

Finite Size Effects In Ferroelectric Nanosystems: Absence Of Mode Softening

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ABSTRACT

We present measurements of the mode softening behavior for $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (PZT(50)) thin films using terahertz time domain spectroscopy (TTDS). The films were grown using pulsed laser deposition (PLD) techniques on silicon substrates to study how reduced size affects the mode softening behavior. At room temperature two modes are observed at 1.1 THz (37 cm^{-1}) and at 2.3 THz (77 cm^{-1}). As the temperature is increased toward T_c we do not see strong mode softening, but rather a spectral weight transfer from the high frequency mode to the low frequency mode. This absence of mode softening is more dramatic than that reported by other investigators[1]. We will discuss the possible sources for this discrepancy. These results suggest a change in lattice dynamics for nanoscale ferroelectric films that may be highly dependent on the sample preparation technique.

Keywords: ferroelectric, mode softening, PZT, terahertz.

1 INTRODUCTION

Ferroelectric systems are currently used for DRAM capacitors, nonvolatile memory elements (FRAM), and switching/routing elements in optical communications systems. Further miniaturization and large-scale application of these systems are limited by apparent finite size effects diminishing the dielectric response. These size effects could arise from a variety of phenomena. Material quality considerations such as an amorphous “dead layer” reducing the net thickness of the material, defects dependent on material’s preparation method, and strain effects induced by the substrate. More fundamental limitations may arise from depolarization field effects and fundamental changes in the balance between short range and Coulomb interactions which determine the nature of the structural phase transition itself. For continued incorporation of these materials into “smart” systems, all of these possible causes of degradation in ferroelectric response at reduced dimensions must be addressed in the actual device materials systems.

The structural phase transition for ferroelectrics is accompanied by a peak in the low frequency dielectric response, ϵ_0 . This temperature dependence in ϵ_0 can be

understood through the Lyddane Sachs Teller (LST) relationship:

$$\epsilon_0 / \epsilon_\infty = \prod_i \omega_{\text{LO}i}^2 / \omega_{\text{TO}i}^2 \quad (1)$$

where ϵ_0 , ϵ_∞ , $\omega_{\text{LO}i}$ and $\omega_{\text{TO}i}$ are the DC dielectric constant, the high frequency dielectric constant, the longitudinal optical (LO) phonon frequency and the transverse optical (TO) phonon frequency respectively. Thus the transverse optical mode softening is accompanied by a rapid increase in the DC dielectric response at the transition temperature. However a systematic study on PbTiO_3 nanoparticles for example has shown that the enhancement in ϵ_0 at T_c , decreases with particle size[2].

In an effort to understand the decrease in dielectric response in small systems, several authors have begun to examine if a) the LST relation holds in these reduced-size systems and b) if the mode softening changes with the system size[1, 3]. The dominant commercial ferroelectric material presently is $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZTx). In particular, it is currently the main material used for FRAM production due to its high saturation polarization P_s , practical coercive field E_c and high T_c . These parameters appear to be optimized for $x \sim 0.5$. Fedorov et al. measured the far-infrared (FIR) response of a $1 \mu\text{m}$ thick PZT(47) sol gel film on a sapphire substrate using standard FTIR transmission spectroscopy. They reported the softening of a room temperature mode at 58.7 cm^{-1} to 30 cm^{-1} at T_c . This mode was attributed to the soft transverse optical mode associated with the structural phase transition.

Here we present results on technological grade PZT(50) films on silicon substrates. We find that for a 500 nm film deposited by PLD, the mode softening is nearly absent, in spite of the film being a high quality ferroelectric at room temperature. These results suggest that as the system is reduced to nanoscale dimensions, not only is mode softening suppressed, but the degree of suppression is dependent on substrate and/or preparation technique.

2 EXPERIMENT

The frequency range for studying mode softening, 0.01 – 3.0 THz (0.3-100 cm^{-1}), has long lacked compact sources and cryogenic detection was required. Spectroscopy in the

FIR requires attention to artifacts due to reflections both in the sample and the measurement system. These impediments are responsible for the scarcity of FIR measurements of mode softening.

TTDS systems based on photoconductive materials are used as spectroscopic tools for a characterizing transport in semiconductors, biomolecular studies, and for probing solute-solvent interactions [4, 5]. These systems typically produce broadband picosecond pulses in the 0.03 THz to 3.0 THz region. With coherent detection schemes, signal to noise ratios as high as 10000:1 for a single pulse have been reported [6]. TTDS is ideally suited for studying the low frequency lattice dynamics that play a critical role in ferroelectric materials. Unlike conventional FIR spectroscopy, which is inefficient below 50 cm^{-1} , TTDS can explore phonon mode softening (which approaches zero frequency at the ferroelectric transition temperature T_c) and central modes down to 2 cm^{-1} (0.25 meV). Since TTDS is a coherent spectroscopic technique that measures the magnitude and phase of the transmitted/reflected electric field (rather than the intensity), the real and imaginary part of the dielectric response can be obtained in a single measurement. A further advantage of TTDS over conventional FIR spectroscopy using a bolometric detector is that TTDS is not affected by the thermal background generated by ferroelectric samples that are commonly heated to temperatures commensurate with their T_c (which can be on the order of $500 \text{ }^\circ\text{C}$). Unlike neutron scattering, which relies on single crystal samples, TTDS can be applied to polycrystalline films and nanoparticles. Raman scattering is also an effective tool for studying lattice dynamics in ferroelectrics, but often the modes of interest (e.g., transverse optical mode in PZT) are not Raman active above T_c , and the low frequency excitations are overwhelmed by the strong scattering background in ferroelectric nanoparticle systems.

We use the current transient radiation that is induced by the illumination of a biased photoconductive switch to generate our THz pulses [7]. A Hertzian dipole antenna with a several μm photoconducting gap at the center is fabricated on semi-insulating GaAs. A large DC bias ($\sim 7.5 \text{ kV/cm}$) is applied across the antenna and when carriers are photo-injected into the gap by short-pulsed laser absorption, a current transient is produced, giving rise to an output pulse of broadband low frequency radiation. The radiating field in the far field is given by the time derivative of the current transient.

Coherent detection of the output field transient is accomplished by electro-optic detection. In electro-optic detection the THz field pulse is coincident with a near-infrared (NIR) probe pulse on an electro-optic crystal. The THz field produces birefringence in the crystal causing the linear NIR polarization to rotate. This polarization rotation is proportional to the sampled THz electric field, where the sampling time is given by the NIR detection pulse width (65 fs). A delay stage of the NIR gating pulse is scanned to

map the THz *electric field* pulse in time. For a transmittance measurement of a sample we have:

$$t = \frac{E_{\text{sample}}(\omega)e^{i\phi_{\text{sample}}(\omega)}}{E_{\text{ref}}(\omega)e^{i\phi_{\text{ref}}(\omega)}} = |t|e^{i\phi_t(\omega)} \quad (2)$$

Given that we have both magnitude and phase information, we can extract the real and imaginary parts of the dielectric constant directly. Here an empty aperture is used as the reference. The time scan of the transmitted THz pulse is set to end before the secondary peak due to reflection within the substrate arrives, thus we do not include etalon for the substrate. However etalon in the ferroelectric film must be included and the real and imaginary parts of the film's dielectric constant are extracted using:

$$t = \frac{t_{af}t_{fs}t_{sa}e^{-2\pi\nu k_f d}e^{i2\pi\nu(n_f-1)d_f}e^{i2\pi\nu(n_s-1)d_s}}{1 - r_{fa}r_{fs}e^{-4\pi\nu k_f d}e^{i4\pi\nu n_f d}} \quad (3)$$

$$t_{ij} = \frac{2\tilde{n}_i}{\tilde{n}_i + \tilde{n}_j} \quad r_{ij} = \frac{\tilde{n}_i - \tilde{n}_j}{\tilde{n}_i + \tilde{n}_j} \quad (4)$$

where t_{ij} and r_{ij} are the Fresnel coefficients for the ij -interface, and \tilde{n}_i (\tilde{n}_j) is the complex index of refraction on the incident (transmitted) side of the interface. The optical interfaces consists of: air, ferroelectric film, substrate, and air are indicated by subscripts f , s , and a respectively. The complex indices of refraction for the film and substrate are

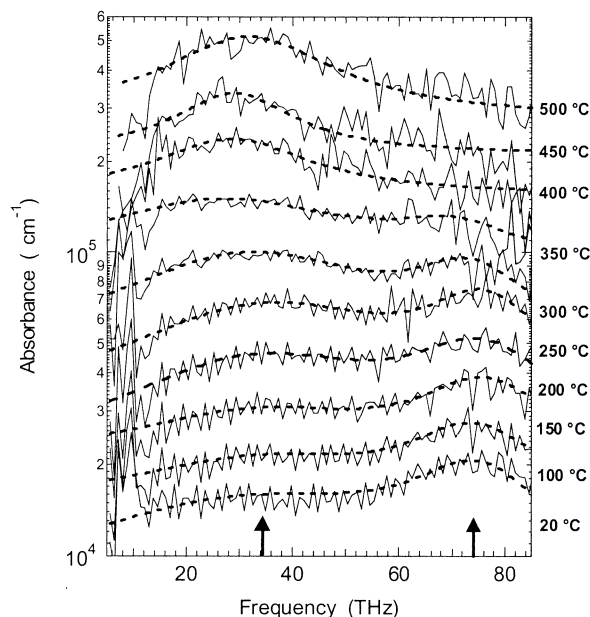


Figure 1: TTDS absorbance for 500 nm PZT film grown by PLD on silicon substrate. The different temperature measurements are offset for clarity.

$n_f + ik_f$ and $n_s + ik_s$, respectively.

The sample consisted of a 500 nm PZT50 film grown by pulsed laser deposition onto a silicon substrate with a 50 nm STO template film. Films grown on a STO buffer layer have enhanced crystallinity and overall ferroelectric properties.

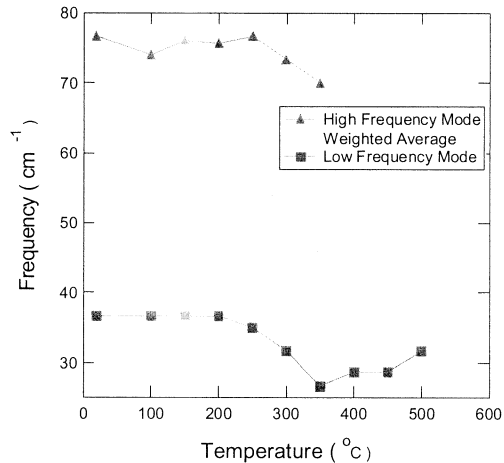


Figure 2: Temperature dependence of the TO mode frequencies determined from the transmission data in Fig. 1. The centroid of the two observed peaks is shown to compare with the Fedorov data.

3 RESULTS

The measured FIR absorbances are shown in Fig. 1. A clear 77 cm^{-1} absorption appears at room temperature. As the temperature is raised, a second absorption line appears at 37 cm^{-1} . The 37 cm^{-1} absorption feature increases in strength as the temperature increases while the 77 cm^{-1} line decreases in amplitude. The exchange of oscillator strength between the two modes suggests the possibility of cubic phase domains forming at temperatures as low as $150 \text{ }^\circ\text{C}$. In the high symmetry state above T_c a single soft mode is observed which is a TO phonon mode. Below T_c , two TO modes corresponding to the lower symmetry tetragonal state are observed. We note that Fedorov et al. do not show the splitting of the TO phonon below T_c . A double Lorentzian line fit is used to analyze the data. In Fig. 2 we show the frequencies of the observed modes as a function of temperature. The softening of both the 77 cm^{-1} and 37 cm^{-1} peak is slight. The Fedorov results for a 1000 nm sol gel film show significant softening [1]. There are several possible causes for the disagreement: 1) thickness difference 2) substrate strain effects and 3) limitations in experimental system and/or fitting procedure. We plot the centroid of our observed peaks as a function of temperature also on Fig 2. This weighted average of the two modes has a temperature dependence resembling the Fedorov data [1] for the PZT47 sample. For samples where the absorption

linewidths are similar to the spacing between the two absorption peaks, the shift in absorption strength with temperature would appear as a shift in a single, averaged absorption frequency. Thus it is conceivable that the same low frequency peak was present in the Fedorov data and that the apparent mode softening was due to the fitting procedure which assumed only one mode. The presence of substrate etalon effects in the Fedorov data may also be

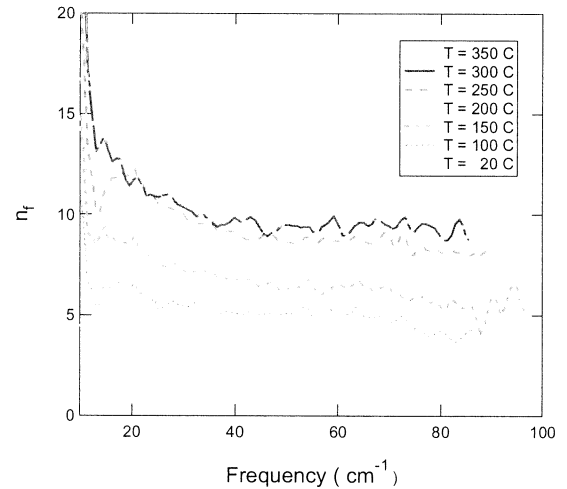


Figure 3: Real part of the index for 500 nm PZT film extracted from transmission data in Fig. 1 using Eq. 2

interfering with their fit. Typical substrate index is ~ 3.3 , with thicknesses $200\text{-}600 \text{ }\mu\text{m}$, giving etalon spacing of $2\text{-}5 \text{ cm}^{-1}$. We also note that 30 cm^{-1} is the lower limit for the Fedorov measurements. The high sensitivity at low frequencies available with the TTDS system greatly enhances our ability to discern the transition behavior at T_c . We use Eq. 3 and a Newton-Raphson fit to extract n_f and k_f for the PZT film as a function of temperature with results shown in Figures 3 and 4. We ignore the absorption due to the substrate in Eq. 3. Neglecting the substrate absorption is an oversimplification and the thermally activated free carrier absorption should be included. We justify this omission in these preliminary results in that the mobility of the Si is sufficiently low that the free-carrier absorption is independent of frequency over the range of the heated measurements. Future measurements will use an uncoated substrate as the reference to remove this complication in the analysis. The extracted k_f again indicates a resonance at 37 cm^{-1} increasing in strength as the temperature approaches T_c .

4 DISCUSSION

Several components of the data are striking. Firstly, the higher frequency absorption is at 77 cm^{-1} rather than $\sim 60 \text{ cm}^{-1}$ as reported by Fedorov et al. Secondly, at relatively low temperatures we see the appearance of a 37 cm^{-1} absorption that has not been reported in the past for the ferroelectric phase. Thirdly, there is a nearly complete

absence of softening of the 77 cm^{-1} mode. A key point is the role of substrate-induced strain. The thermal expansion coefficients $(\Delta L/L)\Delta T = \alpha$ for silicon, sapphire and PZT are $2.6 \times 10^{-6}\text{ K}^{-1}$, $4 - 8 \times 10^{-6}\text{ K}^{-1}$, and $4 \times 10^{-6}\text{ K}^{-1}$ respectively. Both the PLD samples on Si and the sol gel films on sapphire were grown and/or annealed at $600\text{ }^\circ\text{C}$. The PZT film on silicon is under compressive strain at room temperature, however the sol gel film may either be strain free or under tensile strain. Based on the balance between short range and Coulomb interactions, one expects that the mode softening increases and the transition temperature decreases as the pressure increases. This simple relation is consistent with our observations which

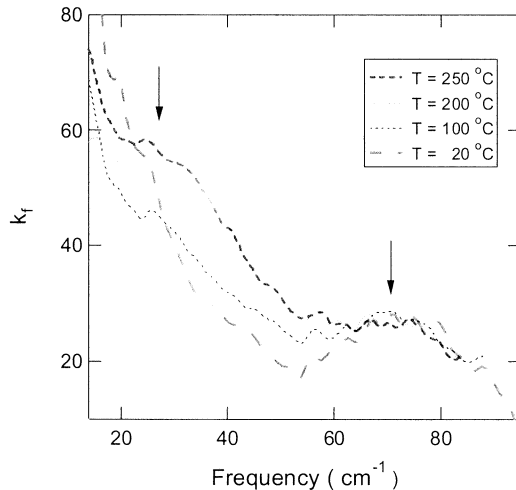


Figure 4: Imaginary part of the index of a 500 nm PZT film extracted from trans-mission data shown in Fig. 1 using Eq. 2.

suggest a $T_c < 400\text{ }^\circ\text{C}$ and an increase in the soft mode frequency to 77 cm^{-1} [8]. With regards to the appearance of the 37 cm^{-1} mode and the near absence of softening, this again may be due to substrate strain and a strongly first order phase transition occurring. If there is a distribution of grains within the film with varying degrees of strain, the transition temperature for the first order phase transition may continuously vary, and the increase in oscillator strength of the 37 cm^{-1} line with increasing temperature is the result of an increasing population of grains undergoing a first order phase transition to the cubic phase. The fact that there is very little mode softening for the 77 cm^{-1} peak may be arising from reduced dimensionality as suggested by the earlier work on thicker films[1-3].

Further systematic measurements as a function of thickness and strain are required to determine if these speculations are correct and to assist in the development of nanoscale films without loss of technologically desirable properties.

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