Soft Mode Dynamics Above and Below the Burns Temperature in the Relaxor Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$

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We report neutron inelastic scattering measurements of the lowest-energy transverse optic (TO) phonon branch in the relaxor Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), and the closely related system Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ (PZN), both of which show a huge increase in piezoelectric character when doped with 8% PbTiO$_3$ (PT). Despite intense research efforts, no consensus on a fundamental understanding of the basic lattice dynamics of these relaxor systems has been established. The identification of a soft transverse optic (TO) mode at the Brillouin zone center, for example, the hallmark of every displacive ferroelectric phase transition including PMN, has proven elusive in both PMN and PZN.

In an effort to solve the soft mode puzzle in the relaxor compounds, we have performed an extensive study of the lattice dynamics of pure PMN using neutron inelastic scattering techniques at temperatures far above $T_{max} = 265$ K, where the dielectric susceptibility exhibits a broad peak. The temperature scale for this study is set by the Burns temperature $T_d \sim 620$ K for PMN, where randomly-oriented regions of local polarization, of order several unit cells in size, begin to condense within the otherwise non-polar crystal structure. Experimental evidence for these so-called polar nanoregions (PNR) was first obtained by Burns and Dacol in 1983 from measurements of the optic index of refraction on both PMN and PZN, as well as other disordered systems. Previous neutron inelastic studies on single crystals of PZN and PZN doped with 8% PbTiO$_3$ (PZN-8%PT) in their respective cubic phases at 500 K have shown that the lowest-energy TO phonon modes are overdamped for reduced wave vectors $q$ less than a characteristic wave vector $q_{wf}$, which is of order 0.2 Å$^{-1}$, but undamped otherwise. It was speculated that the PNR are the underlying cause of this $q$-dependent damping because the TO modes are polar, and thus they should couple strongly to the PNR. Indeed, it is this coupling that is believed to produce the anomalous waterfall feature observed in these and other lead-oxide relaxor systems including PMN. If these speculations are correct, then the search for a soft true mode can only be made above $T_d$ since the anomalous low-$q$ damping makes it impossible to observe the temperature dependence of the zone center TO mode. However, the values of $T_d$ for PZN and PZN-8PT compounds approach their decomposition temperatures, making such measurements difficult. PMN, by contrast, has a much lower Burns temperature compared to that of PZN, making it an ideal system in which to look for the soft mode. We have exploited this fact to study the evolution of the lowest-energy TO branch in PMN at temperatures far above and below $T_d$, thereby providing key insight into the role played by the PNR on the soft mode dynamics in this important relaxor system.

The inset to Fig. 1 shows the TO and TA dispersion curves measured along the cubic [001] direction after heating the PMN crystal in vacuum to 1100 K, well above $T_d$, but safely below the decomposition temperature of $\sim 1370$ K. The data shown in panels (a) and (b) are constant-$Q$ scans measured at $Q = (2.0,0.08)$ and (2.0,0.16), respectively, and indicate that well-defined propagating TO and TA modes are present throughout the Brillouin zone at this temperature. Similar data measured at 800 K were discussed briefly by Naberezhnov et al. who identified the upper curve as a hard TO1 branch, and concluded that it could not be the ferroelectric mode. Based on our PMN data, which cover a larger range in temperature, this conclusion does not appear to be justified. Instead, we demonstrate in this Letter that the lowest-frequency TO mode is in fact the elusive ferroelectric soft mode in this relaxor compound, and that the PNR have a drastic effect on its behavior.
of a long sample stick. The sample stick assembly was then mounted inside the vacuum space of a furnace, and positioned onto the goniometer of the spectrometer. This orientation gave access to reflections of the form \((h0l)\).

![PMN (T = 1100 K)](image)

**Fig. 1.** Constant-\(\vec{Q}\) scans measured at 1100 K \((> T_d)\). Panel (a) shows a well-defined, underdamped TO mode for \(q = 0.08\) rlu. Panel (b) shows well-defined, underdamped TO and TA modes for \(q = 0.16\) rlu. The TA and TO dispersion curves are shown in the inset (lines are guides to the eye).

The neutron inelastic scattering data presented here were obtained on the BT9 triple-axis spectrometer located at the NIST Center for Neutron Research. We used the same experimental configuration as that described in Ref. [4]. The data were taken holding the final neutron energy \(E_f\) fixed at 14.7 meV \((\lambda_i = 2.36\) Å\) while varying the incident neutron energy \(E_i\). Horizontal beam collimations were \(40'\)-\(46'\)-\(S\)-\(40'\)-\(80'\). Constant-\(E\) scans were performed by holding the energy transfer \(\hbar\omega = E_i - E_f\) fixed while varying the momentum transfer \(\vec{Q}\). Constant-\(Q\) scans were performed by holding the momentum transfer \(\vec{Q} = \vec{k}_i - \vec{k}_f\) (\(k = 2\pi/\lambda\)) fixed while varying \(\hbar\omega\).

Single crystals of PMN were grown from high-temperature solution using PbO as flux. The growth conditions were determined from the pseudo-binary phase diagram established for PMN and PbO [9]. A rectangular parallelepiped crystal, with dimensions \(8.7 \times 5.1 \times 2.2\) mm\(^3\) \((0.10\) cm\(^3\)), was prepared with the largest facets oriented parallel to the cubic [100] direction. This crystal was mounted in a molybdenum holder with quartz wool with the [010] axis oriented vertically, and attached to the end of a long sample stick. The sample stick assembly was then mounted inside the vacuum space of a furnace, and positioned onto the goniometer of the spectrometer. This orientation gave access to reflections of the form \((h0l)\).

![PMN (T = 550 K)](image)

**Fig. 2.** Constant-\(\vec{Q}\) scans measured at 550 K \((< T_d)\). Panel (a) shows a damped TO mode for \(q = 0.08\) rlu \(< q_{wf}\). Panel (b) shows well-defined, underdamped TA and TO modes for \(q = 0.16\) rlu \(> q_{wf}\). The inset shows the TA and TO dispersion curves below \(T_d\), the latter of which terminates at the waterfall wave vector (dashed line) at \(q_{wf} \sim 0.12\) rlu.

The data presented in Fig. 2 were taken below \(T_d\), but still in the cubic phase of PMN, to establish consistency with prior results on PZN and PZN-8\%PT [10]. The solid curves shown in the inset were derived from constant-\(Q\) scans, whereas the dashed line representing the waterfall anomaly was derived from constant-\(E\) scans. The waterfall feature is located at \(q = q_{wf} \sim 0.12\) rlu (reciprocal lattice units), where 1 rlu = \(2\pi/\lambda = 1.553\) Å\(^{-1}\). Fig. 2 (a) shows a representative constant-\(Q\) scan measured at \(\vec{Q} = (2, 0, 0.08)\) \((q < q_{wf})\) where, in contrast to that shown in Fig. 1 (a), the TO mode is now strongly damped and appears at lower energy. The solid lines in these and all other panels represent fits of the data to a Lorentzian function of \(q\) and \(\omega\) convoluted with the instrumental resolution function. The TA mode is not visible in panel (a) because it peaks at energies below 3 meV. Fig. 2 (b) shows a similar constant-\(Q\) scan measured at \(\vec{Q} = (2, 0, 0.16)\) \((q > q_{wf})\) for which well-defined propagating TA and TO modes are observed. The peak intensities, which scale with the Bose factor, are notice-
ably lower for the TA mode in Fig. 2 (b) compared to the TA mode in Fig. 1 (b). (To facilitate comparison between figures, all intensity axes have been scaled to the same count rate per unit length.)

A series of constant-$\vec{Q}$ scans were taken in steps of 0.04 rlu over the entire Brillouin zone, and the results are summarized in the inset to Fig. 2. They show that at 550 K propagating TO modes are now only present for wave vectors $q > q_{wf} \sim 0.12$ rlu, and that the waterfall feature has appeared. The dashed line in the inset is used to indicate that the waterfall is in fact not part of the TO dispersion curve since no propagating modes are observed for $q \leq q_{wf}$. We emphasize that these data were taken at 550 K, far above $T_{max} = 265$ K, the temperature at which the dielectric susceptibility of PMN reaches a maximum, yet still below the Burns temperature $T_d \sim 620$ K. Hence while the system is in the cubic phase, it also contains a finite density of nanometer-sized regions of randomly-oriented polarization. The data taken on PMN at this temperature are thus consistent with the picture obtained from earlier neutron studies of PZN and PZN-8%PT. The question remains, however, of whether or not this damping, and the resulting waterfall, correlate with the condensation of the PNR at the Burns temperature.

To answer this question, we show three identical constant-$\vec{Q}$ scans in Fig. 3 measured at the zone center at $\vec{Q} = (2, 0, 0)$ from 1100 K (above $T_d$) down to 600 K (near $T_d$). These data reveal an unambiguous evolution from an underdamped to an overdamped phonon cross section as the temperature is reduced below $T_d$. The TO peak intensity diminishes, and the TO linewidth broadens, with decreasing temperature. Although the damping of the zone center mode begins at temperatures considerably above $T_d$, we note that the mode becomes completely overdamped near or at $T_d$ as shown in the bottom panel of Fig. 3. The increase in the damping of this and other low-$q$ modes is accompanied by the gradual formation of the waterfall. It appears that $T_d$ coincides with the condensation of the dynamical fluctuations of the PNR at $q = 0$ which develop at much higher temperatures.

The temperature dependence of the zone center TO mode energy squared $(\hbar\omega)^2$, shown in the inset to Fig. 3, varies linearly with temperature until $T \sim T_d$. This behavior is consistent with that observed in PbTiO$_3$ and other displacive ferroelectrics, and represents the first definitive identification of a true soft mode in PMN. At present we have no direct experimental measure of the zone center mode frequency below $T_d$. However, we speculate that this mode recovers at very low temperature as has been reported for PZN where, at 20 K, the TO mode scattering cross section peaks at 10.5 meV. A dashed line connects this data point to that for PMN at $T_d$ to suggest how this mode might recover at low temperature.

To establish the temperature dependence of the TO mode damping in greater detail, we present data in Fig. 4 similar to those shown in Fig. 3, but for non-zero $q$. As was the case for the zone center mode, the TO mode at $q = 0.08$ rlu gradually softens with decreasing temperature above $T_d$. Moreover, the top and bottom panels of Fig. 4 indicate that the TO mode is underdamped at high temperature and overdamped at low temperature. However, the presence of a weak phonon peak at 550 K (below $T_d$) in the middle panel of Fig. 4 demonstrates the important fact that TO modes with finite $q$ become overdamped at lower temperatures compared to that for the zone center mode. Hence the temperature dependence of the TO mode damping is $q$-dependent.

![PMN (Q = (2, 0, 0))](image)

Fig. 3. The square of the zone center TO mode energy $(\hbar\omega)^2$ softens linearly (see inset) between (a) 1100 K, (b) 900 K, and (c) 600 K. The FWHM linewidth (horizontal bar) increases from 1.2 meV at 1100 K to 1.8 meV at 900 K, but is too broad to measure reliably at 600 K.

We have identified a soft polar phonon mode in PMN, and established its behavior through the Burns temperature $T_d$. Our identification of the lowest-energy zone center TO mode as the ferroelectric soft mode differs from
that of Naberezhnov et al. who identified it as a hard TO1 mode \[8\]. In their neutron study, they claimed that no underdamped soft TO mode was observed in the vicinity of (221), even at 900 K and large \( q \). However the data we present in Fig.’s 3 – 4 show conclusively that our mode determination is correct. Indeed, the relative intensities of the TO branch measured in different zones are very similar to those found in PbTiO\(_3\). It is important to note that the existence and value for \( T_d \) has been confirmed by a variety of experimental techniques. Neutron powder diffraction data by Zhao et al., for example, provide clear evidence of the PNR in PMN through a marked deviation from the linear dependence on temperature of the unit cell volume near 600 K \[10\]. Also, Naberezhnov et al. observe diffuse scattering at (2,2,0.95) that begins to increase at 650 K, as well as a TA linewidth broadening at the same temperature \[8\]. Our measurements indicate a Burns temperature that lies between 600 and 650 K, and are thus consistent with both of these studies.

Our next goal is to determine how the diffuse scattering in PMN connects to this soft mode picture. Diffuse scattering was first reported in PMN by Vakhrushev et al. \[11\] at room temperature, however the scattering intensities are entirely different from those of the soft optic mode. For example, the scattering near (110) is much stronger than that at (200). In fact, this observation was the main reason that Naberezhnov et al. assigned the lowest-frequency TO branch as a hard TO1 branch \[8,12\]. Although several x-ray studies of the diffuse scattering in PMN have been published \[3-5\], the ionic shifts derived from the neutron diffuse scattering peaks in PMN \[11\] have not yet been confirmed by x-ray scattering. We are trying to reconcile the conflict between the diffuse and soft mode scattering cross sections by considering different models. Finally, the question of how the long-wavelength TO phonon modes recover at low temperatures, as was observed in PZN, remains to be answered. Neutron experiments using a larger PMN crystal are planned to examine this interesting issue.

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