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Phys. Rev. B **83**, 014302 — Published 18 January 2011

DOI: [10.1103/PhysRevB.83.014302](https://doi.org/10.1103/PhysRevB.83.014302)

## Phonon anomalies and phonon-spin coupling in multiferroic $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ thin film

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### Abstract

We present Raman data on both single-crystal and thin-film samples of the multiferroic  $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ . we show first that the number and selection rules of Raman lines is compatible with a face-centered cubic  $\text{Fm-3m}$  structure, as is known in other  $\text{ABO}_3$  relaxors, such as  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ . We then compare Raman data with anomalies in magnetization and dielectric constant near the magnetic phase transition temperature ( $T_N$ ), the diffuse ferroelectric phase transition temperature ( $T_m$ ), and the pseudo-structural phase transition (Burns temperature  $\sim T_B$ ). The temperature evolution of the Raman spectra for PFN film shows measurable changes in phonon positions, intensities, and full width at half maxima (FWHM) near 200 K, 410 K, and 650 K – temperatures that match well with experimentally observed  $T_N$ ,  $T_m$ , and  $T_B$  respectively. The increase in frequency with increasing temperature for the lowest-energy  $\text{F}_{2g}$  phonon mode is particularly unexpected. These changes suggest the transition of crystal structure from an ordered phase to a disordered one near  $T_B$ . The Raman study revealed phonon anomalies in the vicinity of  $T_m$  and  $T_N$  that are attributed to the dynamical behavior of polar nano-regions (PNRs) and spin-phonon coupling due to its relaxor and multiferroic nature respectively, which is well supported by dielectric and magnetic properties of the PFN thin film. Softening of the Fe-O mode was observed near the  $T_N$ . We correlate the anomalous shift of the Fe-O mode frequency with the normalized square of the magnetization sublattice; agreement with the experimental

results suggest strong spin-phonon coupling near  $T_N$  due to phonon modulation of the super-exchange integral, however the shifts in frequency with temperature are small ( $< 3 \text{ cm}^{-1}$ ).

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## I. Introduction

Lead iron niobate (PFN) is a complex perovskite material originally reported by Smolenkii et al. in late 1950s<sup>1</sup>. PFN belongs to the class of materials having two or more order parameters (elastic, electric, or magnetic) coexisting in the same phase. Among single-phase multiferroic materials, very few exhibit significant coupling of their magnetic and electric order and these are quite promising for magnetoelectric (ME) applications<sup>2</sup>. Single-phase multiferroics belonging to the  $AB'B''O_3$  complex perovskite family, such as  $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$  (PFN),  $\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$  (PFT), and  $\text{PbFe}_{0.67}\text{W}_{0.33}\text{O}_3$  (PFW), have gained interest because in these materials magnetic ( $d^5$ )  $\text{Fe}^{3+}$  ions and nonmagnetic ( $d^0$ )  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ , and  $\text{W}^{6+}$  ions have a common B site. The ( $d^5$ ) ion in the  $\text{BO}_6$  octahedral sites leads to ferromagnetic order, while the ( $d^0$ ) ions in similar lattice positions help provide ferroelectric order. Thus, these materials are good candidates to study multiferroicity and possible magnetoelectric (ME) coupling in a single phase material<sup>1,3-5</sup>.

The dielectric, magnetic, and magnetoelectric properties of PFN have been studied in single-crystal, ceramic, and thin-film forms<sup>1,6-15</sup>. Bulk PFN undergoes a paraelectric (PE) to ferroelectric (FE) phase transition with a Curie temperature ( $T_c$ ) between 379 to 385 K<sup>1,6,7</sup>. In the case of PFN films, a diffuse phase transition (DPT) with frequency dispersion has been reported<sup>8-9</sup>. Bulk PFN exhibits a paramagnetic (PM) to anti-ferromagnetic (AFM) phase transition with Néel temperature ( $T_N$ ) of 140 K<sup>10,11</sup>. However, ferromagnetic order has

sometimes been reported at low<sup>12</sup> ( $\sim 9$  K) or even room temperature<sup>13</sup>. Experimentally observed dielectric anomalies due to magneto-electric coupling were reported in PFN single crystals<sup>14</sup>. Monte Carlo simulations of magneto-electric coupling provided reasonable agreement between the simulated and the experimental results of PFN single crystals<sup>15</sup>. Although PFN does not exhibit B-site cation ordering, it shows normal long-range dipole order in the FE phase<sup>16</sup> of single crystals and ceramics. However, PFN films have been reported as magnetoelectric relaxors, that is, having a simultaneous frequency dispersion of both the electrical and magnetic susceptibilities<sup>17</sup> – a relaxor ferroelectric with weak ferromagnetic properties<sup>8,9</sup>. The detailed structural, dielectric, and magnetic properties of the PFN films are reported elsewhere<sup>9</sup>.

Our PFN films were highly oriented with an in-plane epitaxial relationship PFN [100] || LSCO [100] || MgO [100]. The temperature evolution of the dielectric constant showed a diffuse ferroelectric phase transition with frequency dispersion. The dielectric maximum temperature ( $T_m$ ) shifted from 337 K (5 kHz) to 380 K (100 kHz). The frequency dispersion of dielectric constant follows a Vogel-Fulcher law and gives an activation energy of 5.1 meV (equivalent to 62 K) and a freezing temperature of 325 K. The low activation energy of PFN films (62 K) compared to the experimental measuring temperature indicates its non-equilibrium state as in a glassy system<sup>18-19</sup>. Besides the frequency dependent dielectric maxima, we observed two more features in the temperature evolution of the dielectric constant of PFN thin films: One was in the vicinity of  $T_N$ , where a small kink around 170 K was observed; the second was a bump at  $\sim 600$  K near the Burns temperature ( $T_B$ ). We ascribed the former dielectric anomaly to strong spin-dipole coupling which has been already found in PFN single crystals and ceramics<sup>7,12,14</sup>. The later anomaly was associated with structural changes in the sample when it goes through an ordered phase to a disordered one.

In the past decade significant effort has been devoted to understanding the physics of multiferroics and the coupling mechanisms of ferroelectric and magnetic order in ME materials. The usual approach has been to study the dielectric and magnetic properties of multiferroics under applied electric and magnetic fields in a wide temperature ranges. However, extraordinary spin-phonon interaction has been detected in rare-earth manganites by thermal conductivity<sup>20</sup> and thermal expansion<sup>21</sup> measurements. Raman spectroscopy has been shown to be a valuable technique in the study of optical phonon behavior in multiferroic materials. Although phonon studies play an important role in the understanding of ferroelectricity, and this is expected to be influenced by spin correlation<sup>22</sup>, only in recent years has the behavior of optical phonons in multiferroics and magnetoelectric multiferroics materials been studied<sup>23-29</sup>. Our temperature-dependent Raman study of PFN film reveals phonon anomalies in the vicinity of  $T_m$  and  $T_N$  that we ascribe to the dynamical behavior of polar nano-regions (PNRs) and spin-phonon coupling due to its relaxor and multiferroic nature respectively.

One important issue in the physics of ferroelectrics is the understanding of the domain structure. Among the available techniques for studying ferroelectric materials, Piezo-Force Microscopy (PFM) has emerged as a valuable tool for local nano-scale imaging, spectroscopy, and manipulation of piezoelectric and ferroelectric materials<sup>30</sup>. PFM is being used to study the domain structure, its temperature evolution, switching behavior, retention, loss, and electromechanical properties of several ferroelectric materials<sup>30-33</sup>. In this paper, we report the room temperature domain structure and temperature dependent phonon anomaly of PFN film obtained by PFM and Raman spectroscopy respectively. The temperature-dependent Raman spectra will be correlated with magnetic and dielectric properties of PFN film. We observed

phonon anomalies around the temperature of the dielectric maximum ( $T_m$ ) and the temperature of the PM-AFM phase transition  $T_N$ .

## II. Experimental details

Lead iron niobate (PFN) thin films were grown on (100) oriented magnesium oxide (MgO) substrate with lanthanum strontium cobalt oxide (LSCO) as bottom electrode using pulsed laser deposition (PLD) technique. The PFN deposition parameters were as follows: deposition temperature, 600 °C; laser energy, 250 mJ and 200 mT oxygen pressure. In the case of LSCO layer, these parameters were 600 °C, 300 mJ and 300 mT respectively. PFN single crystals of maximum size  $4 \times 3 \times 3 \text{ mm}^3$  were grown by spontaneous crystallization from the mixture of polycrystalline PFN and  $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$  solvent in the appropriate proportions using solution technique. Mixture was sealed in a platinum crucible and then placed into a corundum crucible filled with  $\text{Al}_2\text{O}_3$ . The temperature was rapidly raised to 1200 °C, kept at four hours and then finally cooled to 900 °C at a rate of  $2\text{--}3 \text{ }^\circ\text{C h}^{-1}$ . The detailed of crystal structure and magnetic properties are described elsewhere<sup>34, 35</sup>. The phase formation and crystallographic orientation of the film were analyzed using a Siemens D500 X-ray diffractometer, with  $\text{CuK}_\alpha$  radiation. Dielectric properties were measured as a function of frequency (100 Hz to 1 MHz) and temperature (100 K to 650 K), utilizing an impedance analyzer (HP4294A). A cryostat with a programmable-temperature controller (M/S MMR Technology Inc. model K-20) was used for the temperature-dependent measurements of the above properties. The magnetic measurements were carried out using a superconducting quantum interference device (Quantum Design MPXSP SQUID) magnetometer. The room temperature piezoresponse of the PFN layer was measured by piezoforce microscope (Veeco Dimension 3100).

The Raman measurements were performed in the backscattering geometry using a Jobin-Yvon T64000 Triple spectrometer. The laser line at 514.5 nm from a coherent Iargon ion laser (Innova 90-5) Argon laser was focused in about 2-3  $\mu\text{m}$ -diameter area by using a Raman microprobe with a 80X objective. A liquid-nitrogen-cooled charge-coupled device (CCD) system collected and processed the scattering light. We collected the low temperature spectra in vacuum from 80 to 600 K in steps of 25 K using a  $\text{LN}_2$  cryostat from Linkam and the high temperature spectra from 300 to 900 K in 50 K steps using a High Temperature Linkam module for Raman microprobe.

### **III. Results and Discussion**

#### **A. Domain structure studied by piezo force microscopy**

Room temperature piezoelectric phase loop, topography, amplitude, and phase images of PFN thin films are shown in Figure 1. The PFM images of PFN film were obtained simultaneously under a small ac voltage (3V) with no applied dc bias. In PFM measurements the amplitude and phase images yield information about the strength of piezoelectric response and domain structure respectively. The topography of film revealed ellipsoid-shaped grains with an inhomogeneous size distribution (Fig 1a). The complex domain structure showed bright, dark, and intermediate contrast. The bright/dark regions are associated with opposite polarity whereas several factors contribute to intermediate contrast<sup>30</sup>: The presence of intermediate contrast may due to randomly polarized grains, domains with the polarization vector deviating from the normal to the film plane, nonferroelectric regions, or regions with weak piezoelectric response. Bright (pink) and dark (wine-colored) contrast in Fig.1 suggests the existence of highly polarized areas. These areas must be self-polarized<sup>33</sup> because no dc bias field was applied (this often occurs upon

cooling in ferroelectrics due to strain). At room temperature PFN film is slightly below its freezing temperature (325 K) where the growing domains freeze in (become immobile), so its domain structure reflects a frustrated ferroelectric state. The piezoelectric phase loop (Fig 1d) provided evidence for presence of ferroelectric switching behavior.

### B. Temperature dependent Raman spectra

Raman scattering data for PFN films was obtained in two distinct normal backscattering geometries, VV ( $Z(\underline{XX})Z$ ) and VH ( $Z(\underline{XY})Z$ ). VH denotes incident laser light polarized vertically and scattering light polarized horizontally in the laboratory frame of reference. The room-temperature spectra of both configurations of the single crystal and film are shown in Figure 2. At this temperature the VV configuration of film and crystal consists of two relatively intense peaks at 697 and 781  $\text{cm}^{-1}$ , a weaker peak at 427  $\text{cm}^{-1}$ , and three broad bands at about 204, 260 and 550  $\text{cm}^{-1}$ . The VH configuration consists of two medium-intensity bands at 206 and 261  $\text{cm}^{-1}$ , a broad band at 522  $\text{cm}^{-1}$ , and weak bands that may be due to polarization “leakage” of the phonon modes from vertical polarization. At 300 K the low frequency  $F_{2g}$  mode in the single crystal is intense and well defined but it appears as a shoulder for the film. The splitting of the  $A_{1g}$  mode discussed in the following sections is more prominent in the film than in the crystal. In this article we limit our discussion to the room temperature Raman study of PFN single crystal. Detailed growth techniques, structural and magnetic properties of PFN single crystal were presented elsewhere<sup>34, 35</sup>.

An ideal (primitive Pm-3m) cubic  $\text{ABO}_3$  perovskite structure does not permit any Raman active modes in its first-order vibrational spectra; since each ion is at an inversion center, all long-wavelength vibrational modes are of odd parity. However many complex perovskites like PFN exhibit first-order Raman spectra over a wide temperature range.  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  is a good



example that exhibits an Fm-3m face-centered cubic structure just above its Curie temperature, dependent upon processing conditions<sup>36,37</sup>.

The origin of these Raman-active modes can be explained by the existence of ordered regions with a particular symmetry, disorder in the B-sublattice that breaks the selection rules, or both<sup>38</sup>. Bulk PFN lacks B-cation ordering and behaves as a normal ferroelectric<sup>13</sup>, however relaxor-like behavior has been observed in film<sup>9</sup>. Figs. 3 (a), (b), and (c) show the temperature-dependent Raman spectra of PFN films in the VH, VV, and close look of  $A_{1g}$  modes VV configurations respectively. The Raman spectra are consistent with the Fm-3m symmetry and have  $2 F_{2g} + E_g + A_{1g}$  Raman-active modes and the  $4 F_{1u}$  infrared-active<sup>38</sup>. It is well known fact that PFN crystal is a normal ferroelectric having long range order with tetragonal crystal structure at room temperature where as in thin film form most of the cases<sup>9,17</sup> it shows relaxor ferroelectric with pseudo cubic structure. The assignment of phonon modes in cubic state of relaxor ferroelectric is still controversial and not well understood<sup>36-40</sup>. Although it is common understanding that lead based relaxors are best assigned in Fm-3m cubic structure. Low frequency  $F_{2g}$  mode arises due to lead (Pb) localization, high  $A_{1g}$  mode due to symmetrical stretching of  $BO_6$  octahedral, and modes between  $180\text{ cm}^{-1}$ - $320\text{ cm}^{-1}$  due to cations off center shift in polar nano regions (it is assigned for the cubic  $F_{1u}$  IR active modes). It is worth to note that although temperature dependent and polarized studies allow better understanding of the Raman modes; the collected spectra exhibit low intensity because the set of analyzer-polarizer and half wave plate used in the setup drastically reduces the intensity. Additionally, the quartz window in the cryostat used for temperature dependent studies reduce the laser power on the sample and indeed the scattering signal that by itself is already lower in thin films than ceramics or single crystals.

## C. Phonon anomalies in the high-temperature phase

### C.1. General Observations

Figure 3a shows the VH polarized Raman spectra of PFN films from 83 to 900 K. The main observed features are as follows: (i) at higher temperatures the spectra consist of one strong phonon mode with phonon peak position (fitted)  $\sim 64\text{-}67\text{ cm}^{-1}$  that corresponds to the low frequency  $F_{2g}$  mode, plus two bands centered at about 220 and  $716\text{ cm}^{-1}$ ; (ii) on decreasing temperature, the  $F_{2g}$  mode broadens and is well behaved until 600 K but persists until 500 K. Below 500 K it becomes a shoulder as indicated by the arrow; (iii) the phonon between 150 and  $370\text{ cm}^{-1}$  shows changes on decreasing temperature, the peaks in this region becomes asymmetric at about 600 K and degenerate into two bands that change peak position, linewidth, and intensity; (iv) at lower temperatures (83 K) the spectra exhibits two bands in the frequency region between 380 to  $600\text{ cm}^{-1}$  plus two more bands in the frequency region between 620 to  $820\text{ cm}^{-1}$ .

### C.2. Phonon dynamics at the regime of negative thermal expansion:

The temperature dependence of the  $F_{2g}$  mode is of interest. Normally vibrational modes do not increase frequency with increasing temperature; thermal expansion causes their frequencies to decrease. The well defined  $F_{2g}$  mode is observed at high temperature which almost constant (within the experimental and fitting limit) above  $T_B$  but monotonically decreases with further decrease in temperature, similarly to the deviation of the temperature dependence of the refractive index from the expected linear trend typical of paraelectrics<sup>37,40</sup>. In present case, the observed dependence of phonon between 350 K-520 K can be explained on the basis of thermal dependence change in lattice. PFN does not exhibit thermal expansion from 350-520 K;

instead it undergoes thermal contraction<sup>41</sup>. In such a case the phonon energies should increase (as observed, see Fig.5). However, the magnitude of the increase observed, as well as the underdamping with increasing  $T$  suggests instead that this is a kind of soft mode related to the relaxor transition. Note that a ferroelectric soft mode cannot be of even parity in the paraelectric phase, so the exact role of this vibration in transition dynamics is unclear and merits further study.

### C.3. Phonon dynamics and the Burns temperature

Figure 3b shows the temperature dependent VV polarized Raman spectra of PFN films. For Fm-3m symmetry two Raman-active modes are expected in this configuration: the  $E_g$  and the  $A_{1g}$  mode. At higher temperatures (650 K and above), the  $A_{1g}$  mode appears low intensity and considerable thermal band broadening, but at temperatures near  $T_B$  and below it appears as a well-resolved doublet with peak frequencies at approximately 780 and 700  $\text{cm}^{-1}$ . At higher temperatures damping is strong and the intensities of both peaks in the doublet are almost similar, then the  $A_{1g}$  mode looks like a broad asymmetric peak (see Fig 3c). This shows strong correlation with the Burns temperature, generally considered to be near 650 K. The presence of the  $E_g$  mode in the PFN film Raman spectra is not clearly discerned. The normal vibration analysis of the complex perovskites with Fm-3m symmetry shows that the  $A_{1g}$  mode represents the breathing mode of the oxygen atoms, close to that of a free oxygen octahedron<sup>42</sup>. Siny *et al.*<sup>43</sup> pointed out that the mode frequency of the  $A_{1g}$  mode changes in a series of complex perovskite compounds as a function of the perovskite unit cell and with the changes in ionic radii. Although neither A, B', nor B'' ions move in this  $A_{1g}$  vibration, the mode still reflects subtle changes in the perovskite structure. Only the oxygen ions move, but their spacing and bonding and hence frequencies change with the size of other ions.

In order to investigate more quantitatively the temperature evolution of the observed vibrational modes in PFN film, we analyzed the Raman spectra with the damped harmonic oscillator model (DHO)<sup>42</sup>. Each spectrum have been fitted with the spectral response function<sup>42,43</sup>

$$S(\nu) = \sum_i \frac{\chi_0 \Gamma \nu_0^2 \nu}{(\nu^2 - \nu_0^2)^2 + \Gamma^2 \nu^2} F(\nu, T) \quad (1)$$

where  $F(\nu, T) = [n(\nu) + 1]$  (Stokes scattering) and  $n(\nu) = [\exp(h\nu/kT) - 1]^{-1}$ . The parameters in Eq. (1) amplitude  $\chi_0$  (in arbitrary units), the mode frequency  $\nu_0$ , the damping constant  $\Gamma$ , and the temperature  $T$ , describe each phonon mode as a damped harmonic oscillator. In the fitting routine, these parameters for all Raman bands were taken simultaneously as unconstrained variables. At some temperatures, the Raman spectra at the lowest frequencies were fitted with a Gaussian and a Lorentzian both centered in a zero-frequency shift that allow a better deconvolution of the spectra. Figure 4 (a), (b), (c), and (d) show representative graphs of the fitting routine for VV and VH polarized spectra at high and low temperature, the Gaussian and the Lorentzian are not shown. Due to the high noise to signal ratio and considerable thermal band broadening observed at higher temperatures (above  $T_B$ ) in the VV polarized spectra, first we fit  $A_{1g}$  modes above 650 K for only the small frequency region with two modes and later employed those parameters in the fitting of the spectra as a set of damped harmonic oscillators (Fig. 4d). The fitted data are also presented in the Fig. 5(a) as a function of temperature which indicates a kink near the  $T_B$  that physically represents the thermally assisted Raman shift.

Though we have analyzed most of the observed Raman bands for their energy, FWHM, and integrated intensity, we will show the detailed analysis for the two of the more prominent modes and also prominent  $F_{1u}$  mode particularly near phase transition. The  $F_{2g}$  mode was chosen to elucidate the dynamics of the paraelectric- to-diffuse-ferroelectric phase transition. Since  $A_{1g}$  modes are symmetric, they play no direct role in the high-temperature phase of any symmetry-

breaking phase transition. However we found correlation between the temperature evolution of the  $A_{1g}$  mode and the temperature regimes where mobile polar nanoregions and static polar nanoregions exist in PFN film, and in the vicinity of the paramagnetic to antiferromagnetic temperature phase transition.

Temperature dependent  $A_{1g}$  Raman active modes are illustrated in Fig. 5(a). Temperature evolution of the observed  $A_{1g}$  vibrational modes of PFN film is analyzed by the damped harmonic oscillator model (DHO)<sup>42</sup>.  $A_{1g}$  mode represents the dynamic evolution of the relaxor ferroelectric state in PFN films.  $A_{1g}$  modes fit with two well defined phonon modes below the  $T_B$  and these modes appear low intensity and considerable thermal band broadening above  $T_B$ . The observation of two phonon modes below  $T_B$  matched with the complex B-site relaxor family<sup>43-46</sup> unlike to classical relaxors ( $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ ,  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ ) where only one singlet peak is observed<sup>16,18,37</sup>. The so called two phonon modes behavior was introduced for  $\text{Si}_{1-x}\text{Ge}_x$  systems<sup>45</sup>, later also observed for complex relaxor systems as mentioned above. The low Raman band  $698\text{ cm}^{-1}$  corresponds the Fe-O stretching whereas  $788\text{ cm}^{-1}$  band represents Nb-O stretching. In such system the vibration associated to two band mode do not couple due to their chemical origin. The kink in the Raman shift of two bands above the  $T_B$  is mainly due to the change in the disorder to order state. We observe the Burn temperature and lattice stability for PFN film at 650 K which matched with the kink in the frequencies of doublet support the transformation of disorder to ordered state.

Fig. 5(b) shows the Raman shift of the  $F_{2g}$  mode in the temperature window (100 to 900 K) where it appears as a sharp phonon peak above 500 K and below 500 K where it appears as a shoulder. We deconvoluted through the Gaussian-Lorentzian fit as shown in Fig. 4. The mode frequency (Raman shift) of the  $F_{2g}$  branch exhibited a shift down in frequency by  $\sim 3.0\text{ cm}^{-1}$ ,

however, it decrease in two steps from 900 to 650 K and from 650 to 350 K and below that remains fairly constant. Above  $T_B$  it is practically constant where started softening from  $T_B$  to  $T^*$  due to temperature dependence deviation of refractive index of normal paraelectric materials. Further softening of  $F_{2g}$  mode till 350 K may be due to lattice contraction as can be seen in Fig. 5 (c). Peng *et al.*<sup>41</sup> reported the temperature evolution of the lattice parameter of PFN film grown by PLD technique (similar to us). Here we reproduced the lattice constant behavior of PFN film with the reported value of Peng et al. (Fig. 5c). The evolution of the lattice parameter clearly shows three anomalies at 650, 510, and 200 K. These anomalies were respectively ascribed to the Burns temperature  $T_B$ , at which PNRs begin to nucleate;  $T^*$  related to the appearance of static PNRs, and  $T_N$  as the paramagnetic to anti-ferromagnetic phase transition temperature. Although  $T_N$  for these films is higher than  $T_N$  for bulk (145 K), they ruled out any strain effect on  $T_N$  but attributed the shift in  $T_N$  to variation in the stoichiometric ratio of high-spin  $Fe^{3+}$  cation taking place during film growth. The reported lattices anomalies at  $T_N$  and  $T_B$  are consistent with our own results on the dielectric, magnetic, and Raman studies of PFN film. In addition, 500 K is the crossover temperature from a narrowed  $F_{2g}$  mode at high temperatures to an abruptly broadened shoulder suggesting a qualitative change in coherence length for nanoregions setting in near 500 K.

Regardless of the changes described above in the  $F_{2g}$  and  $A_{1g}$  modes between 600 K- 900 K, the overall spectral signature does not change notably in this temperature range. That is not the case for temperatures below 600 K where new spectral signatures such as new Raman lines and line splittings are observed in both geometries. We inferred above the appearance of a local Fm-3m space symmetry in PFN film. At 600 K and below, the formation of inequivalent oxygen octahedra with  $Fe^{+3}$  and  $Nb^{+5}$  cations reduces this symmetry and causes a doubling of the  $A_{1g}$

mode, as first discussed in tungstates and molybdates with two  $\text{MO}_4$  ions per unit cell<sup>47</sup> and later by so called two phonon modes in different system as described above.

#### **D. Phonons in the low-temperature phase**

##### **D.1. Qualitative behavior**

Fig. 6 shows the band softening of  $216\text{ cm}^{-1}$  (at 100 K) which arises due to off center B site distortion and their local cations displacement. This particular mode softens around  $18\text{ cm}^{-1}$  till 600 K. The major Raman shift takes place near the diffuse phase transitions. All the modes between  $180\text{ cm}^{-1}$ - $320\text{ cm}^{-1}$  arise due to cations off center shift in polar nano regions (it is assigned for the cubic  $F_{1u}$  IR active modes). Among these modes, Nb-O stretching mode ( $216\text{ cm}^{-1}$ ) is more sensitive to ferroelectric long range ordering. The freezing temperature i.e. long range ferroelectric ordering of PFN thin films is around 325 K, below this temperature softening is less prominent. The important questions are; (i) why this mode shows significant softening near diffuse phase transition? (ii) and what is responsible for this effect? Answer may be driven from two different mechanisms. It may be due to; (i) lead site off shift, B-site octahedral tilt, and local cation ordering in polar nano regions, (ii) Cubic phase  $F_{1u}$  infrared active mode (“silent mode”). The second reason is mostly unlike as in.

PFN single crystal and ceramics behave like a normal ferroelectric, its A-site is occupied by lead, the off shift of lead is vital for spontaneous polarization. Since PFN thin film showed relaxor ferroelectric behavior and diffuse phase transition which in turns give some fraction of spontaneous polarization. As we know the two classical ferroelectrics,  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  show spontaneous polarization due to hybridization of 3d states of the B-positioned Ti ions and 2p

states of off center B site oxygens distortion<sup>48</sup>. Lead off shift also gives spontaneous polarization in lead based ferroelectric. Most likely this reason is more responsible for band softening.

On the other hand, the structural change also allows the presence in Raman spectra of the nominally  $F_{1u}$  infrared active mode (“silent mode”) in which the  $B'/B''$  ions participate and it is affected by the mass of those ions. The  $F_{1u}$  mode is located in the frequency region from 150 to 380  $\text{cm}^{-1}$  in  $\text{ABO}_3$  perovskites, e.g. at 173  $\text{cm}^{-1}$  in cubic  $\text{SrTiO}_3$ <sup>47,49</sup>; and, as can be seen in the VH polarized Raman spectra, it splits in two bands. Because Nb ions have a larger mass compared to Fe ions, the band with the lower frequency corresponds to the vibration mode of the Nb-O bond, whereas that with higher frequency is the vibrational mode of the Fe-O bond.

## D.2. Magnetic interactions with phonons

It is worth noting that from 83 to 600 K the magnetic, dielectric, and ferroelectric properties of PFN film were studied and reported elsewhere<sup>9</sup>. The temperature evolution of the dielectric spectra of PFN film showed three anomalies: (1) a kink near the Neel temperature ( $\sim 170$  K); (2) a diffuse phase transition (327 K-380 K) with frequency dispersion near the temperature at which the dielectric maxima occur; and (3) an almost frequency-independent maximum at 600 K, suggesting weak magnetoelectric (ME) coupling, relaxor behavior, and a structural phase transition, respectively<sup>9</sup>. Dielectric properties and magnetic hysteresis revealed the coexistence of relaxor ferroelectricity and weak ferromagnetism at room temperature in PFN films<sup>8,9,17</sup>. Although neither the relaxor state nor the magnetic transitions are accompanied by a transition to a homogeneous single-phase state with long-range order, we still observe phonon anomalies in the vicinity of  $T_N$  and  $T_m$ .



The change in the frequency of the breathing-type motion of both oxygen octahedra as a function of temperature are shown in Figure 7. The intensity and linewidth of both modes follow similar behavior, the intensity increase on decreasing temperature and the linewidth decreases on cooling (see Fig 3c). However, the temperature evolution of the energy for both modes differs significantly, and their changes can be correlated with the magnetic and dielectric properties exhibited by the film. In the low temperature phase (600 to 83 K) phonons respond to the dynamical changes in ferroelectric and magnetic order. We can identify three temperature regions where different trends are observed: region I from 600 to 400 K, region II from 400 to 200 K, and region III from 200 to 83 K. The overall change in the frequency of the Fe-O octahedra ( $\Delta\omega$ ) is  $\sim 3.7 \text{ cm}^{-1}$ , but it does not change monotonically; instead it is perturbed in the full temperature range. When the material enters the temperature region with magnetic order (region III), the frequency of the Fe-O octahedra mode drops. This kind of abrupt decrease may be due to the change in the magnetic ordering around 200 K. The magnetic ordering data are supported by the field-cooled (FC) temperature-dependent magnetization: the M versus T curve shows an abrupt increase of magnetization at 200 K. In addition, PFN film showed a lattice anomaly at 200 K due to the PM-AFM phase transition as observed by Peng *et al*<sup>36</sup>.

### D.3. Model of Granado et al.

Magnetic ordering effects in the Raman spectra of polycrystalline  $\text{La}_{1-x}\text{Mn}_{1-x}\text{O}_3$  were reported by Granado et al.<sup>24</sup> They observed a *softening* of  $\text{Mn}^{3+}\text{-O}^{2-}$  stretching mode below  $T_N$  for orthorhombic  $\text{LaMnO}_3$ . This softening was associated with spin-phonon coupling due to phonon modulation of the super-exchange integral. In a nearest-neighbor approximation, they

found that the frequency change with temperature of a phonon  $\alpha$  due to spin-phonon coupling is given by:

$$(\Delta\omega)_{s-ph} \approx -\frac{2}{m\omega_{\alpha}} \frac{\partial^2 J_{\alpha\beta}}{\partial u^2} \left( \frac{M_{\text{sublattice}}(T)}{4\mu_B} \right)^2 \quad (2)$$

The scaling of the anomalous shift of the frequency of the  $\text{Mn}^{3+}\text{-O}^{2-}$  stretching mode with the normalized square of the magnetization sublattice supports the experimental evidence that the shift is due to spin-phonon coupling. We observed similar scaling behavior on our experimental PFN data and also found a close correlation between the anomalous frequency drop of the Fe-O mode and magnetization at  $T_N$ . The observed softening is interpreted in terms of spin-phonon coupling due to phonon modulation of the super-exchange integral (Figure 8).

#### D. 4. Dielectric behavior and phonons

In the case of the  $A_{1g}$  mode for the Nb-O octahedra, its frequency also decreases on cooling, but the overall change in frequency ( $\Delta\omega \sim 5.5 \text{ cm}^{-1}$ ) is greater than the  $A_{1g}$  mode for the Fe-O octahedra. In Fig. 7 we can see the temperature evolution of the dielectric constant in the same temperature window that the fitted frequency of the  $A_{1g}$  mode, and we find some correlation between them. On decreasing temperature, the spatially averaged homogenous paraelectric state changes into an inhomogeneous phase; the frequency shifts downward smoothly; and the dielectric constant shows a bump (region I). However at the boundary between regions I and II, the frequency has a sudden drop from  $793.5 \text{ cm}^{-1}$  at 450 K to  $791.5 \text{ cm}^{-1}$  at 400 K with further decrease till dielectric maximum temperature. In this region the dielectric constant exhibits relaxor behavior, and the fitting of the frequency dispersion of  $T_m$  with the Vogel-Fulcher law gives a freezing temperature of 325 K. At this point with PNRs frozen-in, the material could be in a mixed ferro-glass state as suggested by the domain structure shown by PFM; on further cooling the frequency of the  $A_{1g}$  mode for the Nb-O octahedra just goes up and

down whereas the frequency of the  $A_{1g}$  mode for the Fe-O octahedra shown the changes discussed above due to the onset of magnetic ordering.

#### **IV. Conclusions:**

We studied the temperature evolution of the Raman spectra of PFN film in a wide temperature range (83-900 K). The approximate local symmetry is Fm-3m. The high-temperature Raman spectra showed changes in phonon positions, intensities, linewidths, and especially kink in the Raman shift of the  $A_{1g}$  doublet around 650 K, suggesting order-disorder behavior near the accepted Burns temperature and lattice constant anomalies. Our study revealed phonon anomalies in the vicinity of  $T_m$  and  $T_N$  that we ascribe to the dynamical behavior of polar nano-regions (PNRs) and spin-phonon coupling due to relaxor ferroelectric and magnetoelectric nature respectively. We established a close correlation between the microstructural features and the dielectric and magnetic properties of PFN film. Lattice anomalies reported for PFN film are consistent with our results on the dielectric, magnetic, and Raman studies of PFN films. Softening of Fe-O mode, change in magnetization sublattice, and their coupling were observed in the vicinity of  $T_N$  scale.

#### **Acknowledgements:**

The authors thank Jian Jun for his help with the PFM measurement and the Center for Intelligent Material System and Structure (CIMSS) at Virginia Tech. M. Correa acknowledges the IFN fellowship that sponsored the PFM studies at CIMSS. This work was partially supported by W911NF-06-1-0183 and DoE FG 02-08ER46526 grants.

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## Figure Captions

Figure 1. (a) Topographic (5x5  $\mu\text{m}$ ), (b) amplitude, (c) phase, and (d) piezoelectric phase loop of PFN thin films

Figure 2. Room Temperature Raman spectra of PFN films and single crystal in VV and VH configurations.

Figure 3: A sequence of the temperature-dependent (83K-900K) Raman spectra of PFN films. (a) VH polarized (b) VV polarized and (c) VV polarized for selected temperatures and specific frequency range.

Figure 4: Example of the spectrum analysis at (a) 750 K and VH polarized, (b) 233 K and VV polarized, (c) and (d) 900 K and VV polarized for selected and full frequency range respectively. The points show experimental data and the red solid line through points represents the results of fitting by the phonon modes by Eq. (1). The solid blue lines represent the constituent components of fitting (phonon modes).

Figure 5: (a) Raman shift of the  $A_{1g}$  mode from 83 K to 900 K (b) Raman shift of the  $F_{2g}$  mode from 83 K to 900 K (c) temperature evolution of the lattice parameter for a PFN film.

Figure 6: Temperature evolution of the frequency, linewidth, and intensity of Nb-O band near  $180\text{-}350\text{ cm}^{-1}$  from 83 to 600 K

Figure 7: Temperature evolution of the frequency, linewidth, and intensity of Nb-O and Fe-O octahedrons from 83 to 600 K, field-cooled (100 Oe) magnetization, and dielectric response as a function of temperature of PFN films.

Figure 8: Softening of Fe-O mode and change in sublattice magnetization,  $\Delta\omega = (1/2\pi)[\omega(T) - \omega(258\text{ K})]$ .

















