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Far-infrared dielectric response of $PbTiO_3$ and $PbZr_{1-x}Ti_xO_3$ thin ferroelectric films

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Abstract. Far-infrared transmittance and reflectance of $PbTiO_3$, $PbZr_{0.53}Ti_{0.47}O_3$ and $PbZr_{0.75}Ti_{0.25}O_3$ thin films deposited by a sol–gel technique on sapphire substrates were measured between room temperature and 650 °C. The spectra were fitted with a classical oscillator model to calculate the dielectric response. Polar-mode parameters are more accurate than data on bulk ceramic materials and are in good agreement with them. An analysis of the soft-mode behaviour and comparison with the low-frequency permittivity data clearly indicate the existence of additional relaxation that is always present in the several cm^{-1} range, even at room temperature.

1. Introduction

The study of far-infrared (FIR) spectra of soft ferroelectric modes has substantially contributed to an understanding of the mechanisms responsible for the existence of ferroelectricity. For high-absorption materials like proper ferroelectrics in the FIR region, only reflectance spectra can be measured on bulk materials [1, 2]. The accuracy of the evaluation of optical constants, in this case, when the reflectivity coefficient is close to one, is strongly limited. This makes it very difficult to study the detailed behaviour of the soft mode. The transmittance and/or reflectance FIR spectroscopy of thin films provides a new possibility of measuring directly and more accurately the parameters of the soft mode and other polar phonons. To our knowledge, there is only one paper [3] on IR spectroscopy of thin ferroelectric films, namely $PbTiO_3$ (PT) on a silicon substrate. It is restricted to room-temperature measurements and does not evaluate the dielectric response. Up until now, there has also only been one paper published [4] on the Raman spectroscopy of thin ferroelectric films of this material where the temperature dependence of soft-mode parameters is discussed.

In this work we have studied FIR properties of thin films of PT, $PbZr_{0.53}Ti_{0.47}O_3$ (PZT-47) and $PbZr_{0.75}Ti_{0.25}O_3$ (PZT-25) using Fourier spectroscopy. We fitted the data with a classical oscillator model to estimate the parameters of the polar phonons and to discuss their temperature behaviour. Our results are compared with data obtained from the literature on bulk materials of the same composition and on the thin films mentioned above.

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2. Experiment and results

Our samples were polycrystalline thin films of $\sim 1\,\mu$m thickness deposited on optically isotropic 0.54 mm thick sapphire substrates with the c axis perpendicular to the substrate plane. The films were prepared by a sol–gel technique [5–7]. The XRD analysis at room temperature proved the tetragonal structure of the PT sample. The nuclear analytic techniques PIXE (particle-induced x-ray emission) and RBS (Rutherford backscattering spectroscopy), and profilometer measurements, were applied to determine the thickness, flatness and homogeneity of our films. Their variation was about 10%. Two different samples for each concentration of Ti and Zr were studied, processed in slightly different ways and/or differing in thickness. Within the limits of our experimental error, the IR-mode parameters were identical for each of these pairs. The temperatures of the transitions from the paraelectric to ferroelectric phase were $T_c \sim 770$ K (PT), $T_c \sim 600$ K (PZT-25) and $T_c \sim 680$ K (PZT-47). At room temperature (RT), the PT sample was tetragonal, the PZT-25 sample was rhombohedral and the PZT-47 sample was a mixture of rhombohedral and tetragonal phases. These results are in good agreement with XRD data on bulk PZT materials.

Transmittance and reflectance spectra in the 30–250 cm^{-1} and 30–3000 cm^{-1} ranges, respectively, were measured using a Bruker spectrometer IFS 113V in the temperature region from RT to 650 °C. The same measurement was done with the sapphire substrate to determine its optical constants, which are necessary for the fitting procedure. The experimental spectra were described using a simple Drude–Lorentz model (sum of classical non-interacting oscillators) for the dielectric function:

$$\epsilon(\omega) = \epsilon_\infty + \sum_{i=1}^{n} \frac{\Delta\epsilon_i \omega_i^2}{\omega_i^2 - \omega^2 + \mathrm{i}\omega\gamma_i} \tag{1}$$

where n is the number of harmonic oscillators, ϵ_∞ is the dielectric constant at high (optical) frequencies, $\Delta\epsilon_i$ is the contribution of the ith mode to the static dielectric constant $\epsilon(0)$, and ω_i and γ_i are the TO frequency and damping of this mode. The full formula including interference fringes was used to calculate reflectance and transmittance coefficients for the measured system comprising the thin film and substrate in the spectral range 30–250 cm^{-1}. The higher-frequency data, where only reflectance measurements could be performed (the substrate is opaque), yielded ambiguous results on the film phonon parameters and we therefore omitted this range in our discussion. Three different measurement techniques were used.

(i) Transmittance spectra measurements of the thin-film–substrate system. An example of this kind of spectrum is given in figure 1. The clearly visible dense interference fringes are due to the interference of the radiation in the substrate. The three broad peaks are caused by phonon absorption in the thin film. The lowest-frequency vibration, which is strongly temperature dependent, is the E-symmetry soft mode. The advantage of this method is the high sensitivity of the measurement to parameters of the soft mode. For example, the frequency of the soft mode can be determined with an experimental error of 0.5 cm^{-1} by this method, which is much better than in the case of the bulk materials.

(ii) Near-normal incidence reflectance spectra of the thin-film–substrate system (figure 2). The same comments as in the previous case are valid. The accuracy of the fit in both methods is illustrated in figure 3 for PT in the E-type soft-mode range. The high-frequency interference shift between measured and fitted spectra is caused by the limited accuracy of the substrate parameters. The two methods described above were used in the temperature range from RT to 250 °C.

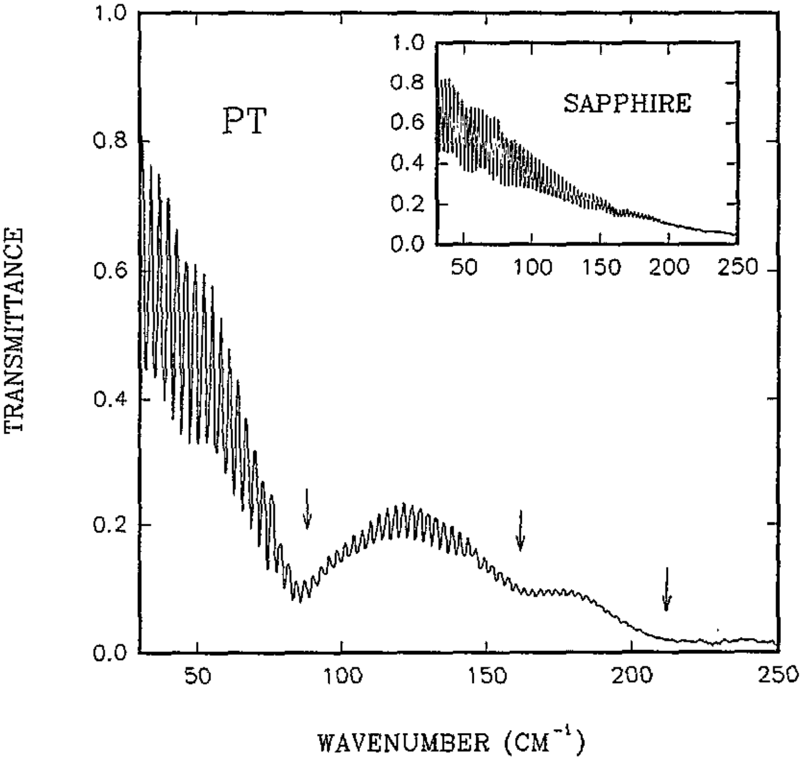

Figure 1. The transmittance spectrum of a PT thin film ($d = 0.47\,\mu m$) on a sapphire substrate at room temperature. Interference fringes in the spectrum are due to radiation interference inside the substrate. The arrows indicate the positions of three thin-film phonons. The insert shows the transmittance spectrum for the substrate without film.

(iii) For higher temperatures, another sample heater of different construction had to be used and an additional difficulty appeared. It was necessary to take into account the influence of the metallic heater surface which was attached to the rear side of the substrate. In this case it was not possible, of course, to measure transmittance, and a more complicated system (thin-film–substrate–vacuum-gap–metal) had to be included in the fitting procedure. The metallic layer was modeled by the Drude formula and its temperature dependence was also considered from measurements of the heater reflectivity without the sample. The power of the given method and the typical spectra which it provides are similar to those presented in (ii). However it is worthwhile mentioning that, because the system became more complex, the accuracy of determining the model parameters decreased.

After finishing the data evaluation it became clear that the polar-mode contribution does not account for the whole value of the low-frequency permittivity. Therefore we completed our measurements by additional transmission measurements in the 8–33 cm^{-1} range using the spectrometer 'Epsilon' based on monochromatic backward-wave-oscillator sources (BWO) [8]. An example of the transmission spectrum (PT at room temperature) in this range is shown in figure 4, together with the fit with and without an additional Debye relaxation of $\omega_r = 7.2\,\mathrm{cm}^{-1}$ (see later).

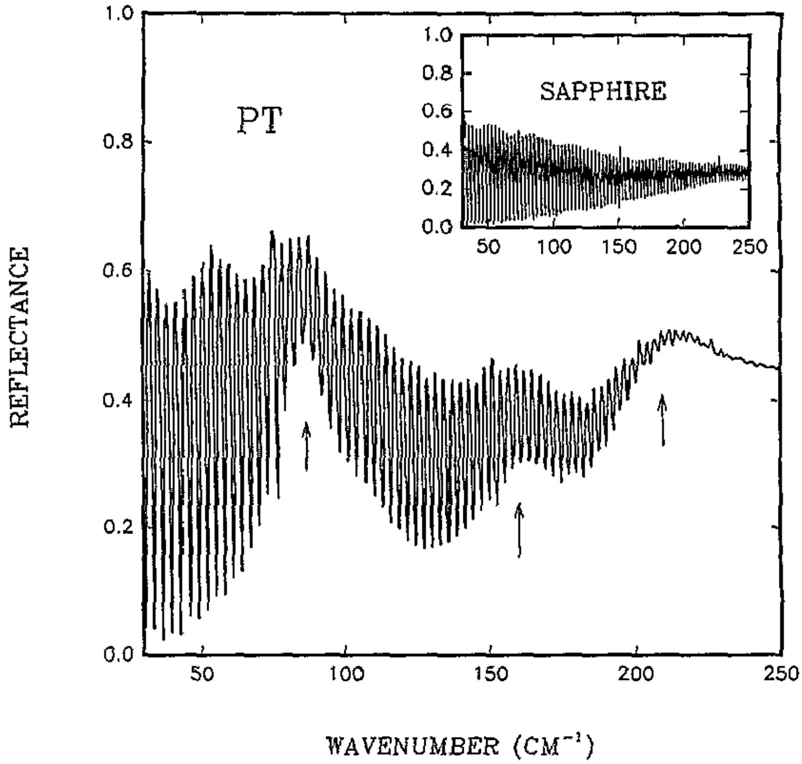

Figure 2. The reflectance spectrum of a PT thin film ($d = 0.47\,\mu m$) on a sapphire substrate at room temperature at nearly normal incidence angle. The arrows indicate the positions of the thin film phonons as in figure 1. The insert shows the same spectrum for the substrate without film. The substrate can be fitted by a single oscillator model with parameters $\omega_0 = 830\,\mathrm{cm}^{-1}$, $\Delta\epsilon = 5.2$, $\gamma = 54.7\,\mathrm{cm}^{-1}$ and $\epsilon_\infty = 3.8$. (Two noise spikes at 150 and 230 cm^{-1} were not considered for evaluation.)

3. Evaluation and discussion

The film phonon parameters determined at RT and 650 °C are given in table 1. Our assignment is based on classic Raman works on PT single crystals [9, 10] where the transverse and longitudinal frequencies of all phonons were evaluated from RT up to T_c (above T_c no mode remains Raman active). It should, however, be noted that whereas the agreement between our data and the Burns–Scott data [9, 10] is good for both observable E modes, our A_1 soft mode is clearly (by 27%) shifted upwards in frequency. Its frequency is temperature independent, its strength is weaker and disappears at higher temperatures. This mode is not observed at all in PZT samples. This strange behaviour has to be explained by the polycrystalline nature of our samples. The polycrystalline film (ceramic) is a mixture of randomly oriented grains with strongly anisotropic dielectric functions (the RT low-frequency permittivity using the Lyddane–Sachs–Teller relation for the E and A_1 modes amounts to ~ 105 and ~ 40, respectively [10]).

Under the assumption of ellipsoidal particles that are much smaller than the radiation wavelength, the dielectric function of such a system can be roughly calculated using the electrostatic effective-medium approximation [11]. For spherical particles the effective dielectric function ϵ_{eff} of a dense uniaxial polycrystal (ceramic) satisfies the equation

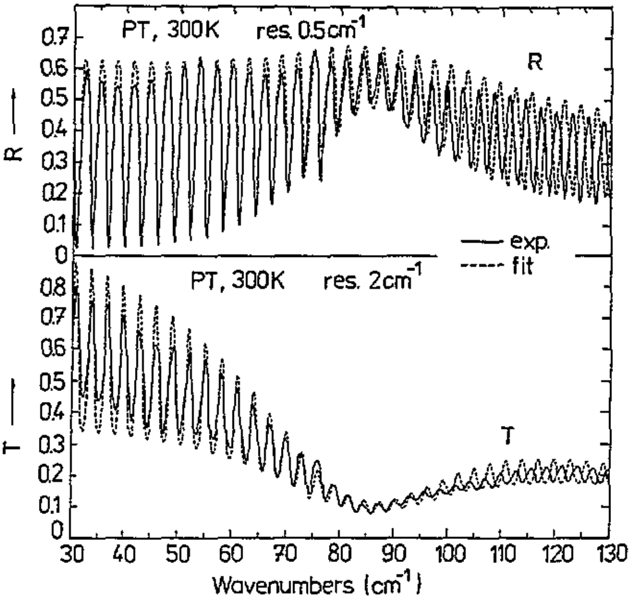

Figure 3. An example of fitting of the reflectance spectra (upper curve) and transmittance spectra (lower curve) of the film–substrate system (PT film, $d = 0.47\ \mu$m).

$$\frac{1}{3}\frac{\epsilon_c - \epsilon_{eff}}{\epsilon_c + 2\epsilon_{eff}} + \frac{2}{3}\frac{\epsilon_a - \epsilon_{eff}}{\epsilon_a + 2\epsilon_{eff}} = 0. \tag{2}$$

The $\epsilon_a(\omega)$ and $\epsilon_c(\omega)$ functions corresponding to the dielectric response perpendicular and parallel to the c axis, respectively, can be approximately taken from Raman data [10] using the three damped harmonic oscillator response (see (1)). The corresponding parameters for PT at RT are listed in table 2. The effective dielectric function calculated from (2) and compared with that determined from our fitted parameters of the PT film is shown in figure 5. The agreement between both functions is by no means perfect; in particular, the shift in the A_1 soft-mode frequency and the difference in the TO2 E-mode strength are pronounced and remain unexplained. However, these differences were also observed in the case of bulk ceramics [2].

Table 1. Low-frequency phonons parameters from the fit.

Mode		RT			650 °C		
		PT	PZT-47	PZT-25	PT	PZT-47	PZT-25
E(TO1)	ω_1	86.4	58.7	59.8	36	39	36
	$\Delta\epsilon_1$	40	87	77	316	72	123
	γ_1	20	54	54	29	31	30
A_1(TO1)	ω_2	161	—	—	—	—	—
	$\Delta\epsilon_2$	4.3	—	—	—	—	—
	γ_2	46	—	—	—	—	—
E(TO2)	ω_3	210	197	200	181	190	195
	$\Delta\epsilon_3$	5.9	13.9	11.1	1.5	1.0	2.6
	γ_3	32	48	36	45	40	37

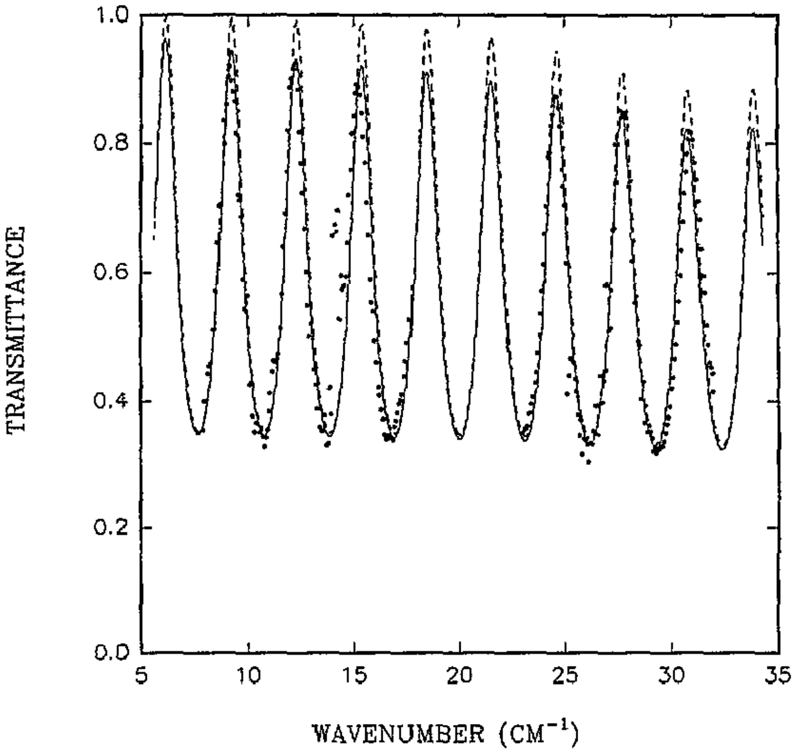

Figure 4. Submillimetre transmission of the PT film at room temperature. ······, experimental data; ——, fit including the relaxation (see table 3); — — —, fit without the relaxation.

The temperature dependence of the E-type soft-mode frequencies in PT, PZT-25 and PZT-47 thin films is shown in figures 6 and 7. The behaviour of PT films is compared, in figure 6, with the frequencies obtained from Raman scattering on bulk PT ceramics [2] and films grown on the Si substrates with a Pt buffer layer [4]. Our data are in good agreement with the results of the early IR and Raman scattering measurements [2] on bulk PT ceramics. There is, however, a clear downward shift in the frequencies of the modes observed in the Raman spectra of PT films [4]. The authors [4] explain this shift by a strain induced from a process of ferroelectric-domain formation. No such effect was observed in our experiments. The temperature dependence of the soft-mode frequency in PZT-25 films (figure 7) also agrees with the data on IR reflectivity of bulk PZT-25 [12]. Concerning PZT-47 (figure 7), to our knowledge no data on IR and Raman scattering spectra for this composition are available. The most striking feature of the soft-mode behaviour is that the softening is very incomplete. The fact that the soft-mode frequency remains finite at T_c may be partly due to the first-order nature of this transition (for PT see the discussion in [10]) and partly due to appearance of an additional low-frequency excitation (central mode).

It is well known [1] that the difference between the values of the low-frequency permittivity and the sum of all optical-mode contributions $\Sigma\Delta\epsilon_i + \epsilon_\infty$ is due to the existence of the central-mode-type dielectric dispersion. The value of $\Sigma\Delta\epsilon_i$ for PT at 550 °C (in the paraelectric phase) is approximately 400, as can be seen in figure 8. The low-frequency dielectric permittivity ϵ_a of the PT single crystals reaches a value nearly ten times higher [13]. The dielectric measurements on thin films of PZT-47 at 10 kHz [14] show that the permittivity at temperatures slightly above T_c is higher than 1.4×10^3. This

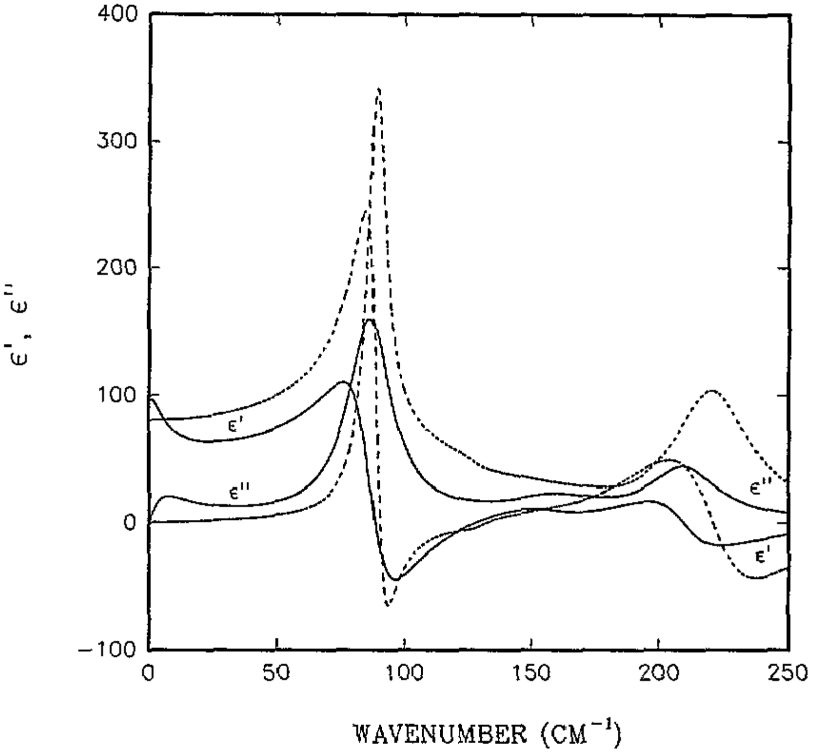

Figure 5. Room-temperature dielectric function of PT from our fit (full curves) and from the effective-medium approximation based on Raman data [10] (broken curves).

Table 2. Polar phonon parameters used for the calculation of the effective dielectric function (from [2, 9]). $\epsilon_\infty = 6.37$.

c response (A_1 modes)			a response (E modes)		
ω_i	$\Delta\epsilon_i$	γ_i	ω_i	$\Delta\epsilon_i$	γ_i
127	28	25	89	65	9
364	4.0	20	221	34	37
651	2.2	30	508	1.7	19

is at least three times higher than the value of $\Sigma\Delta\epsilon_i$, which we obtained by fitting the spectra of the PZT-47 sample (figure 8). The only available information about the low-frequency ϵ_0 of PZT-25 bulk ceramic samples at RT [12] provides a value of $\epsilon_0 \approx 7 \times 10^3$. The value of $\Sigma\Delta\epsilon_i$ obtained in this work for PZT-25 thin films is about six times lower (figure 8). It is seen that the finite value of the soft-mode frequency at T_c (about 30 cm^{-1} for PT and PZT-47 and 15 cm^{-1} for PZT-25) is also caused by the presence of the central mode, as in other proper ferroelectric perovskites [1, 15]. However, for a more quantitative conclusion it would be necessary to measure directly the microwave dielectric dispersion in the paraelectric phase. Corresponding data are, to the authors' knowledge, not known.

The dielectric dispersion up to 10 GHz was measured only in the ferroelectric phase for PZT-40, 48 and 60 by Kersten and Schmidt [16]. These authors found a pronounced relaxation near 1 GHz, which they assigned to a domain wall and morphotropic phase

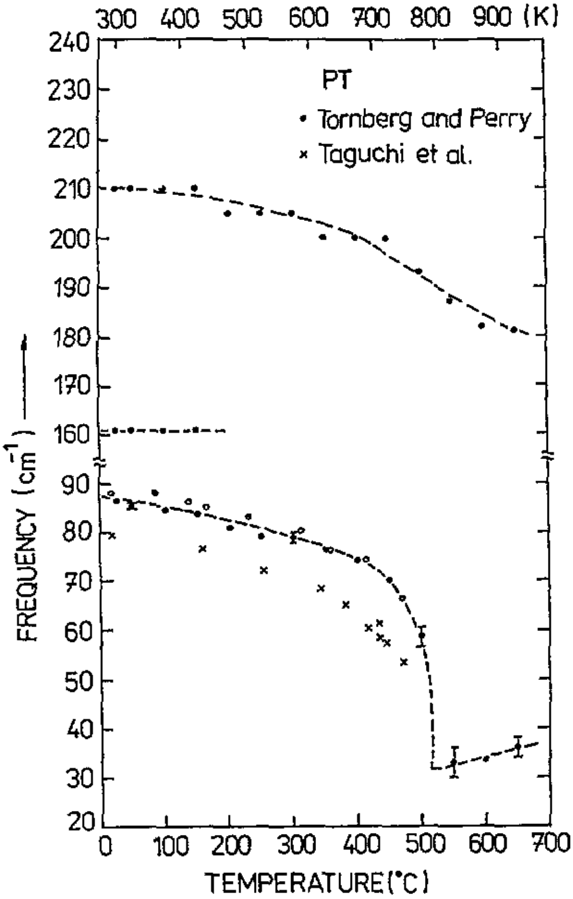

Figure 6. The temperature dependence of the observed phonon frequencies for PT film (*full circles*). *Empty circles represent the* soft E-mode results of Raman scattering in *bulk material; crosses correspond to* Raman data in PT films on Si substrates. The broken curve is to guide the eye (same as in figure 7).

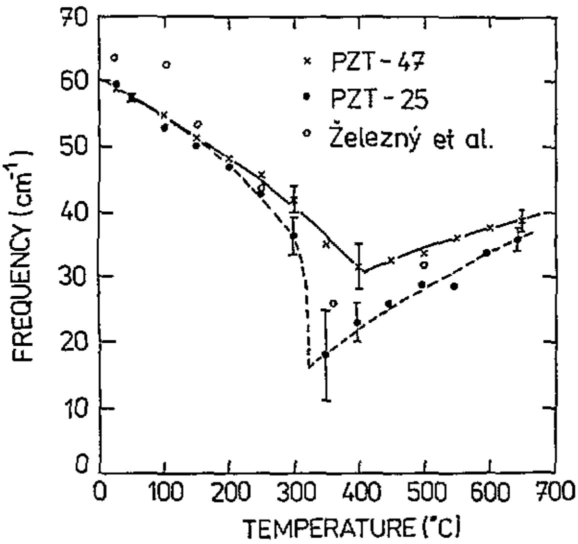

Figure 7. The temperature dependence of the soft E-mode frequency for PZT-25 (full circles) and PZT-47 films (crosses). The empty circles show frequencies in the bulk PZT-25.

boundary fluctuation [16]. However, even above the relaxation frequency, at 10 GHz, the

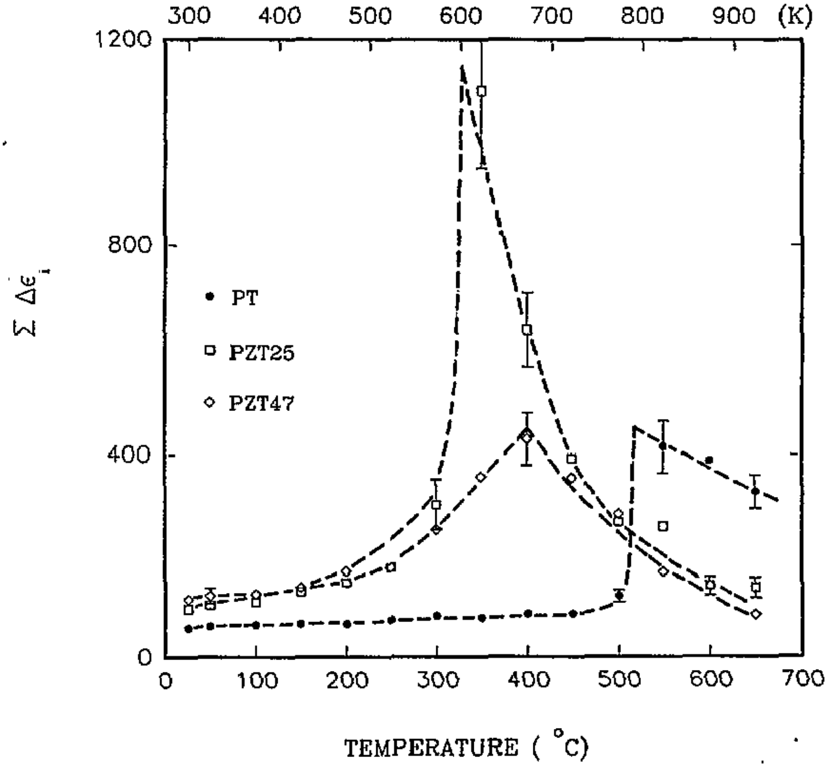

Figure 8. The temperature dependence of the sum of all observed mode contributions. Full circles: PT; squares: PZT-25; diamonds: PZT-47.

permittivity amounted to 200–400, which is definitely higher than our RT low-frequency values. This indicates another dispersion somewhere between 10^{10} and 10^{12} Hz. This motivated us to perform the BWO measurements mentioned above. It turned out that, irrespective of the value of low-frequency permittivity, an additional Debye relaxation with frequency somewhere below 10 cm^{-1} was needed to achieve a good fit to the merged spectra in the 8–250 cm^{-1} range. To determine the parameters of the relaxation unambiguously we would need to include the values of low-frequency (i.e. microwave in our case, to avoid piezoelectric and domain contributions) permittivity into our fit. As these are not known precisely for our samples, the estimated accuracy of the fitted relaxation frequency is limited to about ±10% in the case of PT and ±20% in both other cases. The resulting parameters for PT are shown in table 3 and corresponding dielectric contributions plotted in figure 9. For PZT-47 the relaxation frequency drops to $\sim 5\,cm^{-1}$ and $\Delta\epsilon_r$ increases to ~ 300 at room temperature. For PZT-25 the relaxation frequency is even lower (1–2 cm^{-1}) and $\Delta\epsilon_r$ even higher (~ 1000). However, slightly above $T_c \sim 300\,°C$, $\Delta\epsilon_r$ in our best fit dropped to zero. This seems to be connected with the appreciably lower soft-mode frequency (figure 6) and its corresponding higher dielectric strength (figure 7) than in both remaining samples. To determine more precisely the central-mode parameters would require still lower-frequency measurements.

In view of the microwave data for PZT [16] it seems probable that the microwave dispersion is broad and cannot be described by a single Debye relaxation. This behaviour is typical of relaxor ferroelectrics and dipolar glasses; this behaviour becomes more

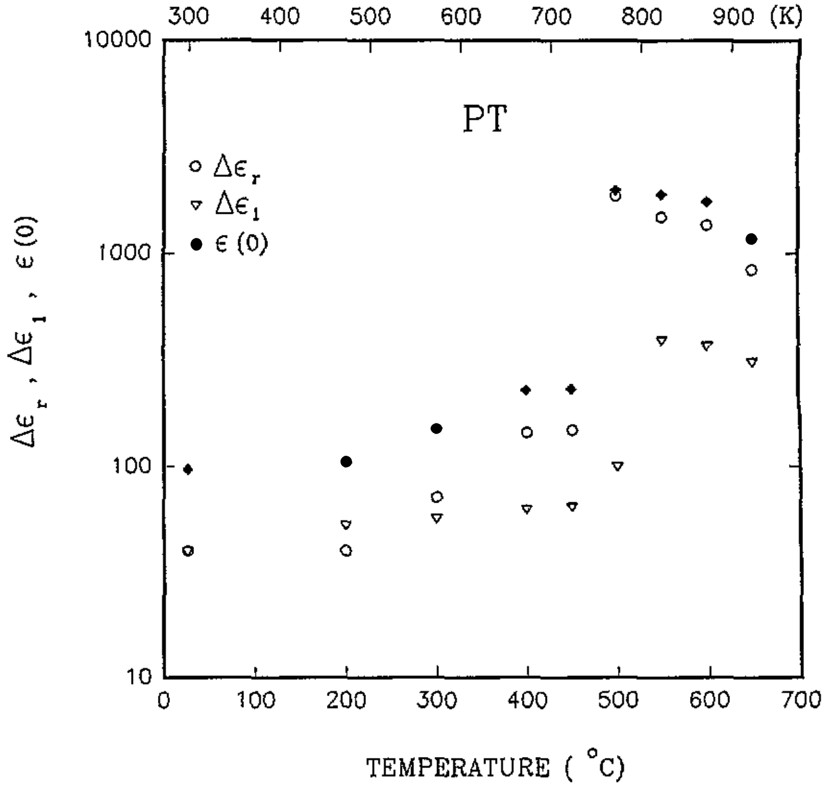

Figure 9. Temperature dependence of the soft-mode ($\Delta\epsilon_1$; triangles) and central-mode ($\Delta\epsilon_r$; circles) dielectric contribution and of total permittivity ($\epsilon(0)$; diamonds) in PT (see also table 3).

Table 3. Temperature dependence of the soft (subscript 1) and central (subscript r) mode parameters in PT. $\epsilon(0)$ is the sum of all mode contributions plus $\epsilon_\infty = 6.4$.

T (°C)	ω_1	γ_1	$\Delta\epsilon_1$	ω_r	$\Delta\epsilon_r$	$\epsilon(0)$
26	86	20	40	7.2	40	97
200	81	22	53	7.2	40	105
300	79	24	57	7.2	71	151
400	74	26	63	7.2	146	230
450	70	27	65	7.2	150	234
500	59	28	101	7.2	1871	1990
550	33	27	400	7.2	1485	1900
600	34	35	376	7.2	1364	1753
650	36	29	316	10	843	1171

pronounced as the ferroelectric phase transition becomes diffusive. In our case the largest diffusivity appears for the PZT-47 sample, presumably also because this composition is a mixture of two ferroelectric phases and a transition from the rhombohedral to tetragonal phase is steeply dependent on the exact Zr–Ti content [17].

Recently Fontana and co-workers [15] reported on the existence of the dynamical central peak from Raman scattering on a single-domain PT crystal. However, their estimate of its characteristic frequency (~ 1 GHz) is about two orders of magnitude below ours, and their central peak seems to appear only above about 300 °C. We note, however, that their central peak is not fully experimentally resolved and their conclusion on the narrow central peak width is based on the assumption that the ratio of the central- and soft-mode strength is the same in Raman and IR spectra. Dropping this not fully justified assumption, even our much higher values for the central-mode width seem not to contradict the Raman data. An alternative possibility would be a different dynamical behaviour of polycrystalline thin films and behaviour of single-domain single crystals, or different manifestations of the central-mode phenomena in light-scattering and IR experiments. However, we have no physical arguments in favour of these latter explanations.

4. Conclusions

It was demonstrated that both transmission and reflection spectroscopy can be successfully used to determine the FIR dielectric response of semitransparent ferroelectric films.

The accuracy of the determination of the soft- and central-mode parameters is higher than can be obtained from reflectivity spectroscopy on bulk proper ferroelectrics.

The soft mode does not account for the total low-frequency permittivity in any of the three compositions investigated (PT, PZT-47, PZT-25).

Central-mode-type dielectric dispersion in the several cm^{-1} range is always present in our samples.

Whereas the phase transition in PT is sharply first order, phase transitions in PZT-25 and PZT-47 show increasing features of diffuseness.

Acknowledgments

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