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Soft and central mode behaviour in $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ relaxor ferroelectric

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Abstract

The relaxor ferroelectric $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) is investigated by means of dielectric and Fourier transform far infrared transmission spectroscopy in the frequency range from 10 kHz to 15 THz at temperatures between 20 and 900 K using mostly thin films on infrared transparent sapphire substrates. While the thin film relaxors display reduced dielectric permittivity at low frequencies, their high frequency lattice response is shown to be the same as for single-crystal/ceramic specimens. In contrast to the results of inelastic neutron scattering, the optic soft mode is found to be underdamped at all temperatures. On heating, the TO1 soft phonon follows the Cochran law with an extrapolated critical temperature of 670 K near to the Burns temperature. Above 450 K the soft mode frequency levels off near 50 cm^{-1} and above the Burns temperature it slightly hardens. Central-mode-type dispersion assigned to the dynamics of polar nanoclusters appears below the Burns temperature at frequencies near to but below the soft mode and slows down and broadens dramatically on cooling, finally, below the freezing temperature of 200 K, giving rise to frequency independent losses from the microwave range down. A new explanation of the phonon ‘waterfall’ effect in inelastic neutron scattering spectra is proposed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Lead magnesium niobate $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) was initially studied by Smolenskii *et al* [1, 2] at the end of the 1950s, and since that time it has been considered as a model system for relaxor ferroelectrics (RFE). The interest in this topics was enhanced after the publishing of the paper of Park and Shrout [3] who showed that $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{--PbTiO}_3$ (PMN–PT) and $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{--PbTiO}_3$ (PZN–PT) mixed crystals exhibit ultrahigh strain and piezoelectric behaviour. The model system PMN shows high and broad maxima of real and imaginary parts of the complex permittivity $\varepsilon^*(T) = \varepsilon'(T) - i\varepsilon''(T)$ which shift with increasing measuring

frequency to higher temperatures. The dielectric anomaly is not accompanied by any phase transition to a polar state, and the structure remains cubic down to liquid He temperatures [4]. Nowadays it is generally accepted that the strong dielectric dispersion, which in RFE occurs in the broad spectral GHz to mHz range [5, 6] at temperatures around and below that of $\epsilon'(T)$ maximum T_{\max} , is a consequence of the dynamics of polar nanoclusters, which appear several hundred degrees above T_{\max} at the Burns temperature T_d [7]. Although many papers have been devoted to RFE (see e.g. reviews by Cross [8], Ye [9], Samara [10] and Kamba [11]), the quantitative knowledge of the complex dielectric behaviour of RFE is still not satisfactory. The dynamics of polar nanoclusters was studied predominantly at low frequencies below 1 MHz at temperatures near T_{\max} . However, the mean relaxation frequency increases up to the microwave range at higher temperatures and is expected to appear even in the THz range near T_d [5, 11]. This frequency range merges with the polar lattice vibration response; therefore the study of lattice dynamics, especially at high temperatures, is very important for understanding the peculiar properties of RFEs.

Naberezhnov *et al* performed the first study of the lattice dynamics of PMN single crystal by means of inelastic neutron scattering (INS) [12]. They observed a transverse optic phonon branch TO1 which softens on cooling to $T_d \approx 620$ K. Below T_d the softening ceased and a strong central peak appeared. Gehring *et al* revealed that below T_d the TO1 branch dived into the transverse acoustic (TA) branch at a specific wavevector $q_{WF} \approx 0.20 \text{ \AA}^{-1}$ and no TO1 phonon could be resolved in the INS spectra at lower q [13, 14]. Gehring *et al* named this effect the ‘waterfall’ effect and explained it by the presence of polar clusters below T_d . According to their arguments, when the wavelength of the TO1 mode becomes comparable to the size of polar clusters, the phonon cannot propagate and thus becomes overdamped. Simultaneously, it was observed that the damping of the TA mode increased remarkably below T_d [12, 15]. The waterfall effect is not specific only to PMN; it has been observed in other relaxors or relaxor based crystals like PZN, PZN–PT and PMN–PT [10, 14]. The line shape of TA and TO1 phonon peaks in INS experiments were successfully explained by the coupling of the two modes using the assumption that the TO linewidth (damping) is wavevector and temperature dependent [16]. Hlinka *et al* repeated the INS measurements on PZN–PT and discovered that the critical waterfall wavevector depends on the Brillouin zone, where the experiment is performed [17]. Therefore, they claimed that the waterfall effect is not correlated with the size of polar nanoclusters but could be explained as an apparent effect in the framework of a model of bilinearly coupled harmonic oscillators representing the acoustic and heavily damped optic phonon branches and the fact that there are different dynamical structure factors in different Brillouin zones.

Wakimoto *et al* revealed that the soft TO1 mode recovers (i.e. underdamps) in the INS spectra below 220 K and its frequency hardens according to the Cochran law with decreasing temperature [15, 16]. This result was somewhat surprising because such behaviour is typical for displacive ferroelectric transitions below T_c , but PMN remains paraelectric down to liquid He temperatures [4]. This means that the soft mode behaviour provides evidence about the ferroelectric order in polar clusters. On the other hand, it is interesting to note that 220 K coincides with the ferroelectric phase transition temperature T_c of PMN cooled under an electrical bias field [18]. The question remains of how the TO1 zone centre soft mode behaves between T_c and T_d , where it is not resolved in the INS spectra. Direct experimental data are missing, which was the motivation for our Fourier transform infrared (FTIR) studies in the broad temperature range.

Some time ago we investigated FTIR reflectivity of PMN–29%PT and PZN–8%PT single crystals and, in contrast to INS data, our studies revealed underdamped TO1 phonon at all temperatures between 10 and 530 K [19]. This discrepancy was explained by the different

q vectors probed in IR and neutron experiments. The IR probe couples with very long wavelength phonons ($q \approx 10^{-5} \text{ \AA}^{-1}$) which see the homogeneous medium averaged over many nanoclusters, whereas the neutron probe couples with phonons whose wavelength is comparable to the nanocluster size ($q \geq 10^{-2} \text{ \AA}^{-1}$) [19]. Recently, we also investigated PMN single crystal by means of FTIR reflection spectroscopy and observed an underdamped TO1 mode at all temperatures below 300 K which obeyed the Cochran law [5, 20]. Unfortunately we were not able to unambiguously evaluate the FTIR data above room temperature, because the reflection band from the TO1 soft mode (SM) overlaps with that of the central mode (CM). Therefore we decided to perform more sensitive FTIR transmission measurements on a thin PMN film.

2. Experimental details

PMN single crystals are opaque in the far IR range due to the strong polar mode absorption down to thicknesses of the order of $1 \mu\text{m}$. Therefore the PMN thin films were prepared by chemical solution deposition on sapphire substrate, fully transparent in the far IR range. The PMN film was 500 nm thick and a plane-parallel sapphire substrate of $6 \text{ mm} \times 8 \text{ mm}$ size and $490 \mu\text{m}$ thickness with both faces optically polished was used. The film was polycrystalline with a predominantly (111) out-of-plane orientation and a grain size of 60 nm. Details about the thin film preparation and their characterization can be found elsewhere [21].

The in-plane dielectric response of the film was measured using a planar capacitor with standard photolithographically produced gaps of $10 \mu\text{m}$ between Cu/Cr electrodes sputter deposited on the surface of the PMN film. The capacitance and loss tangent of the electrode/film/substrate stack were measured using an HP4284A impedance analyser at frequencies from 10 kHz to 1 MHz at temperatures between 375 and 175 K. The permittivity of the film was calculated from the electrode/film/substrate stack capacitance according to Vendik [22] with an estimated error of $\pm 10\%$.

The unpolarized FTIR transmission spectra were taken using an FTIR spectrometer Bruker IFS 113v at temperatures between 20 and 900 K with the resolution of 0.5 cm^{-1} . A helium-cooled Si bolometer operating at 1.5 K was used as a detector, while an Optistat CF cryostat with polyethylene windows was used for cooling, and a commercial high temperature cell SPECAC P/N 5850 for the heating. The spectral range investigated was determined by the transparency of the sapphire substrate: at 20 K up to 450 cm^{-1} (0.3–15 THz); at 900 K the sample was already opaque above 160 cm^{-1} (see figure 1(a)).

High frequency and microwave (MW) dielectric spectra were obtained on PMN single crystal using an Agilent HP 4291B impedance analyser (1 MHz–1.8 GHz; 100–520 K) and by a waveguide resonance and non-resonance method using fixed-frequency generators (7–74 GHz, 100–800 K) [5, 23].

3. Results and discussion

An example of FTIR transmission spectra of the PMN thin film on a sapphire substrate at selected temperatures is shown in figure 1(b). Dense oscillations in the spectra are due to interferences in the substrate, while broad minima correspond to frequencies of polar phonons. The transmission decreases on heating, mainly due to the increase in multi-phonon absorption of the sapphire substrate. An unusual increase in transmission below 50 cm^{-1} was observed on heating above 700 K, which will be explained below by the disappearance of the CM above T_d .

The spectra of a bare substrate and of the PMN film on the substrate were determined for each temperature studied. For a given temperature, the transmission spectrum of the bare substrate was first fitted with a sum of harmonic oscillators using Fresnel formulae for coherent

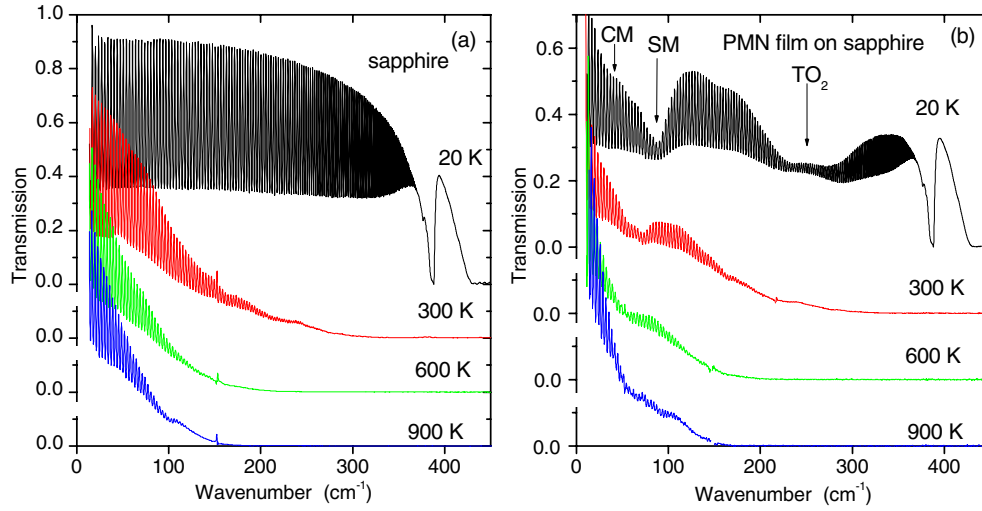


Figure 1. Temperature dependence of FTIR transmission spectra of (a) the sapphire substrate (thickness 490 μm) and (b) the 500 nm thick PMN film deposited on the sapphire substrate. Frequencies of the central mode (CM), TO1 soft mode (SM) and TO2 phonon in PMN are marked. The absorption peak near 380 cm^{-1} is the phonon peak from the sapphire.

Table 1. Parameters of polar modes in PMN thin film obtained from the fit of FTIR transmission spectrum at 20 K. Frequencies ω_j and dampings γ_j are in cm^{-1} , $\Delta\epsilon_j$ is dimensionless, $\epsilon_\infty = 6.0$. The list of polar mode parameters is not complete, because, due to the opacity of the substrate at high frequencies, the phonons above 400 cm^{-1} observed in single crystals [20] are not seen.

No	ω_j	$\Delta\epsilon_j$	γ_j
CM	39	95	73
1	65	6	37
2 (SM)	87	13	34
3	153	1.5	56
4	239	7.7	113
5	276	0.9	42
6	298	0.3	36
7	347	0.3	29

transmission of a plane-parallel slab (i.e. taking into account the interference effects) [24]. The resulting fitted sapphire parameters were then used for the fit of the PMN/sapphire two-layer system. The complex transmittance of the two-layer system was computed by the transfer matrix formalism method including interference effects [25].

The complex dielectric function expressed as the sum of damped quasi-harmonic oscillators has the form [27]

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty + \sum_{j=1}^n \frac{\Delta\epsilon_j \omega_j^2}{\omega_j^2 - \omega^2 + i\omega\gamma_j} \quad (1)$$

where ω_j , γ_j and $\Delta\epsilon_j$ denote the frequency, damping and contribution to the static permittivity of the j th polar mode, respectively. ϵ_∞ describes the high frequency permittivity originating from the electronic polarization and from polar phonons above the spectral range studied. The mode parameters at 20 K are listed in table 1. The TO2 mode near 230 cm^{-1} is not seen at high temperatures due to opacity of the substrate, but at lower temperature it can be well resolved

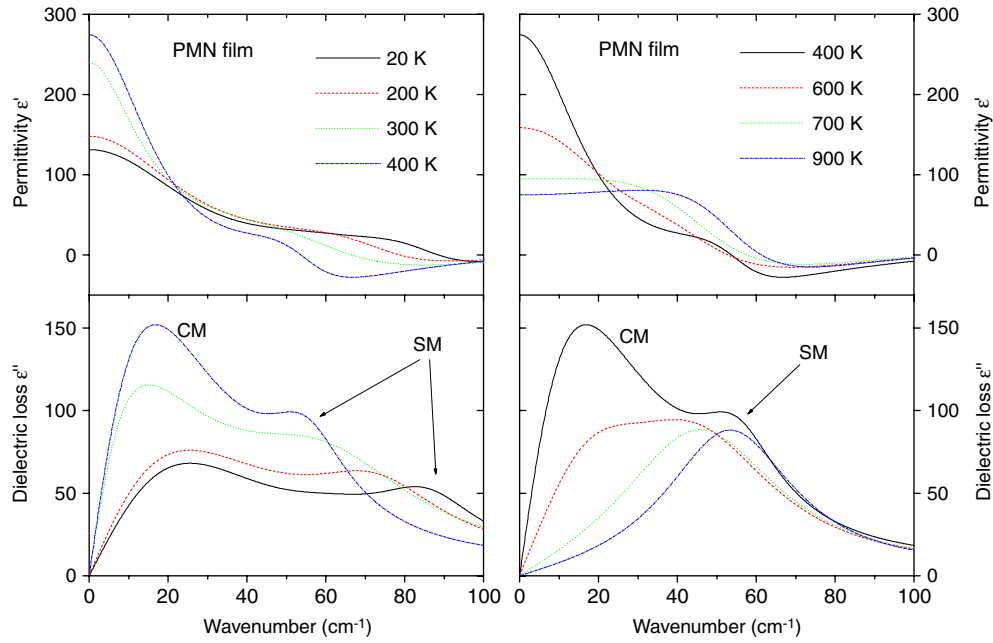


Figure 2. Complex dielectric spectra of PMN obtained from the fits of FTIR transmission spectra at various temperatures.

and finally even its splitting is seen due to breaking of symmetry in polar clusters. Let us note that the factor-group analysis and the mode activities in the spectra of different phases of complex perovskite ferroelectrics were published in [19].

The $\varepsilon^*(\omega)$ spectra calculated from the fit of the transmission spectra of PMN/sapphire are shown in figure 2. For our discussion it is instructive to discuss the dielectric loss $\varepsilon''(\omega)$ spectra, because the frequencies of loss maxima characterize the excitations, in our case the SM and CM frequencies, even in the case of their overdamping. Their temperature dependences are shown in figure 3. The TO1 mode slightly softens from 60 cm^{-1} (900 K) on cooling, but below 450 K it starts to harden and follows the Cochran law

$$\omega_{\text{SM}}^2 = A(T_d - T) \quad (2)$$

with the extrapolated critical temperature $T_d = (671 \pm 10) \text{ K}$ and $A = (11.9 \pm 0.2) \text{ K}^{-1}$. This temperature is close to the Burns temperature 620 K reported for PMN single crystals [9]. The SM frequency in the thin PMN film shown in figure 3 agrees with that in the bulk sample measured by means of FTIR reflectivity below 300 K [5, 20] and INS spectroscopy below T_c and above T_d [15]. The temperature dependence of the TO1 mode frequency obtained from the INS spectra is plotted for comparison in figure 3 as open circles and very good agreement with the FTIR data (full symbols) is seen. Only above T_d are the TO1 frequencies in INS spectra somewhat lower than in FTIR spectra, probably because of their high inaccuracy due to their high damping in INS spectra. Generally it is seen that the lattice vibrations are not appreciably influenced by the possible strain, microstructure and defects in the film, and that the *lattice response of relaxors in thin films does not differ appreciably from that in single crystals*. The situation differs from the situation in incipient ferroelectrics [26] where the soft mode in films, which represents the substantial contribution to the static permittivity, is strongly influenced by strains and microstructure. On the other hand, in relaxors the main contribution to permittivity

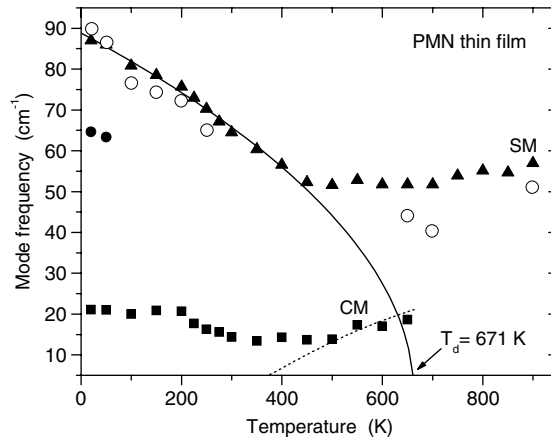


Figure 3. Temperature dependences of the SM and CM frequencies. Solid and open points mark modes obtained from FTIR transmission and INS spectra, respectively. The CM is overdamped; therefore the frequency of the loss maximum corresponding to $\omega_{\text{CM}}^2/\gamma_{\text{CM}}$ is plotted. The Cochran fit of the SM is shown by the solid line; the slowing down of the CM is shown schematically by the dashed line.

stems from the dispersion due to polar cluster dynamics below the phonon frequencies; see below.

Note the appearance of a new mode near 65 cm^{-1} which is seen below 50 K. It probably occurs due to the local symmetry of polar or chemical clusters, but its detailed assignment is uncertain since its frequency slightly differs from that of the lowest frequency Raman mode. Also the assignment of the other weak modes at 153 , 298 and 347 cm^{-1} is open to further discussion.

It is important to note that the damping of the SM is only slightly temperature dependent. It increases from 34 cm^{-1} (at 20 K) to 50 cm^{-1} (at 300 K) and at higher temperatures it remains temperature independent within the accuracy of our fits. These results show that the SM is *underdamped* in the whole temperature range investigated, which is in contradiction with the INS spectra where the *overdamped* zone centre TO1 SM is seen between T_c and T_d [15]. Let us note that, by definition, overdamping of the phonon mode occurs when the ratio of the damping γ_j and frequency ω_j becomes higher than 2 [27]. In this case the frequency of the $\varepsilon''(\omega)$ maximum does not correspond to ω_j but rather to ω_j^2/γ_j . The discrepancy between the SM damping in INS and FTIR spectra will be explained below.

Below the Burns temperature $T_d \cong 670 \text{ K}$ the FTIR transmission below 40 cm^{-1} decreases remarkably due to a new overdamped excitation appearing below the SM frequency. It is responsible for the increase in the low frequency ε'' (and ε') on reducing the temperature to 400 K. We believe that this relaxational excitation originates from the dynamics of polar clusters in PMN; let us call it a CM in analogy with the scattering experiments. The CM frequency rapidly decreases on cooling so the fit to the overdamped oscillator becomes only approximate, especially at lower temperatures when the relaxation frequency lies below our frequency range. To get insight into this dispersion, we have performed dielectric measurements between 1 MHz and 56 GHz down to 100 K on single-crystal PMN specimens (see figure 4). One can see the CM near 10 GHz at 350 K, while it slows down to 10 MHz at 260 K. Simultaneously the relaxation broadens. The mean relaxation frequency ω_R obeys the Vogel–Fulcher law

$$\omega_R = \omega_\infty \exp \frac{-E_a}{T - T_{\text{VF}}}. \quad (3)$$

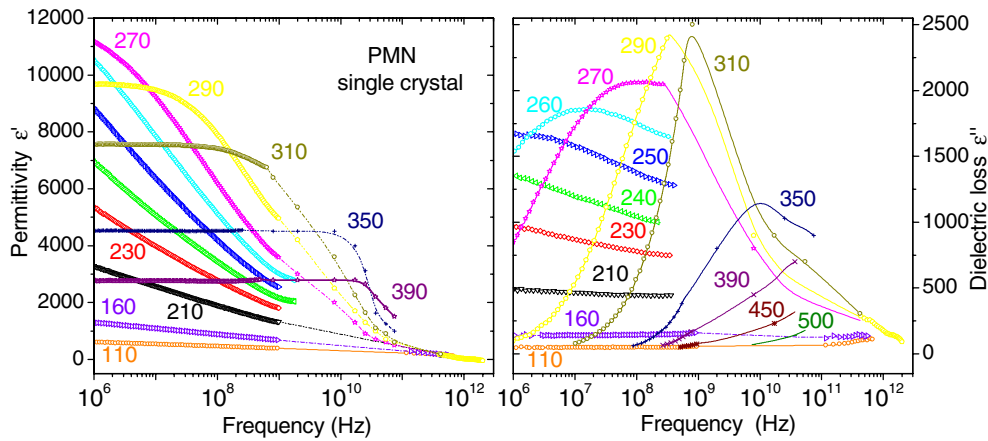


Figure 4. Frequency dependence of the complex permittivity of PMN single crystal in the high frequency and MW range at various temperatures (in kelvins).

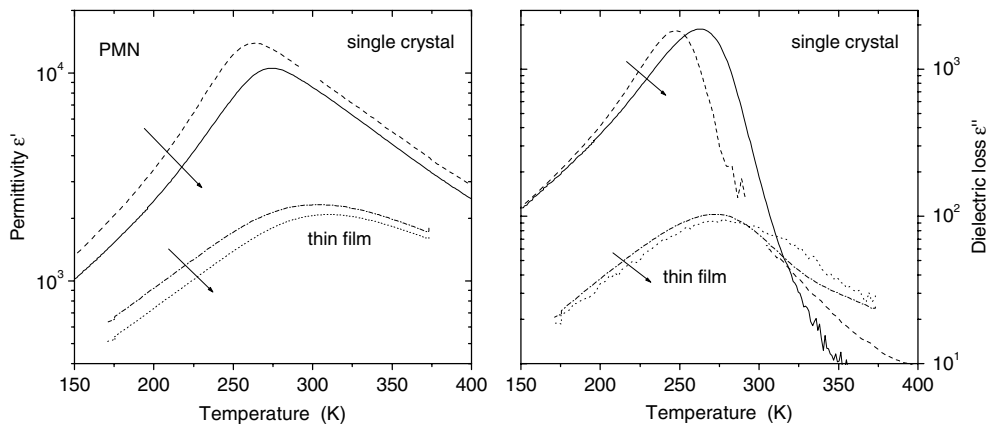


Figure 5. Comparison of the temperature dependence of the complex permittivity of PMN single crystal (from [5]) and PMN thin film obtained at 10 kHz and 1 MHz (arrows mark the increase in frequency). The dielectric response of the thin film was obtained in the plane of the film.

with the freezing temperature $T_{VF} = 200$ K, activation energy $E_a \sim 800$ K and high temperature limit of the relaxation frequency $\omega_\infty \sim 5.7$ THz ($=190$ cm^{-1}) [5]. At lower temperatures the loss maximum becomes so broad that only frequency independent dielectric losses can be seen. It can be fitted with a uniform distribution of relaxation frequencies, much broader than the experimental frequency window [28]. We believe that this is due to the influence of random fields on the distribution of activation energies for breathing of polar clusters [5].

We measured also the in-plane dielectric response of PMN thin film on sapphire between 10 kHz and 1 MHz. A comparison of dielectric data obtained for single crystal and thin film is shown in figure 5. Relaxor behaviour was observed also in the thin film, but the dielectric maximum is approximately five times lower than in single crystal and T_{max} is roughly 50 K higher, similar to recent reports for PMN films measured in the out-of-plane or parallel plate capacitor configurations [29]. This means that the dielectric strength of the CM is smaller in

the thin film. This is probably due to the size effect influence on the dynamics of polar clusters known also in ceramics with different grain size [30]. However, measurements of epitaxial films and films with different stress conditions also showed reduced dielectric response [31] as compared to single-crystal materials, so a detailed study of the impact of external factors leading to a reduced dielectric response in thin films is needed in order to address these questions. Nevertheless, in both single crystal and thin film at T_d the CM appears near the SM frequency and its mean relaxation frequency dramatically slows down on cooling to T_{VF} . The CM slows down faster in thin film; therefore T_{max} is shifted up. The huge temperature dependence of the CM and its broadening is responsible for the diffuse and frequency dependent maxima of $\epsilon^*(T)$ in both single crystal and thin film. Egami [32] has shown that large displacements of Pb ions play the main role in creation of the local dipole moment in nanoclusters below T_d . Therefore we can roughly assign our CM to strongly anharmonic hopping of Pb ions.

From the fit to our FTIR spectra the CM has the highest dielectric strength $\Delta\epsilon_{CM}$ at 400 K. At lower temperatures its frequency lies below our frequency range (see the dashed line in figure 3); therefore $\Delta\epsilon_{CM}$ apparently decreases on cooling, although it should reach a maximum at T_{max} . Yet another broad excitation remains at the low frequency end of our FTIR spectra down to 20 K where its loss maximum stabilizes near $\omega_{CM}^2/\gamma_{CM} = 20 \text{ cm}^{-1}$. A possible assignment could be to the activation of low energy phonons from the entire Brillouin zone (in this case phonons from the acoustic branches) as a consequence of breaking of the translation symmetry due to compositional disorder at the perovskite B sites and/or a locally doubled unit cell in chemical clusters.

Vakhrushev and Shapiro [33] reported that not the TO1 SM but another quasi-optic mode near 3.5 meV exhibits softening on cooling to T_d . Their results are not generally accepted because other authors [15] have seen softening of the TO1 mode. Nevertheless, it is true that the temperature behaviour of the SM does not explain the Curie–Weiss behaviour of the static permittivity above T_d [16] and another soft polar phonon or relaxation is needed. If the CM existed above T_d , it could not be connected with the polar clusters. Anyway, its intensity, if any, should be very low or its frequency should lie at lower values, because we did not observe this additional mode in FTIR spectra.

Next we may comment on the behaviour of the TO1 mode and its apparent contradiction with previous reports from using neutron scattering techniques. From the results discussed herein, we suggest a plausible explanation for the discrepancy between the SM mode observed by INS and FTIR techniques. INS spectroscopy has a lower energy and q resolution than FTIR spectroscopy; therefore INS spectroscopy may not resolve the splitting of the SM below T_d into SM and CM, as is seen in figure 2. It ‘sees’ only one excitation, which apparently becomes overdamped below T_d . Only below T_c does the CM slow down so much that the SM response is no longer overlapped by the CM and therefore the SM reappears in the INS spectra.

Our suggestions can be supported by simulation of INS spectra from our $\epsilon''(\omega)$ spectra. INS spectra $I(\omega)$ are proportional to $(1+n)\epsilon''(\omega)$, where $n = 1/(\exp(\hbar\omega/kT) - 1)$ is the Bose–Einstein factor. The convolution with the instrumental resolution function of the neutron spectrometer causes additional enhancement of the experimental intensity at low (<3 meV) frequencies, which is not taken into account. Nevertheless, the simulated $I(\omega)$ spectra plotted at several temperatures in figure 6 support our idea. A clear phonon peak is seen near 7 meV at 900 K, but this peak is overlapped with the CM at lower temperatures. The TO1 phonon clearly appears again at 20 K near 11 meV. Figure 6 can be compared with experimental data, e.g. figure 3 in [15], where it is clearly seen that the intensity of the SM in the INS spectra is much lower than the total INS intensity at 500 K, where only the CM was distinguished.

We can also explain why the waterfall effect appears at different wavevectors q_{WF} in different Brillouin zones [17]. The central peak is most intense at the Γ point of the Brillouin

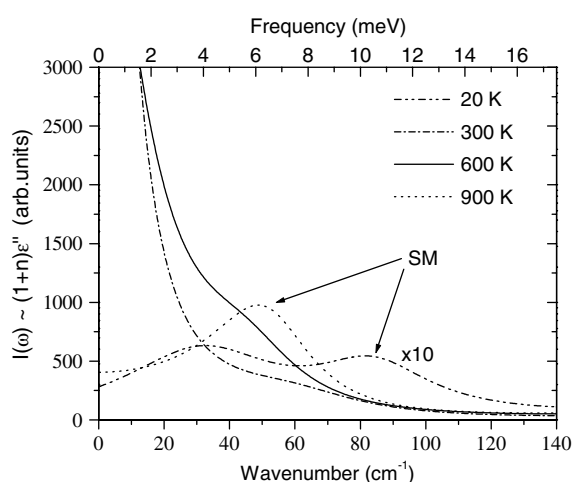


Figure 6. Theoretically calculated inelastic neutron scattering spectra at selected temperatures. The signal is very small at 20 K; therefore it was multiplied by 10. Note that experimental INS spectra are frequently presented only above 3 meV.

zone and distinctly loses its intensity with increasing wavevector. Above q_{WF} the central peak could be so weak that the TO1 phonon branch appears in the INS spectra. The central peak in INS spectra appears remarkably stronger in the 020 Brillouin zone than in the 030 zone [17], so also q_{WF} in the 020 zone is larger than in the 030 zone.

4. Conclusion

It was shown that the polar phonon behaviour appears the same in FTIR spectra of PMN single crystal and thin film so the possible strain and defects in the thin film have no appreciable influence on polar phonons. However, the low frequency dielectric response in the thin film is much reduced compared with that for single crystals, which should be assigned to differences in the polar cluster dynamics or, in other words, in CM behaviour. In contrast to INS data, FTIR spectra of PMN revealed an underdamped SM at all temperatures between 20 and 900 K. The SM frequency, which softens only partially, obeys the Cochran law up to 450 K, then levels off near 50 cm^{-1} and slightly hardens above 650 K. An overdamped CM appears in the FTIR spectra below the Burns temperature and slows down to the MW and lower frequency range on cooling. Its temperature behaviour was directly investigated by high frequency and MW dielectric spectroscopy down to 100 K. It is suggested that the waterfall effect in INS spectra can be explained by overlapping of the SM response with the CM response, which causes apparent overdamping of the SM in INS spectra. A new heavily damped excitation near 20 cm^{-1} appears in the FTIR spectra below $\sim 200 \text{ K}$, probably due to the activation of some short wavelength phonons as a consequence of breaking of the translation symmetry in the B-site disordered PMN.

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