered by the onset of the electric transition or by the application of an electric field.

In general, for ferroelectromagnet materials, the change in electrical ordering caused by the ferro-paraelectric phase transition or by an external electric field produces a redistribution of the electron spins; this leads to a change in the magnetic moments, and therefore a variation in magnetic properties [4].

Electron paramagnetic resonance (EPR) is the most powerful spectroscopic method available for obtaining local structural information and symmetry of paramagnetic ions incorporated in the structure [6]. This technique allows the investigation of the nature of magnetic phases in materials at different temperatures [7,8].

To our knowledge, however, studies of PFN material with EPR technique are scarce. Recently, we published a preliminary EPR study of PFN at low temperature [8], where a weak ferromagnetic signal (WFS) is observed. This WFS is attributed to canting of Fe^{+3} ion sublattices in the antiferromagnetic matrix, and is associated with the magnetoelectric effect.

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In this paper, we study the changes in the EPR line shape of PFN powders; these changes were quantified by means of the following parameters: peak-to-peak linewidth (ΔH_{pp}), g -factor, and integrated intensity (I_{EPR}) as a function of temperature, through ferro-paraelectric transition. All these parameters show evidence of a diffuse phase transition.

2. Samples preparation and experimental details

The samples used in this study were prepared by the columbite precursor method. The PFN powders were synthesized from commercially available oxides. In this method, stoichiometric Fe_2O_3 (99% purity) and Nb_2O_5 (99.99% purity) were mixed by ball milling for 8 h followed by calcination in air at 1200 °C for 2 h, to obtain the monoclinic FeNbO_4 precursor [9]. PbO (98% purity) was added and mixed by ball milling for 4 h and calcined at 800 °C for 2 h. Sintering was carried out at 1050 °C for 2 h in a PbZrO_3 atmosphere, obtaining PFN powders. The X-ray diffraction powder analysis showed a single PFN phase [9].

EPR measurements were 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 8000 G. The EPR spectra were recorded while warming the sample in the 300–500 K temperature range. The spectrometer was modified by connecting X and Y input voltmeters that in turn are connected to a PC enabling digital data acquisition [10]. During all the experiments a speck of DPPH was used as a g -marker whose signal was subsequently subtracted digitally to facilitate line shape fitting.

3. Results and discussion

Fig. 1 shows EPR spectra (dP/dH vs. magnetic field) recorded in the 300–500 K temperature range. We observe a single broad symmetric

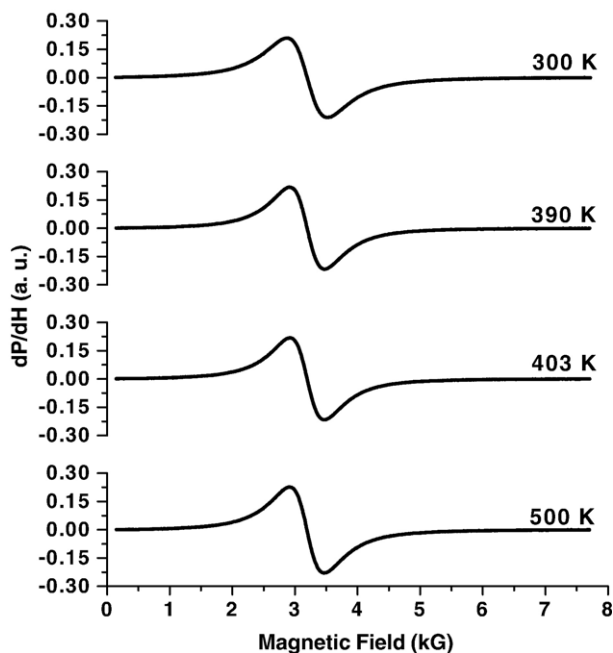


Fig. 1. EPR spectra of $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ powders for selected temperatures.

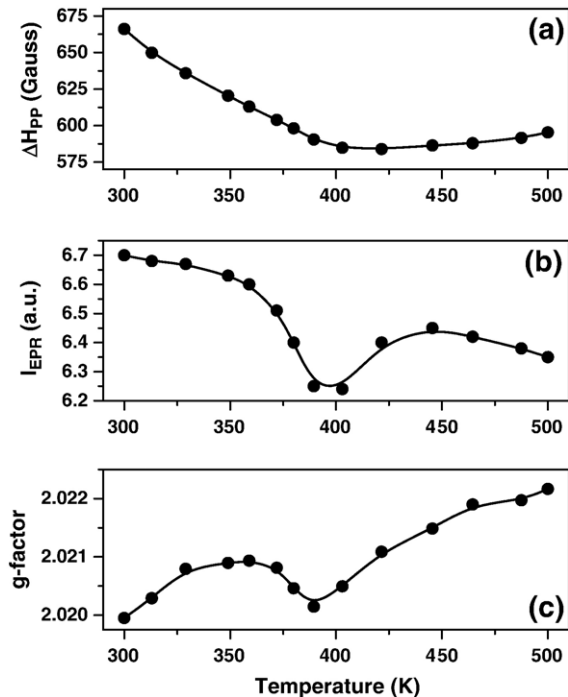


Fig. 2. Temperature dependence of (a) the peak-to-peak linewidth — ΔH_{pp} , (b) the integral intensity — I_{EPR} and (c) the g -factor of PFN. Solid lines are guides for the eye only.

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 (dP/dH) is fitted into the two-component Lorentzian equation accounting for the contributions from the clockwise and anticlockwise rotating components of the microwave magnetic field [11,12]. The temperature dependences of the EPR parameters obtained from these fits are plotted in Fig. 2.

Fig. 2(a) shows the temperature dependence of the peak-to-peak linewidth (ΔH_{pp}) for PFN powders. Starting from room temperature, as temperature increases, ΔH_{pp} decreases continuously until 403 K. In this region of temperature, the material is paramagnetic [1–4,9], and the paramagnetic absorption decreases as temperature increases [13,14]. As temperature increases further, $T > 403$ K, ΔH_{pp} shows a weak increase. We associate this behavior with the structural change, which accompanies the ferro-paraelectric phase transition [1–3,15]; this structural change creates variations in the vicinity of the Fe^{+3} ions, which result in a reorganization of the spin–spin and spin–magnetic field interactions.

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. 2(b). In this figure, we can establish two behavior regions that are limited to the 390–403 K temperature range. We associate this feature with the ferro-paraelectric phase transition. The change in electrical ordering caused by the ferro-paraelectric phase transition leads to a redistribution of the electron spins, which in turn, produces a change in the magnetic moments. Also, this phase transition is in concomitance with the structural change, affording the variation of the Fe-O-Fe angle that defines these magnetic interactions.

Fig. 2(c) shows the behavior of the g -factor vs. temperature. Our experiments give g -values greater than that of a free electron ($=2.0023$) along the entire temperature range. The g -factor shows an increase in the 300–359 K range, and as the temperature increases further, the g -factor decreases, with a minimum at 390 K ($g_{\min}=2.0201$). We associate this

behavior to the diffuse character of the ferro-paraelectric transition [15], which is detected starting from 359 K. The additional g -factor increase (from 390 K to 500 K; $g=2.0222$) is associated with the paramagnetic behavior of the Fe ions.

The phase transition mentioned above is diffuse, i.e., the transition region is extended throughout a wide temperature range. This characteristic can be ascribed to the random distribution of Fe^{+3} and Nb^{+5} ions, which leads to the fluctuations of the composition, thus forming many microscopic regions with slightly different Curie temperatures. The existence of these microscopic regions broadens the transition over a wide temperature range [15,16]. The Curie temperature obtained by the technique EPR (between 390 K and 403 K) is in a good agreement with the reported values [9,15].

4. Conclusions

The changes in ΔH_{pp} , I_{EPR} and g -factor parameters in the EPR spectra for PFN, within the region between 390 K and 403 K, can be interpreted in terms of a diffuse ferro-paraelectric phase transition. This transition promotes a spin redistribution of Fe^{+3} ions, which creates changes in the paramagnetic microwave absorption of the ferroelectromagnet PFN.

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