Dynamics of polar clusters in relaxor ferroelectrics

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Abstract. The paper brings results of far infrared transmission studies of relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ and $PbSc_{1/2}Ta_{1/2}O_3$ thin films performed at temperatures between 10 K and 900 K. The spectra clearly show that the lowest-frequency polar optic phonon softens (partially) neither towards the temperature of dielectric-constant maxima, nor towards the freezing temperature, but towards the Burns temperature. This indicates that it represents the ferroelectric soft mode inside the polar clusters. The dielectric relaxation, which expresses the dynamics (flipping and breathing) of polar clusters, appears in THz range below the Burns temperature. This relaxation dramatically slows down to sub-Hertz region on cooling to freezing temperature near 200 K (in PMN) or to T_c (in PST). Another heavily damped excitation remains in the spectra below 30 cm^{-1} down to 10 K. This mode was assigned to the E component of the split F_{1u} soft mode.

1. INTRODUCTION

Ferroelectric relaxors, in particular complex perovskites with the general formula $PbB'_{1/3}B''_{2/3}O_3$ and $PbB'_{1/2}B''_{1/2}O_3$, are of great interest due to their excellent dielectric, electrostrictive, and pyroelectric properties [1,2]. Nowadays it is generally accepted that the strong dielectric dispersion, which in relaxor ferroelectrics (RFEs) occurs in the broad spectral range from GHz to mHz range at temperatures around and below that of permittivity maximum T_m, is a consequence of the dynamics of polar nanoclusters, which appear several hundred degrees above T_m at the Burns temperature T_d [3]. Dynamics of polar clusters was studied predominantly at low frequencies below 1 MHz at temperatures near T_m. 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. 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.

We will discuss here two model representatives of the RFEs, lead magnesium niobate $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and lead scandium tantalate $PbSc_{1/2}Ta_{1/2}O_3$ (PST). No ferroelectric (FE) phase transition occurs in PMN without bias electric field, while PST exhibits a spontaneous FE transition. Its temperature depends on the ordering of B-site ions (Sc and Ta). Disordered PST undergoes FE transition at $T_c \sim 270$ K, while T_c of the ordered sample appears near 300 K without typical relaxor behavior above T_c [4,5].

Lattice dynamics of PMN was studied in detail by means of inelastic neutron scattering (INS). Naberezhnov et al.[6] observed a low-frequency transverse optic phonon branch TO1 which softens on cooling to $T_d \cong 620$ K. Below T_d the softening ceased and a strong central peak appeared. Gehring et al. [7] revealed that below T_d the TO1 branch dived into the transverse acoustic branch at a specific wave vector $q_{WF} \sim 0.20$ Å and no TO1 phonon could be resolved in the INS spectra at lower q. Gehring et al. named this effect "waterfall" and correlated the value of q_{WF} with the size of polar clusters. According to their arguments, when the wavelength of the TO1 phonon becomes comparable to the size of polar clusters, the phonon cannot propagate and thus becomes overdamped. The waterfall effect

is specific not only for PMN, it was observed also in other relaxors or relaxor based mixed crystals like PZN, PZN-PT and PMN-PT [8]. Hlinka et al. [9] repeated the INS measurements of PZN-PT and revealed different q_{WF} in different Brillouin zones. Therefore, they claimed that the waterfall effect is not correlated with the size of polar clusters but it could be explained as 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 structure factors in different Brillouin zones.

Wakimoto et al. [10] revealed that the soft TO1 mode recovers (i.e. underdamps) in the INS spectra below 220 K and its frequency ω_{SM} hardens according to the Cochran law

$$\omega_{SM} = A\sqrt{T_d - T} \tag{1}$$

on decreasing temperature T. This result was somewhat surprising because such a behaviour is typical for displacive FE transitions below T_c, but PMN remains paraelectric down to He temperatures. It means that the soft mode (SM) behaviour provides evidence for the FE order in polar clusters. On the other hand, it is interesting to note that 220 K coincides with the FE phase-transition temperature in PMN cooled under electrical bias field. The question remains, how does the TO1 zone centre SM behave between the freezing temperature T_f (or T_c) and T_d, where it is not resolved in the INS spectra? Direct experimental data are missing, which was motivation for our infrared (IR) studies in the broad temperature range, because the SM should be IR active.

Recently, we have investigated the IR reflectivity spectra of PMN single crystal and observed at all temperatures below 300 K an underdamped SM which obeyed the Cochran law [11]. Unfortunately we were not able to evaluate unambiguously the IR spectra above room temperature, because the reflection band from the SM overlaps with that of the lower-frequency central mode (CM). Therefore we decided to perform more sensitive IR transmission measurements on a thin PMN film. The same type of experiment we did also with several PST films of different B-site order.

2. EXPERIMENTAL

PMN and PST thin films (thickness about 500 nm) were prepared by chemical solution deposition on sapphire substrates (thickness 490 µm), which are transparent in the far IR range. The films were polycrystalline with the grain size about 60 nm. Details about the films preparation and their characterization can be found elsewhere [12]. IR transmission spectra were taken using a FTIR spectrometer Bruker IFS 113v at temperatures between 20 and 900 K with the resolution of $0.5\,cm^{-1}$. A He-cooled Si bolometer operating at 1.5 K was used as a detector. The spectra of a bare substrate and of the PMN film on the substrate were determined for each temperature studied. The transmission spectrum of the bare substrate was first fitted with a sum of harmonic oscillators using Fresnel formulae for coherent transmission of a plane-parallel slab. The resulting fitted sapphire parameters were then used for the fit of the PMN/sapphire two-layer system.

3. RESULTS AND DISCUSSION

IR transmission spectra of PMN thin film are show at selected temperatures in Figure 1. Dense oscillations in the spectra are due to interferences in the substrate, while broad minima correspond to frequencies of polar phonons in the film. The transmission decreases on heating, mainly due to the increase in multi-phonon absorption of the sapphire substrate. The complex dielectric spectra $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ of PMN calculated from the fit of the IR transmission spectra of PMN/sapphire are shown in Figure 2. It is seen that the phonons contribute to the static permittivity by less than 300, but because the experimental low-frequency permittivity is one to two orders of magnitude higher [11], it shows that some microwave or lower-frequency relaxation is responsible for the high permittivity in RFE. The frequencies of dielectric loss ε'' maxima correspond to the mode frequencies. Their temperature dependences are
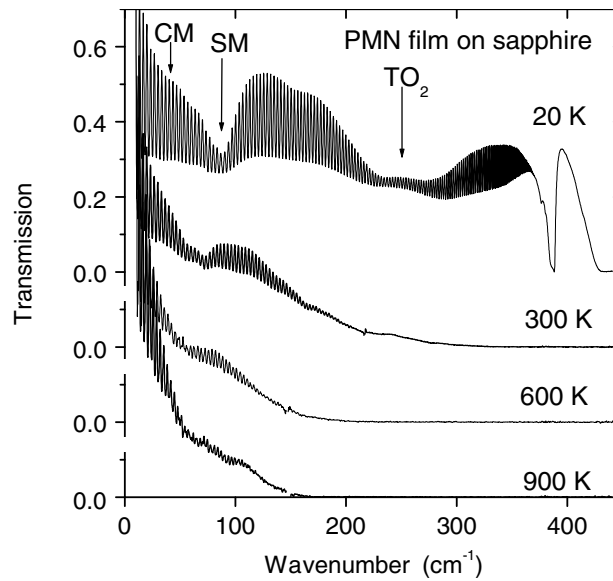
Figure 1. Far IR transmission spectra of the PMN thin film on a sapphire substrate. Frequencies of the central mode (CM), TO1 soft mode (SM) and TO2 phonon are marked. Transmission minimum near $380\,cm^{-1}$ corresponds to the phonon frequency of the substrate.
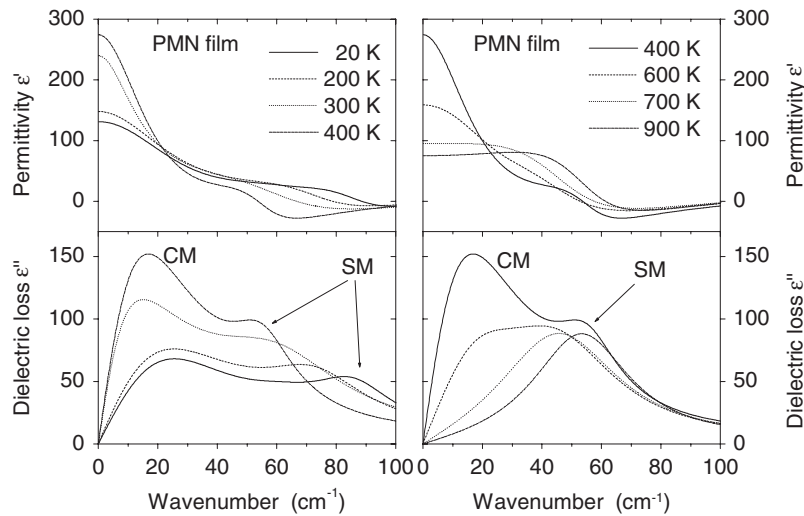

Figure 2. Complex dielectric spectra of PMN thin film obtained from the fit of the IR transmission.

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 with the extrapolated critical temperature $T_d = (671 \pm 10)\,K$ and Cochran constant $A = (11.9 \pm 0.2)\,K^{-1}$. T_d temperature is close to the Burns temperature 620 K reported for PMN single crystals, therefore we believe that we really see the ferroelectric SM in polar clusters. We note that the SM frequency in the thin PMN film agrees with that in the bulk crystal obtained by means of IR reflectivity below 300 K. The same frequencies were seen also in INS spectra [10] below 220 K and above T_d, they are plotted also in Figure 3. It shows that the SM parameters are not appreciably influenced by possible strain or size effect in thin films.
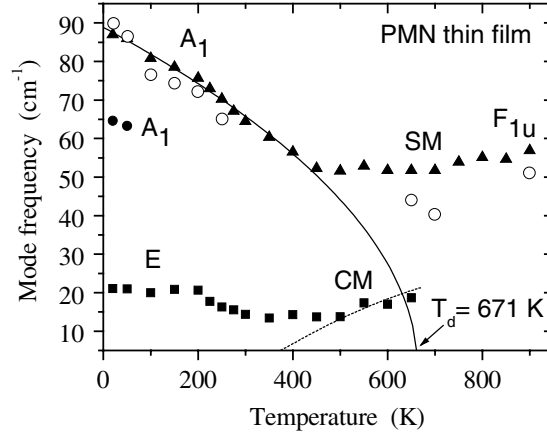
Figure 3. Temperature dependences of the mode frequencies below $100\,cm^{-1}$. Solid and open points mark modes from IR transmission and INS[10] spectra, respectively. CM is overdamped, therfore the frequency of loss maximum corresponding to $\omega^2_{CM}/\gamma_{CM}$ is plotted. The Cochran fit of the SM is shown by the solid line, slowing down of the CM is schematically shown by the dashed line.

A new heavily damped excitation arises in the spectra below T_d near $25\,cm^{-1}$ and its frequency decreases on cooling. We believe that this mode originates from the dynamics of polar clusters, therefore we call it CM in analogy with the scattering experiments. CM frequency rapidly slows down to lower frequency range and obeys the Vogel-Fulcher law with the freezing temperature T_f near $200\,K$ [11]. This mode and its anomalous broadening on cooling is responsible for the RFE behaviour near T_m. Its detail temperature behaviour was described in Ref. 11. Nevertheless, another overdamped mode remains in the far IR spectra near $20\,cm^{-1}$ down to He temperatures. Its origin is under debate. It could be explained by activation of the acoustic phonon branches due to the local unit cell doubling or translation symmetry breaking, but, more probably, it can be just the low-frequency component of the split SM. The SM is triply degenerate above T_d (symmetry F_{1u}), but in the polar phase or in polar clusters below T_d it should split into the stiffer A_1 component, which hardens according to Cochran law on cooling, and the softer E component, which may remain at low frequencies.

It is important to note that the damping of the A_1 component 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 investigated temperature range, in contradiction with the INS spectra where overdamped SM was seen between $220\,K$ and T_d (therefore there are no open circles between these temperatures in Figure 3). The discrepancy between the SM damping observed by INS and IR techniques can be understood as follows. INS spectroscopy has a lower energy and q resolution than IR spectroscopy, therefore INS spectra may not resolve the splitting of the SM below T_d into SM and CM, as it is seen in Figure 2. It sees only one excitation, which apparently becomes overdamped below T_d. Below $220\,K$ the CM slows down so strongly that the SM response is no longer overlapped with the CM and therefore the SM re-appears in the INS spectra. However, INS experiments indicate that the CM is quasistatic with the frequency less than $0.1\,\mu eV$ 13,14 ($0.3\,GHz$), which does not correspond to our IR results neither to dielectric spectra 11 in the microwave range. One can argue that this discrepancy can be explained by the different q vectors probed in IR (dielectric) spectra and neutron experiments. The IR probe couples with very long-wavelength phonons ($q \approx 10^{-5}\,Å^{-1}$), whereas the INS spectroscopy has much lower q resolution ($q \geq 10^{-2}\,Å^{-1}$) and therefore the signal is integrated from much larger q space. It would mean that the SM damping and/or CM width are very strongly q dependent near centre of Brillouin zone, which is not very realistic. But dielectric dispersion in THz and microwave range is most probably caused by

breathing of polar clusters, i.e. by vibrations of cluster walls. If we assume that the cluster walls have the same thickness as ferroelectric domain walls, i.e. in units of lattice parameter, the volume of cluster walls is small compared with the total volume. Therefore vibrations of cluster walls may not contribute strongly to INS spectra and the CM seen in dielectric spectra is not appreciated in the INS spectra.

Let us briefly mention the results of IR transmission of 78% ordered PST thin film (see Figure 4a). IR transmission spectra and their temperature dependence are qualitatively very similar to the PMN film. The phonons have somewhat lower damping in PST than in PMN, presumably due to higher order in the B sites. It allows to see a well pronounced splitting of the SM in the FE phase. Temperature dependences of the polar mode frequencies are plotted in Figure 4b. Again a new overdamped excitation (CM) appears near $30\,cm^{-1}$ below $T_d = 700\,K$. It softens to T_c(its temperature dependence was studied in detail in the microwave and MHz frequency range in Refs. 15,16), but still a heavily damped mode remains near $30\,cm^{-1}$ down to He temperatures. We note that the mode parameters correspond very well to parameters obtained from the bulk IR reflectivity spectra [17]. It again indicates that the phonon parameters are not influenced by strain or size effect in our thin film. Comparison of our spectra with Raman scattering data allowed us to assign the modes seen in IR spectra. The mode near $80\,cm^{-1}$ corresponds to the A_1 component of the F_{1u} SM. The mode near $60\,cm^{-1}$ is not only IR active but also strongly Raman active, therefore it is probably the A_1 component of F_{2g} mode seen above T_c in Raman spectra. The higher-frequency A_1 mode near $80\,cm^{-1}$ follows the Cochran law with T_d near $700\,K$. Because the mode near $60\,cm^{-1}$ has the same symmetry A_1, both modes are bilinearly coupled which results in partial softening also of the lower-frequency mode due to the mode repulsion. The mode near $30\,cm^{-1}$ can be assigned (as well as in PMN) to the E component of the polar SM (of F_{1u}symmetry in the paraelectric phase). This mode should remain IR active up to $T_d \approx 700\,K$ due to the dielectric anisotropy in polar clusters, but it is probably overlapped by the CM at temperatures between T_c and T_d.
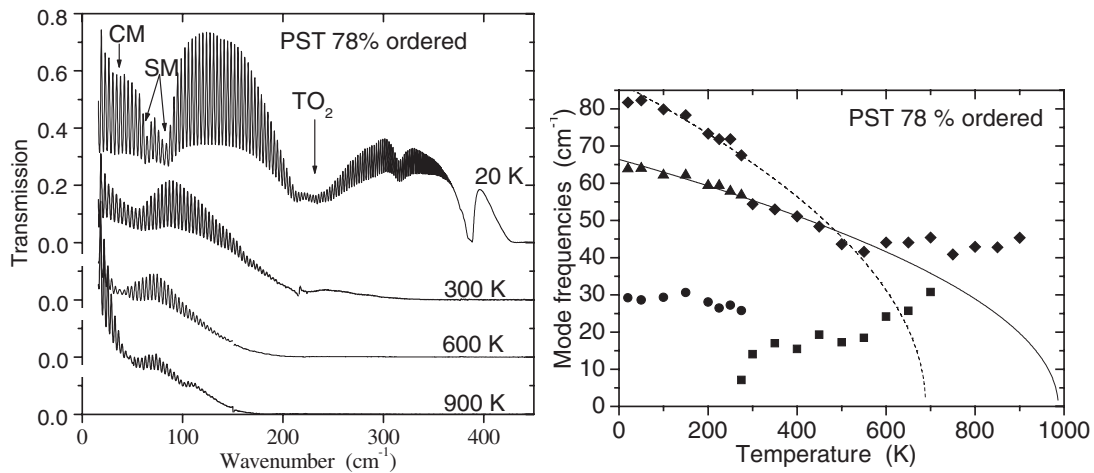

Figure 4. (a) IR transmission spectra of the PST thin film (500 nm thick) deposited on sapphire substrate (thickness 490 μm). (b) Temperature dependences of the polar mode frequencies in 78% ordered PST film. Two kinds of the Cochran fit of the SM are discussed in the text.

4. CONCLUSIONS

Our IR transmission spectra of PMN and PST thin films show qualitatively the same behaviour: soft TO_1 phonon of the F_{1u} symmetry in the cubic phase splits on cooling below the Burns temperature. Its A_1 component hardens and follows the Cochran law with the extrapolated critical temperature near the Burns temperature. The low-frequency E component is clearly seen at low temperatures, but it should remain

active up to T_d, where it is screened by the overdamped CM of comparable frequency. CM stemming from dynamics of polar clusters, appears below the Burns temperature and slows rapidly down to T_c or T_f. This behaviour appears general for the perovskite relaxor ferroelectrics.

Acknowledgments

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