Anisotropic Dielectric Function in Polar Nanoregions of Relaxor Ferroelectrics

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The Letter suggests treating the infrared reflectivity spectra of single crystal perovskite relaxors as fine-grained ferroelectric ceramics: locally frozen polarization makes the dielectric function strongly anisotropic in the phonon frequency range and the random orientation of the polarization at nanoscopic scale requires taking into account the inhomogeneous depolarization field. Employing a simple effective medium approximation (the Bruggeman symmetrical formula) turns out to be sufficient for reproducing all principal features of room temperature reflectivity of $Pb(Mg_{1/3}Nb_{2/3})O_3$. One of the reflectivity bands is identified as a geometrical resonance entirely related to the nanoscale polarization inhomogeneity. The approach provides a general guide for systematic determination of the polar mode frequencies split by the inhomogeneous polarization at the nanometer scale.

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In recent years, there has been enormous effort in studying single crystals with intrinsic nanoscopic inhomogeneity, since such materials often show very interesting properties. It was even proposed that the clustered, inhomogeneous states encountered, for example, in high-T_c cuprates, colossal magnetoresistive manganites, nickelates, cobaltites, diluted magnetic semiconductors, or ferroelectric relaxors, should be considered as a new paradigm in condensed matter physics [1]. In the case of relaxors, the peculiar dielectric properties of relaxor materials were associated with the presence of small polar clusters—so called polar nanoregions (PNR's)—already in the pioneering work of Burns and Dacol [2]. However, because of their small size and random nature, we still lack a clear understanding of their size distribution, thickness, and roughness of their boundaries, their connectivity, shape anisotropy, distribution of the associated dipolar moments, their fractal self-similarity, their dynamics, and so on. PNR's are often represented as small islands submerged in a nonpolar matrix, possibly appearing and disappearing again in time. On the other hand, the recent piezoelectric scanning microscopy investigations [3] of the surface of $PbTiO_3$-doped relaxors rather invoke a picture of a fine, hierarchical, and essentially static "nanodomain" structure. It strongly suggests that the common perovskite relaxors are actually quite densely filled by quasistatic polar nanoregions, and that the former picture with a prevailing nonpolar matrix can perhaps be appropriate only at high temperatures around the so-called Burns temperature [2,4].

Throughout this Letter we will have in mind common perovskite relaxors like $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Zn_{1/3}Nb_{2/3})O_3$, $Pb(Sc_{1/2}Ta_{1/2})O_3$, $(Pb, La)(Zr, Ti)O_3$, and similar systems. Various experiments show that the dipolar moments in these relaxors are caused mainly by ionic off-center displacements. It is difficult to get reliable information about the directional distribution of these displacements, but the *amplitude* of the relevant ion displacements (e.g., Pb in PMN) is quite well defined [5,6] and it is of the same order as in normal ferroelectrics. We will assume that these local displacements are more or less parallel within each PNR (one would have trouble defining PNR if it were not the case), and that the PNR's are at the time scale of our interest essentially static [7] (i.e., the ions vibrate around their displaced but fixed positions, except perhaps for those at PNR boundaries). Under such conditions, the homogeneous frozen polarization (dipole moment density) P_F can be well defined within each PNR, as well as the locally homogenous dielectric function $\epsilon(\omega)$, describing the contribution of polar vibrations inside a given PNR.

It is obvious that the cubic (and in harmonic approximation isotropic) environment of ions in perovskite structure is broken by their off-center displacements. Since the displacements are aligned within a given PNR, parallel ($\| P_F$) and perpendicular ($\perp P_F$) ionic fluctuations are strongly inequivalent. In fact, it is quite likely that the parallel fluctuations feel a more stiff potential, as in the case of usual ferroelectrics. Within a given PNR, one may thus expect that the ionic contributions make the $\epsilon(\omega)$ tensor strongly anisotropic. For simplicity, we will assume that the anisotropy is uniaxial, so that the $\epsilon(\omega)$ tensor has only two principal components, $\epsilon_\|$ and $\epsilon_\perp$ (parallel and perpendicular to P_F). The aim of this Letter is to demonstrate that infrared (IR) reflectivity spectra of common perovskite relaxors can be rather well understood by taking into account this anisotropy.

In the view of the above considerations, it seems reasonable to analyze the influence of PNR on the polar phonon modes under the following simplifications: (i) PNR's are frozen at phonon frequencies, (ii) the PNR size is much smaller than the IR wavelength, (iii) the volume of the sample is fully covered by PNR's, (iv) the shapes of PNR's are roughly spherical, (v) P_F and $\epsilon(\omega)$ within a given PNR are homogeneous, (vi) $\epsilon(\omega)$ has uniaxial anisotropy (principal axis $\| P_F$), (vii) orientations of principal axes are random, and (viii) all PNR's have the same $\epsilon(\omega)$.

It is known that the reflectivity calculations for the samples with dielectric inhomogeneities (spatial fluctuations of dielectric function) at scales smaller than the wavelength of the probing radiation can be performed within the effective medium approach [8]. In this approach, the medium is fully characterized by a homogeneous (averaged) effective dielectric function, $\epsilon_{\rm eff}$, which could be in principle evaluated directly from the original heterogenous dielectric function. In view of the simplifications already made, it seems sufficient to use here a rough approximation, known as the effective medium approximation (Bruggeman symmetrical formula for binary composites), where $\epsilon_{\rm eff}$ is given by the implicit equation [9]

$$\frac{2}{3}\frac{\epsilon_\perp - \epsilon_{\rm eff}}{\epsilon_\perp + 2\epsilon_{\rm eff}} + \frac{1}{3}\frac{\epsilon_\parallel - \epsilon_{\rm eff}}{\epsilon_\parallel + 2\epsilon_{\rm eff}} = 0. \tag{1}$$

The IR reflectivity of a thick (opaque) sample is then evaluated from the standard formula

$$R = \left|\frac{\sqrt{\epsilon_{\rm eff}} - 1}{\sqrt{\epsilon_{\rm eff}} + 1}\right|^2. \tag{2}$$

As a matter of fact, we exploit here the equivalence [10] of our model with that of a dense random binary composite of spherical particles with isotropic dielectric functions equal to $\epsilon_\parallel$ and $\epsilon_\perp$, and the relative appearance of 1:2 volume ratio [10].

It can be expected that the principal polar modes of PNR's in perovskite relaxors are those originating from the 3 F_{1u} polar modes of the parent cubic structure. The uniaxial anisotropy induced by the frozen polarization split each of these triply degenerate modes in an $\mathrm{A}_1 + \mathrm{E}_1$ pair (we assume a strong anisotropy limit leading to $C_{\infty v}$ symmetry for any $P_{\rm F}$ direction). The principal components of the dielectric tensor can be thus conveniently parameterized assuming the factorized form [11] for the generalized damped harmonic oscillator model:

$$\epsilon_\parallel = \epsilon_{\parallel,\infty}\prod_{j=1}^{3}\frac{(\omega^2_{\mathrm{A_1,LO}j} - \omega^2 - i\omega\gamma_{\mathrm{A_1,LO}j})}{(\omega^2_{\mathrm{A_1,TO}j} - \omega^2 - i\omega\gamma_{\mathrm{A_1,TO}j})}, \tag{3}$$

where $\omega_{\mathrm{A_1,TO}j}$ and $\omega_{\mathrm{A_1,LO}j}$ is, respectively, the transverse and the longitudinal frequency of the jth mode polarized along the local polarization direction, $\gamma_{\mathrm{A_1,TO}j}$ and $\gamma_{\mathrm{A_1,LO}j}$ are the corresponding damping parameters and $\epsilon_{\parallel,\infty}$ is the corresponding component of the high frequency permittivity tensor. The $\epsilon_\perp$ tensor component determined by E_1 modes is defined analogously.

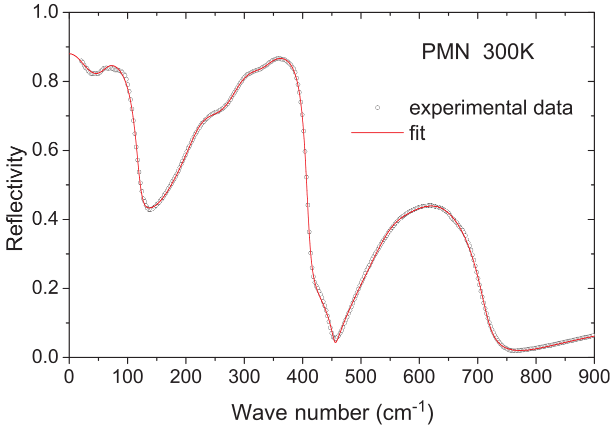

FIG. 1 (color online). IR reflectivity spectra of the PMN single crystal. Circles stand for the room temperature data of Ref. [11] (mistakenly denoted as 20 K there), solid line stands for the fit with the model (1)–(3), parameters are given in Table I.

As an example, let us now apply the model [Eqs. (1)–(3)] to our room temperature reflectivity data of PMN, [11] reproduced in Fig. 1. The real and imaginary part of the resulting effective permittivity is shown in Fig. 2 and it is obviously very similar to that obtained from the standard multioscillator fit technique [11]. Clearly, the three principal bands (below 100, near 220, and at 550 cm^{-1}) correspond to the three TO polar modes of the average cubic structure. Each of these bands has a tail or a bump on the

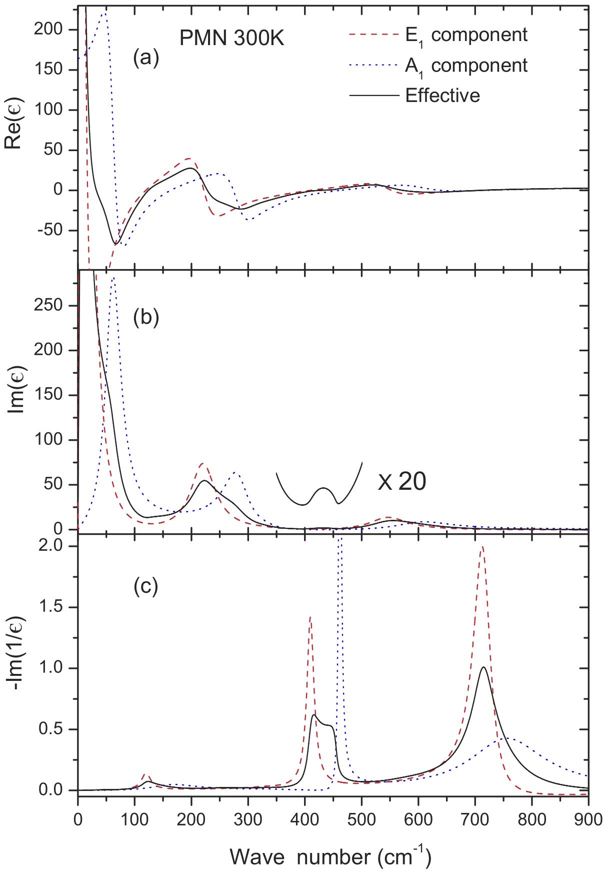

FIG. 2 (color online). Spectra of the real (a) and imaginary (b) part of the permittivity and of the imaginary part of the inverse permittivity (c) calculated from the model defined by Eqs. (1)–(3) with the adjusted parameters given in Table I. Solid line corresponds to the effective macroscopic permittivity $\epsilon_{\rm eff}$, dashed and dotted lines correspond to the $\epsilon_\perp$ and $\epsilon_\parallel$ components of the local permittivity, respectively.

high frequency side. It is natural to assign the principal peaks to the doubly degenerate E_1 components and the high frequency wings to the stiffened A_1 components of the three polar modes. Similarly, the positions of the corresponding three LO bands can be roughly read out from the plot of the imaginary part of the inverse permittivity.

A complete set of mode parameters, as obtained by adjusting the model [Eqs. (1)–(3)] to the measured reflectivity spectrum, is given in Table I. The high frequency dielectric tensor was assumed isotropic, since even in $PbTiO_3$ its two principal components differ by less than 1% [12]. It was set to $\epsilon_{\|,\infty} = \epsilon_{\perp,\infty} = 5.75$, deduced from the available (average) refractive index data of PMN [13]. Furthermore, the visual agreement was much improved by adding a weak mode near 335 cm^{-1} (introduced as identical in both $\epsilon_{\|}$ and $\epsilon_{\perp}$). The agreement is fairly good and the number of the parameters is adequate, except for the frequency of the overdamped E_1(TO1) soft mode, which obviously cannot be reliably determined from data measured above 20 cm^{-1}. The value selected here makes the total phonon contribution to the effective static dielectric permittivity of the order of 1000, which is in qualitative agreement with our previously published analysis [11,14,15]. (There is an additional strong relaxation in the GHz frequency region [14] which is most likely due to the fluctuations of PNR boundaries, but it is not in the focus of this Letter.) All the parameters appear quite realistic—the mode frequencies are reasonably close to that of $PbTiO_3$, given for comparison in Table I, and the trends are in agreement with the smaller frozen polarization [16] in PMN with respect to the spontaneous polarization of $PbTiO_3$.

TABLE I. Intrinsic frequencies and damping parameters (ω, γ) of polar modes of PMN obtained from the fit of the reflectivity spectrum shown in Fig. 1 with the model defined by Eqs. (1)–(3) ($\epsilon_{\|,\infty} = \epsilon_{\perp,\infty} = 5.75$), in comparison with the corresponding mode frequencies of room temperature $PbTiO_3$.

PMN (this work)			$PbTiO_3$ (Ref. [12])	
Label	ω [cm^{-1}]	γ [cm^{-1}]	label	ω [cm^{-1}]
E_1(TO1)	17	34.7	E (TO1)	87.5
E_1(LO1)	120.4	19.8	E (LO1)	128.0
E_1(TO2)	221.4	53.9	E (TO2)	218.5
?(LO)	334.1	56.6		
?(TO)	336.0	54.3		
E_1(LO2)	409.7	15.1	E (LO2)	440.5
E_1(TO3)	545.8	80.5	E (TO3)	505.0
E_1(LO3)	714.6	35.8	E (LO3)	687.0
A_1(TO1)	63.8	32.5	A_1(TO1)	148.5
A_1(LO1)	166.6	95.1	A_1(LO1)	194.0
A_1(TO2)	284.0	53.8	A_1(TO2)	359.5
?(LO)	334.1	56.6		
?(TO)	336.0	54.3		
A_1(LO2)	461.5	4.8	A_1(LO2)	465.0
A_1(TO3)	603.8	117.3	A_1(TO3)	647.0
A_1(LO3)	757.2	160.1	A_1(LO3)	795.0

We do not know for sure the origin of the weak feature near 335 cm^{-1}. In principle, the local homogeneous polarization can induce IR activity also for the E_1 mode derived from the remaining F_{2u} (silent) optic mode. However, the IR dielectric strength of this mode in usual ferroelectric perovskites is known to be extremely weak [12]. Another possibility is that this spectral feature is related to the random occupancy on (ABO_3) perovskite *B* sites. As a matter of fact, there is also a weak IR active mode expected around this frequency [11] due to the *B* site short range ordering of NaCl-type, which activates the R'_{25} Brillouin zone corner mode of the parent cubic structure (antiparallel vibrations of inequivalent ions at neighboring *B* sites). The strength of this mode is determined by a compromise between its relatively strong intrinsic strength inside of the ideally ordered regions (Born charges at inequivalent *B* sites are quite different) and relatively small degree of this *B* site order. This mode was in fact quite clearly seen in the IR spectra of compounds with a larger degree of *B* site order, like PST and similar systems with 1:1 *B* site stoichiometry [17,18], so that it is perhaps the most likely interpretation.

The imaginary part of effective permittivity [Fig. 2(b)] seems to indicate another weak but clear mode with TO frequency near 400 cm^{-1}. The origin of this mode was a puzzle since realistic calculations [11] show that no TO mode is expected around this frequency. Interestingly, the effective medium model proposed here reproduces this band without assuming any intrinsic TO frequency near 400 cm^{-1}. Such modes, so called geometrical resonances, are actually interfacial modes intimately related to the heterogeneity of the medium, and they are known, for example, from IR spectra of ceramics of anisotropic materials [19]. This purely geometric resonance related to the double reflectivity minimum near 400 cm^{-1} appears to be pronounced due to a relatively large splitting of the LO2 mode in comparison with its damping, and it is a generic feature present in many other relaxor perovskites.

A systematic analyses of IR reflectivity data of other relaxor perovskites as well as of temperature dependences within this model are now in progress. In PMN, the frequency of the A_1(TO1) mode increases on temperature lowering and it is obvious that this mode coincides with that which was denoted soft mode in the previous low temperature IR [11,14,15] and neutron studies [20]. On the contrary, the E_1 component of the TO1 mode seems to remain rather soft in all perovskite relaxors. Actually, it would be extremely helpful to develop an appropriate averaging scheme also for the polar modes in Raman scattering and inelastic neutron scattering spectra, in order to form a solid basis for comparison. For example, it seems to us that Raman bands denoted [21] as A–F could be related to the polar modes A_1(TO1), A_1(LO3), LO1, TO2 + silent, TO3, and LO2 modes, respectively. At the present stage however, a direct quantitative comparison is difficult and could be even misleading.

The present model can be modified in many ways. For example, one may consider an elongation of PNR along the direction of the frozen polarization or to consider the contribution of the residual nonpolar matrix, both possible using the analogical effective medium schemes developed for ceramics [22]. More interestingly, one can hope to incorporate a more realistic information about the geometry of PNR structure within a more sophisticated effective medium approach. At the level of the crude approximation [Eq. (1)], it actually does not matter whether the directions of the frozen polarization are completely random or whether they tend to be oriented preferentially along a family of high symmetry directions (most likely 111 or 100). None of these modifications is expected to have a drastic influence on the intrinsic phonon frequencies as determined here, but it is possible that it may explain the spectra assuming smaller damping parameters.

In conclusion, IR spectroscopy brings evidences of splitting of polar optic modes in perovskite relaxors. We deduce that at phonon frequencies and at the length scale of PNR's, the dielectric function is strongly anisotropic. It is demonstrated on the PMN crystal case that a simple effective medium model can reproduce the average permittivity and reflectivity spectra fairly well. The effective medium approach also explains the pseudo-TO mode near 400 cm^{-1} as a consequence of nanoscopic heterogeneity. It is believed that the model can be used for systematically estimating the frequencies of the three principal polar modes in perovskite relaxors and their A_1–E_1 splitting due to the underlying polarization, provided the reflectivity data are known in a sufficiently broad interval (20–1000 cm^{-1}).

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