Ferroelectric ordering in the relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ as evidenced by low-temperature phonon anomalies

S. Wakimoto,[1,*] C. Stock,[1] R. J. Birgeneau,[1] Z.-G. Ye,[2] W. Chen,[2] W. J. L. Buyers,[3] P. M. Gehring,[4] and G. Shirane[5]
[1]*Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7*
[2]*Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*
[3]*Neutron Program for Materials Research, National Research Council of Canada, Chalk River, Ontario, Canada K0J 1J0*
[4]*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*
[5]*Department of Physics, Brookhaven National Laboratory, Upton, New York 11973*
(Received 1 March 2002; published 29 April 2002)

Neutron scattering measurements of the lowest-energy TO phonons in the relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) are reported for $10 \leqslant T \leqslant 750$ K. The soft mode, which is overdamped by the polar nanoregions below the Burns temperature $T_d = 620$ K, surprisingly recovers below 220 K. The square of the soft-mode energy $(\hbar\omega_0)^2$ increases linearly with decreasing temperature and is consistent with the behavior of a ferroelectric soft mode. At 10 K, $\hbar\omega_0$ reaches 11 meV, the same value observed in ferroelectric $Pb(Zn_{1/3}Nb_{2/3})O_3$ at low T. An unusual broadening of the TA phonon starts at T_d and disappears at 220 K, coincident with the recovery of the TO mode. These dynamics suggest that a well-developed ferroelectric state is established below 220 K.

DOI: 10.1103/PhysRevB.65.172105 PACS number(s): 77.84.Dy, 61.12.−q, 64.70.Kb, 77.80.Bh

Both $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and the Zn analog (PZN) are disordered perovskites of the form $PbBO_3$ that possess fascinating dielectric properties. Termed ''relaxors,'' each exhibits an unusual dielectric response that peaks broadly at a temperature $T = T_{\max}$ that is strongly frequency dependent ($T_{\max} = 265$ K at 1 kHz for PMN). When doped with ferroelectric $PbTiO_3$ (PT), both compounds exhibit dramatic increases in their already exceptional piezoelectric properties.[1] Each compound is characterized by quenched chemical disorder on the perovskite B site which is occupied by Mg^{2+} (or Zn^{2+}) and Nb^{5+} cations.[2] It is well known that the mixed-valence character inherent to both PMN and PZN is required for the dielectric relaxation and ''diffuse transition'' in a temperature range around $T_{\max}$. Despite these similarities, PMN and PZN are surprisingly different. Whereas PZN is a ferroelectric that transforms from a cubic to a rhombohedral phase at 410 K,[3] PMN remains, on average, cubic below $T_{\max}$ down to 5 K.[4] To date the true ground state of PMN remains an enigma.

Neutron measurements of the lattice dynamics and diffuse scattering in these relaxor systems have proven to be invaluable in the effort to solve the relaxor problem. Pioneering work by Vakhrushev and co-workers[5–7] yielded critical information about the diffuse scattering and low-frequency transverse optic (TO) phonons in PMN at high temperatures. Recent neutron inelastic scattering measurements on PZN and PZN doped with PT in the cubic phase have revealed an anomalous damping of the TO phonons that only occurs at reduced wave vectors q less than a characteristic value $q_{wf} \sim 0.2$ Å^{-1}, which gives rise to the so-called ''waterfall'' feature.[8,9] The origin of this damping was speculated to result from the presence of local regions of randomly oriented polarization that couple strongly to polar TO modes. These small regions of polarization, also known as polar nanoregions (PNR's), were inferred in 1983 by Burns and Dacol from measurements of the optic index of refraction in different relaxor systems, including PMN and PZN.[10] The most remarkable aspect of their finding was that the PNR's start forming at a temperature T_d, also known as the Burns temperature, that is several hundred degrees higher than $T_{\max}$ (or T_c).

Gehring *et al.* demonstrated that at temperatures above T_d, where there are no PNR's, the low-q TO modes in PMN exhibit a normal optic phonon dispersion and are not overdamped.[11] This provides direct evidence of the correlation between the PNR's and the anomalous phonon damping. Subsequently, Hirota *et al.*[12] proposed a simple model that resolves the puzzling diffuse scattering problem in PMN by introducing the concept of a ''phase-shifted condensed soft mode.'' Recent improvements in crystal growth have made such measurements possible using larger crystals. From these experimental facts, we know that the PNR's are directly connected with the soft-zone-center TO mode.

In this paper we extend our previous phonon research down to 10 K using a large high-quality single crystal of PMN, the same as that used in Ref. 12. Our results clearly show the recovery of the TO mode at 220 K in addition to two distinct phonon anomalies which provide definitive evidence of ferroelectric ordering in PMN and thus shed light on the ground state of PMN.

Neutron scattering experiments were performed on the C5 triple-axis spectrometer located in the NRU reactor at Chalk River Laboratories. Inelastic measurements were carried out by holding the momentum transfer $\vec{Q} = \vec{k}_i - \vec{k}_f$ constant, while scanning the energy transfer $\hbar\omega = E_i - E_f$ by fixing the final neutron energy E_f at 14.6 meV and varying the incident energy E_i. Horizontal beam collimations from reactor to detector were 32′-32′-S-48′-60′ (S=sample). Highly oriented pyrolytic graphite (HOPG) (002) crystals were used as monochromator, analyzer, and higher-order filter. A 3.25-g (~ 0.4 cc) single crystal of PMN was prepared by a top-seeded solution growth technique from PbO flux. The crystal was mounted in either a high-temperature furnace or a closed-cycle helium refrigerator such that reflections of the form $(h0l)$ lay in the scattering plane. The room-temperature lattice parameter of PMN is $a = 4.04$ Å, so that 1 reciprocal lattice unit (r.l.u.) $= 2\pi/a = 1.555$ Å^{-1}.

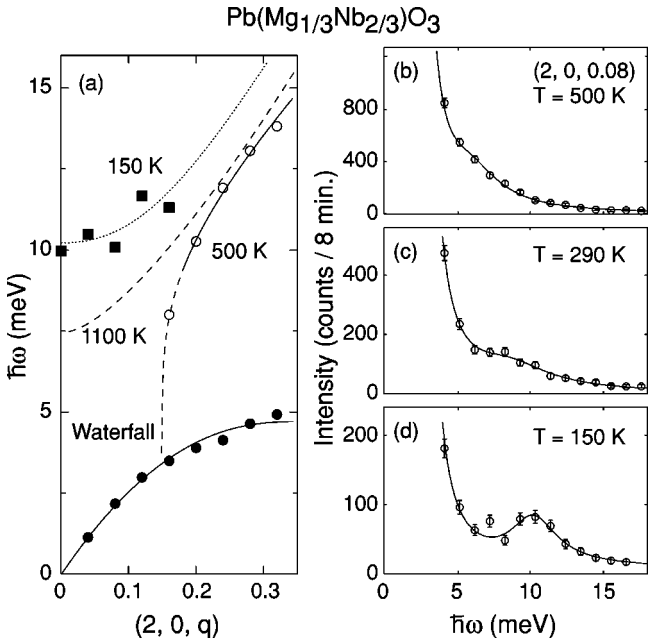

FIG. 1. (a) TO-phonon dispersion at 150 K (solid squares), 500 K (open circles), and 1100 K [dashed line (Ref. 11)]. Solid circles show the TA-phonon dispersion at 500 K. Constant-$\vec{Q}$ scan profiles at (2, 0, 0.08) are shown at (b) 500 K, (c) 290 K, and (d) 150 K. Solid lines in (b), (c), and (d) are fits of the data to a resolution-convoluted Lorentzian function. When compared to those at (2, 0, 0), these profiles suggest that higher-q TO modes recover before those at lower-q upon cooling below T_c.

One of the most important findings of the present study is the recovery of the soft mode at low temperature. As shown in a previous neutron scattering study, this mode becomes overdamped at T_d when the PNR's first condense.[11] The recovery of the TO branch is summarized in Fig. 1(a) together with the TO branch at 1100 K from Ref. 11. Circles and squares represent the phonon energies at 500 K and 150 K respectively. While the TO modes are overdamped or heavily damped for $q \leqslant q_{wf} \sim 0.16$ r.l.u. at 500 K, these modes are underdamped at 150 K, and exhibit a normal TO dispersion. Phonon profiles at (2, 0, 0.08) ($q \leqslant q_{wf}$) are shown at three different temperatures in Figs. 1(b), 1(c), and 1(d). It is clear that the TO mode is nearly overdamped at 500 K and strongly damped at 290 K, but has recovered an underdamped character at 150 K.

Figure 2(a) summarizes the temperature dependence of the TA linewidth Γ at (2, 0, 0.2), which begins to broaden significantly near T_d and is in good agreement with the results of Naberezhnov *et al.*[7] and Koo *et al.*[13] Upon further cooling we obtain the new result that the broadening peaks around 400 K and decreases until it finally disappears around 220 K. Similar results are observed at $q = 0.12$ and 0.16 r.l.u.; however, the broadening at $q = 0.2$ r.l.u. was studied in more detail since the effect is most prominent there. Examples of TA-phonon profiles at (2, 0, 0.2) are shown in the three right-hand panels of Fig. 3. Clearly the TA-phonon linewidth at 500 K is larger than it is at either 150 or 750 K. It is quite interesting to note that the temperature at which the broadening vanishes (220 K) is very close to the temperature at

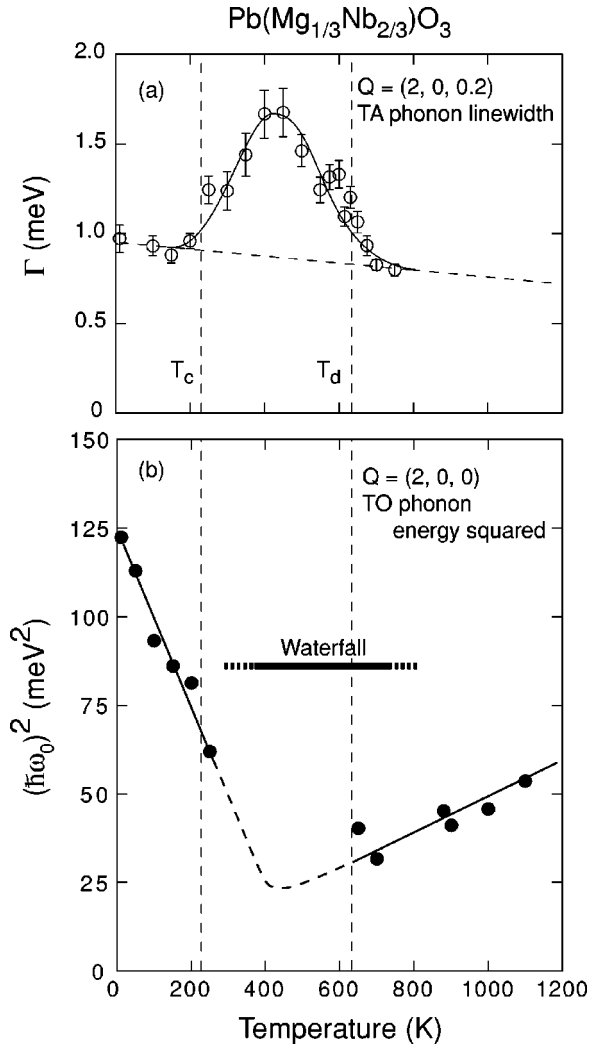

FIG. 2. (a) TA-phonon linewidth Γ at (2, 0, 0.2) obtained from resolution-corrected fits to a Lorentzian function. (b) Temperature dependence of the TO-soft-phonon energy squared. Vertical dashed lines correspond to $T_c = 213$ K and $T_d = 620$ K. The temperature range where the waterfall feature appears is indicated by the thick horizontal line. The other dashed and solid lines are guides to the eye.

which PMN becomes ferroelectric ($T_c = 213$ K) when cooled in the presence of a sufficiently large electric field $E > E_c$.[2]

Figure 2(b) combines the temperature dependence of the zone-center TO-phonon energy squared $(\hbar\omega_0)^2$ measured at (2, 0, 0) at low temperatures with that reported at high temperatures by Gehring *et al.*[11] When compared with Fig. 2(a) a truly striking picture emerges. As indicated by the dashed vertical lines passing through both panels (a) and (b), the onset of the TA-phonon broadening near T_d coincides with the temperature at which the zone-center mode becomes overdamped. On the low-temperature side, the TO mode reappears around 220 K, which is effectively the same temperature ($\sim T_c$) at which the TA broadening vanishes. Thus these data show that the lattice dynamics of PMN is intimately connected with the condensation of the PNR at T_d as

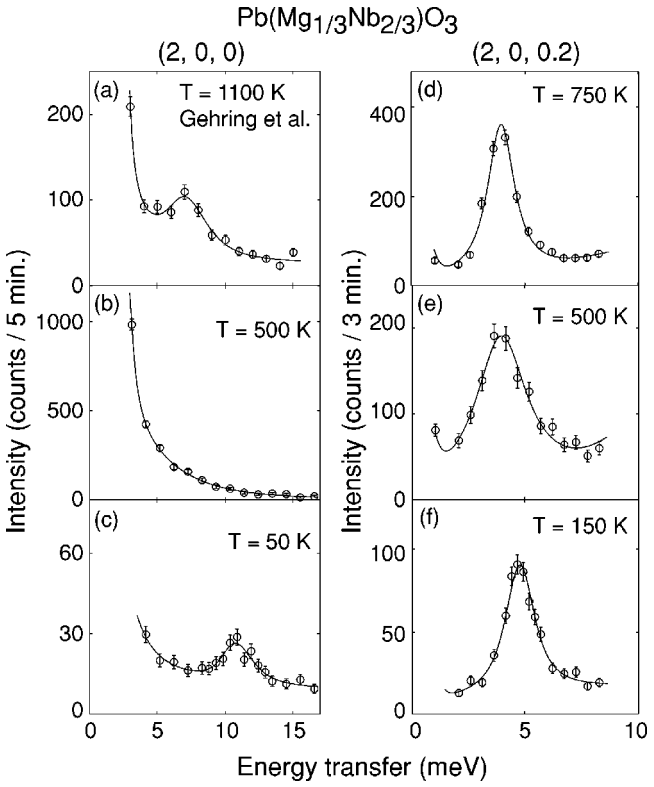

FIG. 3. Temperature evolution of the TO-phonon profile at (2, 0, 0) (left column) and TA-phonon profile at (2, 0, 0.2). Solid lines are fits to a resolution-convoluted Lorentzian function. The data for 1100 K at (2, 0, 0) by Gehring *et al.* (Ref. 11) were taken using a smaller (0.10 cm^3) crystal.

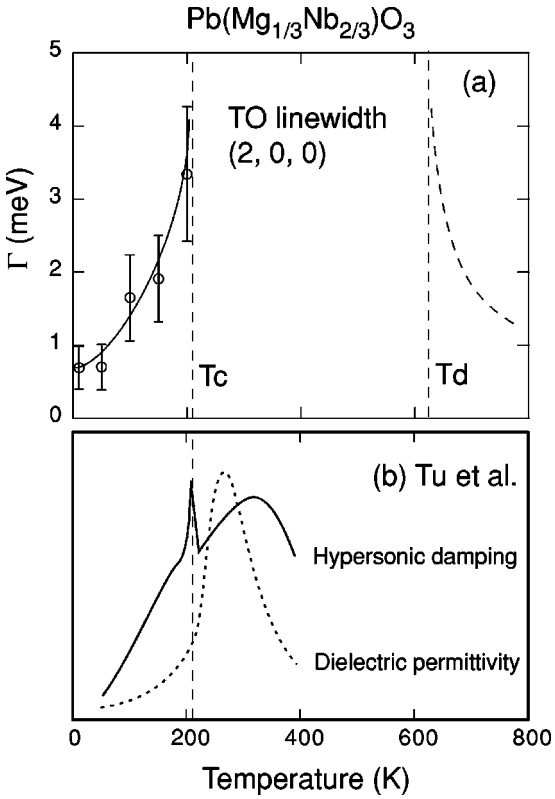

FIG. 4. (a) Temperature dependence of the TO linewidth Γ at (2, 0, 0). (b) Schematic figure of the hypersonic damping (solid line) and dielectric constant (dotted line) vs temperature from Tu *et al.* (Ref. 18). The vertical dashed line indicates $T=T_c$.

well as with the ferroelectric transition temperature T_c (for $E>E_c$).

At high temperatures ($T>T_d$), the zone-center TO mode has been shown to soften in a manner consistent with that of a ferroelectric soft mode.[11] It was not possible to determine the energy $\hbar\omega_0$ of the zone-center mode over a wide range of temperatures below T_d due to its overdamped nature [see Fig. 3(b)]. At temperatures below 220 K, however, the TO mode is no longer overdamped, and the phonon profiles could be fit to a Lorentzian function of q and ω convolved with the instrumental resolution function. From these fits we have established that $(\hbar\omega_0)^2$ increases linearly with decreasing temperature. This is a seminal point since, in a normal ferroelectric material, the linear relationship between $(\hbar\omega_0)^2$ and the inverse dielectric constant $1/\epsilon$ is well established above and below T_c.[14] It should also be noted that $\hbar\omega_0$ reaches 11 meV at 10 K, a value identical to that for ferroelectric PZN at low temperature.[15] This suggests that a ferroelectric state is eventually established in PMN too. This point will be discussed in detail later.

The three left-hand panels of Fig. 3 trace the evolution of the zone-center TO mode at (2, 0, 0). We observe a well-defined propagating mode at 1100 K, but a subsequently overdamped mode at 500 K, which then completely recovers an underdamped character at 50 K. The dramatic recovery of the soft mode below 220 K occurs relatively quickly with decreasing temperature. By comparison, the recovery of the underdamped soft mode in PZN is slower, as it is readily observed only at temperatures below ≈ 100 K.[15] The quick recovery in PMN is also clearly demonstrated in Fig. 4(a), which shows the temperature dependence of the soft-mode linewidth Γ. Below T_c, Γ decreases quickly and becomes very small at low temperature.

In Fig. 2 we demonstrate the occurence of two distinct phonon anomalies in PMN near 220 K. The most remarkable of these is the linear increase of the square of the soft-mode energy that begins below 220 K. This behavior is typical of many ferroelectrics in their ordered states. Yet PMN is known to retain an average cubic structure through 220 K, and even down to very low temperature.[4] The soft-mode behavior shown in Fig. 2 appears to contradict the currently accepted picture of PMN because it implies that a phase transition takes place from a relaxor state to a short-range-ordered ferroelectric (noncubic) state at T_c.

Relaxor-to-ferroelectric phase transitions have been observed in other lead-oxide compounds such as chemically disordered $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) (Ref. 16) and $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) (Ref. 17). They usually occur at a temperature T_c that is lower than the temperature of the maximum permittivity, $T_{\max}$. The difference between $T_{\max}$ (at 1 kHz) and T_c is about 15 K in PST and PSN, and is significantly smaller than that observed in PMN (≈ 50 K). In addition, both PST and PSN have relatively sharp dielectric permittivity $\epsilon(T)$ peaks (small diffuse character) compared to that in PMN. The only data on PMN that show an

anomaly at $T_c = 213$ K upon ZFC is the peak in the hypersonic damping shown in Fig. 4(b).[18] It has also been reported that a macroscopic ferroelectric phase can be induced in PMN upon cooling in a small electric field and that, once induced, the ferroelectric phase and the related polarization vanish upon zero-field heating as a first-order transition at $T_c = 213$ K.[19,20] These results suggest that PMN may exhibit a ferroelectric phase, which, however, does not achieve long-range order when zero-field cooled. Therefore, the soft-mode behavior reported here is not entirely unexpected. It does, however, reveal the ferroelectric phase transition near T_c in terms of the dynamics.

There remains the question of why a sharp structural phase transition is not observed in PMN by x rays, even though a ferroelectric phase is implied from the low-temperature lattice dynamics. One possible answer concerns the length scale of the rhombohedral ferroelectric phase. Quite simply, a length scale of order ~ 100 Å will appear as long-range order in neutron phonon measurements but as short-range order to x rays. In fact, ferroelectric regions of order 100 Å in size have been reported by de Mathan *et al.*[4]

PMN is a special relaxor compound given its unusually broad dielectric relaxation and the large temperature difference between $T_{\max}$ and T_c. We believe that an important clue to understanding the low-temperature properties of PMN lies in the concept of the phase-shifted condensed soft mode recently proposed by Hirota *et al.*[12] In this work the PNR's are shown to result from condensation of the soft TO mode at T_d through a model that reconciles the differences between the structure factors of the soft mode and the diffuse scattering by introducing a uniform ionic shift of the PNR's along their polar axis relative to the surrounding cubic matrix. This phase shift persists to low temperatures as shown by the structural work of de Mathan *et al.*[4] It is important to note that the relative intensities of the diffuse lines reported by de Mathan *et al.* are in excellent agreement with the phase-shifted condensed soft-mode results of Hirota *et al.* The uniform phase shift idea provides an additional energy barrier to the formation of a long-range-ordered ferroelectric state. We speculate that the combination of this energy barrier and the random field effects introduced by the PNR's prevent PMN from entering into a pure ferroelectric state.

Finally, we discuss the relationship between $(\hbar\omega_0)^2$ and $1/\epsilon(T)$. In Fig. 2(b), the dashed line is drawn so that $(\hbar\omega_0)^2$ has a minimum at ~ 400 K, where the TA-phonon linewidth is largest. Since $(\hbar\omega_0)^2$ is linearly related to $1/\epsilon(T)$, one might guess that the minimum value of $(\hbar\omega_0)^2$ would occur at $T_{\max} = 265$ K. However, this value of $T_{\max}$ is obtained at a measuring frequency of 1 kHz. By comparison, $T_{\max} = 305$ K at a measuring frequency of 100 MHz.[21] Our neutron measurements probe the dynamical response function of PMN at frequencies on the order of THz. Since $T_{\max}$ is by definition strongly frequency dependent in relaxors, the temperature of 400 K may possibly correspond to $T_{\max}$ on the THz scale.

To understand the relaxor-to-ferroelectric phase transition in PMN (and those in other relaxors), we intend to carry out a series of neutron experiments which includes a systematic comparison of the lattice dynamics in PMN, PMN-xPT, PSN, and PZN. These experiments will provide useful information about the microscopic mechanism of relaxor ferroelectricity. Recent studies[13,22] of PMN-xPT have already documented very interesting changes in the phase transition with increasing $PbTiO_3$ content x.

We thank A. A. Bokov, K. Hirota, J.-M. Kiat, B. Noheda, and K. Ohwada for stimulating discussions. Work at the University of Toronto is supported by the Natural Science and Engineering Research Council of Canada. We acknowledge financial support from the U.S. DOE under Contract No. DE-AC02-98CH10886 and the Office of Naval Research under Grant No. N00014-99-1-0738.

*Corresponding author Electronic address: waki@physics.utoronto.ca

[1] S.-E. Park and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997).
[2] See review article, Z.-G. Ye, Key Eng. Mater. **155-156**, 81 (1998).
[3] J. Kuwata, K. Uchino, and S. Nomura, Ferroelectrics **37**, 579 (1981); Jpn. J. Appl. Phys., Part 1 **21**, 1298 (1982).
[4] N. de Mathan, E. Husson, G. Calvarin, J. R. Gavarri, A. W. Huwat, and A. Morell, J. Phys.: Condens. Matter **3**, 8159 (1991).
[5] S. B. Vakhrushev, B. E. Kvyatkovksy, A. A. Naberezhnov, N. M. Okuneva, and B. Toperverg, Ferroelectrics **90**, 173 (1989).
[6] S. B. Vakhrushev, A. A. Naberezhnov, N. M. Okuneva, and B. N. Savenko, Phys. Solid State **37**, 1993 (1995).
[7] A. Naberezhnov, S. Vakhrushev, B. Doner, D. Strauch, and H. Moudden, Eur. Phys. J. B **11**, 13 (1999).
[8] P. M. Gehring, S.-E. Park, and G. Shirane, Phys. Rev. Lett. **84**, 5216 (2000).
[9] P. M. Gehring, S.-E. Park, and G. Shirane, Phys. Rev. B **63**, 224109 (2000).
[10] G. Burns and F. H. Dacol, Solid State Commun. **48**, 853 (1983).
[11] P. M. Gehring, S. Wakimoto, Z.-G. Ye, and G. Shirane, Phys. Rev. Lett. **87**, 277601 (2001).
[12] K. Hirota, Z.-G. Ye, S. Wakimoto, P. M. Gehring, and G. Shirane, Phys. Rev. B **65**, 104105 (2002).
[13] T.-Y. Koo, P. M. Gehring, G. Shirane, V. Kiryukhin, G. Lee, and S.-W. Cheong, Phys. Rev. B **65**, 144113 (2002).
[14] G. Shirane, J. D. Axe, and J. Harada, Phys. Rev. B **2**, 155 (1970).
[15] P. M. Gehring (unpublished).
[16] F. Chu, N. Stter, and A. K. Tagantsev, J. Appl. Phys. **74**, 5129 (1993).
[17] F. Chu, I. M. Reaney, and N. Stter, J. Appl. Phys. **77**, 1671 (1995).
[18] C.-S. Tu, V. Hugo Schmidt, and I. G. Siny, J. Appl. Phys. **78**, 5665 (1995).
[19] Z.-G. Ye and H. Schmid, Ferroelectrics **145**, 83 (1993).
[20] G. Calvarin, E. Husson, and Z.-G. Ye, Ferroelectrics **165**, 349 (1995).
[21] T. Tsurumi, K. Soejima, T. Kamiya, and M. Daimon, Jpn. J. Appl. Phys., Part 1 **33**, 1959 (1994).
[22] B. Dkhil, J. M. Kiat, G. Calvarin, G. Baldinozzi, S. B. Vakhrushev, and E. Suard, Phys. Rev. B **65**, 024104 (2002).