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Temperature dependence of E-symmetry phonon–polaritons in $PbTiO_3$

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Abstract. We have studied in the temporal domain E-symmetry phonon–polaritons of $PbTiO_3$ perovskite. Their dependence as a function of temperature is investigated up to the ferroelectric phase transition to cubic symmetry. Knowledge of the behaviour of the two lowest polariton branches allows us to estimate accurately their oscillator strength evolution. The values deduced for the static dielectric constant are in agreement with spectral domain values obtained using the Lyddane–Sachs–Teller relation but not with those from capacitance measurements performed at 1 KHz and 1 MHz.

1. Introduction

Knowledge of the temperature dependences of physical parameters from a material close to phase transitions is very instructive from the viewpoint of describing its structure. In this respect a lattice dynamics behaviour study is of primary concern. In fact, the role played by the two mechanisms generally involved in a structural phase transition, which are of displacive and order–disorder form, has been clarified in the past by their spectroscopic signature in the spectral and/or temporal domain.

The availability of ultrashort laser pulses enables us nowadays directly to drive low-frequency phonon modes coherently, and among them the so-called ferroelectric modes which are known to participate mainly in ferroelectric phase transition mechanisms. Moreover, the use of a transient grating experimental scheme gives direct access to the phonon–polariton region. Knowledge of this dispersive regime, which is typical of polar crystals, enables us to estimate in an easy manner the contribution from the low-frequency modes to the static dielectric constant. Comparison with capacitance techniques for the measurement of the overall dielectric constant can therefore provide precise insight into the vibrational motion contribution taking place at different temperatures.

The case of ferroelectric $PbTiO_3$ is particularly relevant in this context. It has been claimed for a long time that this crystal is a textbook example [1] of a displacive-type phase transition from tetragonal symmetry at room temperature to cubic symmetry at $T_c \simeq 490\,^{\circ}\mathrm{C}$. Moreover, a temperature dependence study [2] of the high-frequency (10^8–10^{10} Hz) clamped dielectric permittivity has confirmed values deduced from the Raman data of Burns and Scott [1]. Nevertheless, several other studies revealed that the situation is more intricate.

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(i) The potential of this crystal is highly anharmonic [3].

(ii) A central mode has been detected by conventional Raman scattering [4] at temperatures close to T_c.

(iii) This relaxational signature is in agreement with older [5] and newer [6] capacitance measurements performed at 1 KHz and 1 MHz.

(iv) The presence of local distortions has been evidenced using x-ray absorption fine-structure measurements [7].

In order to confirm tentatively and to explain these findings, we have investigated in the temporal domain the temperature dependence of the dispersion from E-symmetry phonon–polaritons in $PbTiO_3$ and deduced from a simple model the contributions of the two lowest branches to the static dielectric constant.

The paper is organized as follows. In section 2, we describe the experimental set-up and give rough results on the lattice mode dispersion as a function of temperature. In section 3, we discuss the model that we used to calculate the contribution of the two lowest branches to the static dielectric constant and compare our results with directly measured overall values. Finally in section 4, we present the conclusions of our work.

2. Experiment

2.1. Experimental set-up

The experimental set-up used to drive and detect phonon–polaritons is known as a transient grating scheme. It is characterized by a three-beam geometry. Pulses are issued from a colliding pulse mode-locked laser and amplified in several dye cells. The wavelength of the laser is centred at 620 nm; the temporal pulse width is 50 fs, and the repetition rate is 20 Hz. The useful energy per pump pulse is 1 μJ.

In order to drive true TO modes of E-symmetry, as opposed to quasi-modes, the two-pump-beam mean propagation direction is along the x axis and their polarizations along the y and z axes, respectively. The driven phonon susceptibility tensor element therefore corresponds to the yz (b) component; the phonon–polariton propagation is located in the x–z plane and its polarization along y. The change in the polariton wavevector value q is obtained by tuning the angle between the pump beams. In contrast with the case of symmetric modes, its value is dependent on the anisotropy of the crystal and on its dispersion inside the pump spectral width [8]. The refractive indices that the two pump beams p_1 and p_2 experience, namely n_o (ordinary) and n_e (extraordinary), are different. Therefore, the excited phonon vector q is described by two components $q_\parallel$ and $q_\perp$, respectively, along and perpendicular to the mean direction of propagation of the beams. As the dispersion of $PbTiO_3$ is small, even at wavelengths close to 620 nm, one can write in a first approximation

$$\begin{aligned} cq_\perp &= 2\omega_l \sin(\theta/2) \\ cq_\parallel &= \omega_l[(n_o^2 - \sin^2(\theta/2))^{1/2} - (n_e^2 - \sin^2(\theta/2))^{1/2}] \end{aligned} \tag{1}$$

where θ is the angle between the pump beams, external to the crystal, and ω_l the central frequency of the laser. Neglecting the dispersion in the refractive indices leads to an approximation in the q-value lower than the error performed in its actual measurement, say ± 2 cm^{-1}.

Temporal characteristics of the transient grating are detected via the diffraction, at the Bragg angle, of a probe beam which is focused inside the spot of the pumps. The signal s is measured in a background free direction; it is therefore proportional to the square of the response function of the material under study. This assessment is of prime importance, as it

governs the attribution of the signal Fourier transform (FT) peaks to specific combinations of vibrational frequencies.

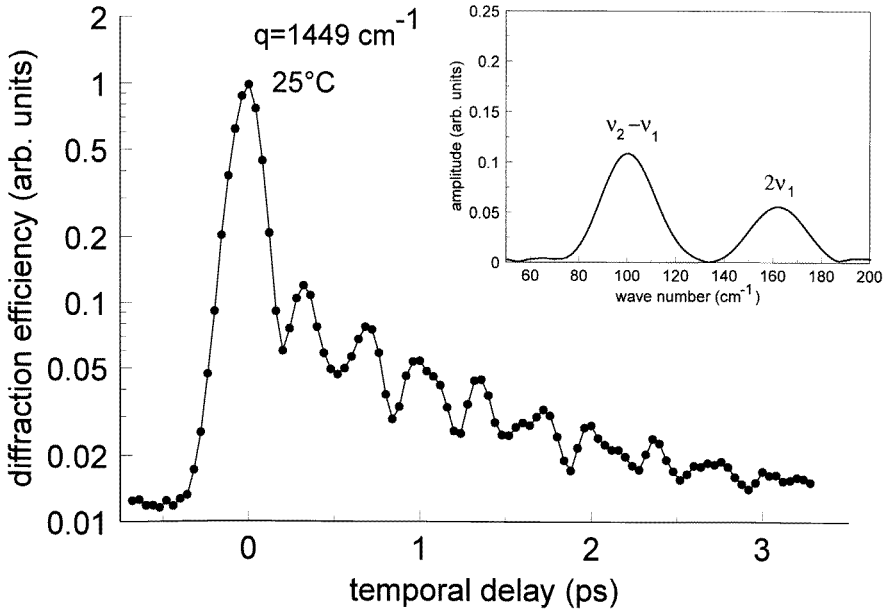

Figure 1. Diffraction efficiency of the signal as a function of time delay between pump and test pulses, at a q-value of 1449 cm^{-1} and 25°C; the inset corresponds to the FT of the temporal signal.

2.2. Experimental results

We performed time-resolved measurements at different temperatures (25, 190, 260, 315, 390, 415, 460 and 500 °C) and wavevector values (482, 1043, 1449, 1891 and 2391 cm^{-1}). We present in figure 1 an example of the time-resolved signal obtained at $q = 1449$ cm^{-1} and 25°C. In all cases studied, the FT curves consist of at least two lines. As previously demonstrated in a study of the polariton behaviour of E-symmetry modes from $PbTiO_3$ at room temperature [9], this is a consequence of the excitation of the two lowest polariton branches of lead titanate.

Attribution of the various peaks to specific combinations of phonon–polariton modes is based on the definition of the response function of the crystal. The most general form can be written as

$$R(t) = \delta(t) + \sum_i A_i \sin(2\pi\nu_i t) \exp\left(\frac{-t}{\tau_i}\right) + \sum_j B_j \exp\left(\frac{-t}{\tau_j}\right) \qquad (2)$$

where ν_i, τ_i and A_i are the frequency, relaxation time and amplitude, respectively, of the i phonon–polariton, and τ_j and B_j are the characteristic time and amplitude, respectively, of the j relaxational mode. Debye relaxation responses are used to describe the possibility in lattice dynamics for ions to be transported from site to site of a given symmetry. They correspond to the order–disorder contribution to the phase transition. Comparable studies on other perovskites, conducted mainly in the spectral domain [10], reported the existence of

complementary relaxational contributions, the temporal counterparts of which were located in the picosecond (or subpicosecond) and the nanosecond regimes.

The FT peak assignments have been made in continuity with [9]. In all cases, the two combinations $\nu_2 - \nu_1$ and $2\nu_1$ are present. Owing to the quadratic nature of the signal, the range of detectivity of processes with a small efficiency is enhanced, compared with a linear signal, by heterodyne interaction with any other more efficient process having close temporal characteristics. No peak has been detected that corresponds to the ν_1 or ν_2 frequency; this means therefore that no relaxational temporal response having a characteristic time located in the picosecond or femtosecond regime is present.

Mode softening takes place for the two vibrational frequencies investigated. The decrease in frequency, on approaching T_c, of the two soft-modes does not behave according to the relation

$$\Omega^2 = A(T - T_c) \tag{3}$$

which is specific to a second-order mechanism. The behaviour is roughly the same at each value of the wavevector studied; mode frequencies drop abruptly to zero at the phase transition temperature, as expected for a first-order mechanism. The E-mode temperature dependence is nevertheless somewhat flatter than that of the A_1 ferroelectric mode [1, 11].

At this stage, the lattice dynamics behaviour of E-symmetry modes is consistent with a displacive character for the phase transition to cubic symmetry.

3. Phonon mode contribution to the dielectric constant

In order to estimate the contribution from the phonons to the evolution of the dielectric constant as a function of temperature, we first discuss the model to be used for a general description of the dielectric function. The frequency dependence of the phonon–polariton response is written in the spectral domain as

$$\varepsilon_{ph}(\Omega) = \sum_i \frac{S_i \omega_{TO_i}^2}{\omega_{TO_i}^2 - \Omega^2 - \mathrm{i}\Omega\gamma_{TO_i}} \tag{4}$$

with the index i indicating a transverse optic mode of frequency ω_{TO_i}, strength S_i and damping γ_{TO_i}. The contribution from Debye relaxational modes is described as

$$\varepsilon_D(\Omega) = \sum_j \frac{S_j}{1 - \mathrm{i}\Omega\tau_j} \tag{5}$$

with S_j and τ_j the strength and characteristic time, respectively, of the mode j. The overall dielectric function is then given by

$$\varepsilon(\Omega) = \varepsilon(\infty)[1 + \varepsilon_{ph}(\Omega) + \varepsilon_D(\Omega)] \tag{6a}$$

and the static dielectric constant as

$$\varepsilon(0) = \varepsilon(\infty)\left[1 + \sum_i S_i + \sum_j S_j\right]. \tag{6b}$$

As we measured the phonon–polariton dispersion, our results are very sensitive to the value of the dielectric constant $\varepsilon(0)$. Therefore, the contribution S of each driven mode to the static dielectric constant can be accurately deduced from an analysis of the phonon–polariton dispersion. As stated by Barker and Loudon [12], the polariton response is given by the function

$$R(q, \Omega) = \mathrm{Im}\left\{\frac{1}{c^2q^2/\Omega^2 - \varepsilon(\Omega)}\right\} \tag{7}$$

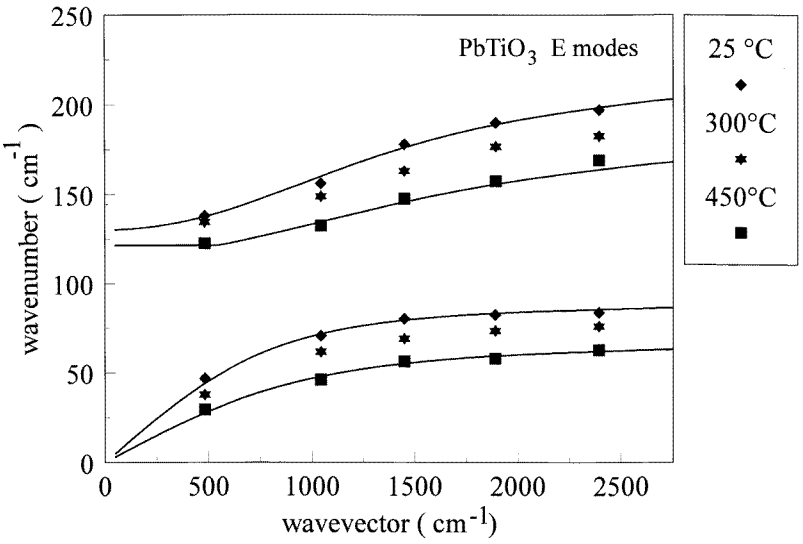

Figure 2. q-function values of phonon–polariton frequencies extrapolated at temperatures for which the dispersion curves have been fitted: ——, results from the fit to equations (4), (6) and (7) for the two extreme cases studied.

the maxima of which give the polariton dispersion.

A fit to the polariton dispersion curves described by equation (7), and using equations (6) and (4), led to measurement of the $\varepsilon(0)$ evolution as a function of temperature until the phase transition to cubic symmetry. In the fitting procedure used to estimate the S_i parameters, values for ω_{TO_1}, γ_{TO_1}, ω_{TO_2}, and γ_{TO_2} are taken from the literature. The third branch cannot be reached in our experiment. Its contribution to the dielectric constant, which is known to be very small, was taken to be a temperature-independent constant term, say $S_3' = 0.3$ [1]. In order to work with the minimal number of unknown parameters, contributions from a relaxational mode and from coupling to either of the phonon modes have not been taken into account as in our previous work at room temperature. Another argument for the use of the simplest model is that we are interested in the temperature evolution of $\varepsilon(0)$, even if the actual value at room temperature is not perfectly described. In figure 2 are plotted some of the frequency polariton values deduced from an analysis of the FT of the temporal response and extrapolated at temperatures at which $\omega_{TO_i}(T)$ and $\gamma_{TO_i}(T)$ are available [1], and the corresponding fitted curves. The resulting S_i oscillator strength values are collected in table 1, together with the values from other calculations [1, 4] and capacitance experimental data at 1 MHz [6].

There is noteworthy agreement between the calculated values deduced from dispersion curve fitting and application of the Lyddane–Sachs–Teller (LST) relation, the differences between the LST values being a consequence of different TO and LO wavenumber attributions. We therefore corroborate that the third polariton branch contribution can be taken as constant and is negligible with respect to the two lower branches. It can also be pointed out that the contribution from the second branch increases significantly with increasing temperature, even if its evolution is weaker than that from the first branch. The lowest-energy branch cannot therefore describe by itself the E-symmetry part of the ferroelectric phase transition.

Table 1. Temperature dependence of oscillator strengths and static dielectric constant. S_1 and S_2-values are fitted from equations (4), (6) and (7); $\varepsilon(0)$-values calculated in this work are obtained using $\varepsilon_\infty = 6.36$ in equation (6); the ε_a (LST) published values have been deduced from the LST relation; the ε_a(exp)-values correspond to clamped measurements [6] at 1 MHz.

T (°C)	S_1	S_2	S_3'	$\varepsilon_\infty(1+\sum S_i)$	ε_a(LST) [1]	ε_a(LST) [4]	ε_a(exp) [6]
25	9.0	4.5	(0.3)	94	111	106	106
100	9.5	4.5	(0.3)	99	126	112	112
200	14.0	5.0	(0.3)	129	144	121	121
300	16	6	(0.3)	148	163	130	130
400	20	7	(0.3)	180	196	160	320
450	30	8	(0.3)	250	246	200	1090

Finally, the temporal study of the polariton dispersion curves fails totally to explain the drastic evolution of $\varepsilon(0)$ close to T_c, as observed by capacitance measurements at 1 MHz frequency by Fontana *et al* [4]. The discrepancy starts at temperatures around 400°C, well below the highest temperatures reached in our experiments. Several points are worth consideration. Fontana *et al* [4] claimed the existence of a central peak, the damping γ_r of which reaches a value of 0.05 cm^{-1} near T_c, i.e. a characteristic time τ_r of 2.2 ns. The process in this temporal range is hardly detectable using femtosecond pulses, as the signal efficiency is proportional to $(1/\tau)^2$. Nevertheless, as explained and demonstrated in the spectral domain by Sokoloff *et al* [10] for $BaTiO_3$and $KNbO_3$, this signal would have a counterpart in the subpicosecond temporal regime, which we have not detected. Such a short time domain would be in agreement with the findings published by Bakker *et al* [13] who used a value of 250 fs for a theoretical description of the central mode in $LiTaO_3$.

4. Conclusion

The low-wave vector regime of phonon–polaritons from $PbTiO_3$ has been examined by coherent excitation and detection in the temporal domain. This paper investigated the temperature dependence of the two lowest E-symmetry mode frequencies. The contributions of these modes to the static dielectric constant up to the ferroelectric phase transition to the cubic phase have been examined in detail. Evaluation of the oscillator strengths allowed us to determine the contributions of the two soft modes to the static dielectric constant. Results agree with previous estimations made using the (LST) relation from spectral domain measurements of LO and TO frequencies.

Nevertheless, the softening character does not permit us to recover the temperature-dependent $\varepsilon(0)$-values obtained by capacitance techniques and also through recent Raman scattering studies which ascertained the presence of a central peak on approaching T_c. No temporal counterpart of this peak (which would correspond to an exponential tail) has been observed in our time-resolved experiments, for which the quadratic nature of the detection scheme allows us to enhance small signals by intrinsic heterodyne interaction with higher-efficiency processes. Several explanations can be tentatively put forward. It is well known that the occurrence of a central peak does not imply Debye-type dispersion. Polarization fluctuations which are visible in Raman spectra at zero frequency can be a consequence of the joint action of a low-lying frequency ω with sufficient weight and of the weighting factor $1/\omega$ accompanying the Boltzmann constant. This hypothesis implies the existence of at least one low-frequency extra-mode. Such a broad resonance has been observed in $LiTaO_3$

[13] by a time-resolved study of phonon–polaritons. Work is in progress to look at this feature for even lower wavevector values by using a one-pump technique. The existence of a Debye relaxator with a weight too small to be seen directly can also be detected indirectly through coupling to oscillatory modes; this would result in a modification of intrinsic oscillator damping [13, 14]. Search for such a coupling requires accurate knowledge of the experimental phonon–polariton damping. Unfortunately the fit of this parameter is quite a complicated problem in our case and is not, at the present, definitely completed. The two driven modes have strongly different behaviours as function of q because the phonon- or light-like character evolutions of the two branches are not the same. The lowest-lying phonon branch behaviour goes from light like at $q \simeq 0$ to phonon like at high q-values; in contrast, the second branch changes from phonon like (LO–TO degeneracy) to phonon like (TO mode), with an intermediate light-like region. So the relative velocity changes can lead to a more or less efficient interference between the two phonon–polaritons and accordingly to a varying modulation of the diffracted signal. These points are the subject of the present research with an ultimate goal of clearly estimating the ability for time-resolved techniques to confirm and even to explain thoroughly spectral domain attainments in the case of intricate lattice dynamics problems.

As is the case for any physical property of a material, its overall characteristics may be divided into contributions from different symmetry subgroups of the crystal space symmetry. For example, in the $KNbO_3$ ($BaTiO_3$) ferroelectric, published data in the spectral [11] and the temporal [15] domains show a heavily damped soft mode for B_2 (E) symmetry, and a relaxational mode for A_1 (A) symmetry; this symmetry-dependent behaviour turns out to be consistent with a specific model of phase transition. For $PbTiO_3$, we have shown that experimental findings, as could be deduced for time-domain experiments, lead to overall identical behaviours from A_1- and E-symmetry lowest-frequency modes. Nevertheless, comparison with clamped dielectric constant values only agree for the A_1-symmetry contribution [11], which corresponds to the dielectric constant ε_c along the ferroelectric axis.

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