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Dielectric constants of bulk ferroelectric PZT measured by THz time-domain spectroscopy

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Abstract

The complex permittivity of bulk ceramic ferroelectric of nominal composition $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$ was measured in the range 0.2-2 THz using transmission time-domain spectroscopy. The results indicate strong absorption and dispersion in this frequency range often seen in highly disordered and polar materials. The results are compared to equivalent thin film data in the literature, and significant differences in the real and imaginary permittivity suggest that substrate clamping and degree of polarisation of the ferroelectric thin film materials affect dielectric properties even at these high frequencies.

Introduction

Wireless communication technologies are continuously expanding to ever-higher frequencies. Experimental wireless links have already been demonstrated at frequencies up to 300 GHz [1]. These technological developments will demand advances in dielectric and other functional materials for passive and possibly active devices, whose design will require accurate knowledge of dielectric properties at sub-THz and THz frequencies.

Ferroelectric and piezoelectric materials underpin a wide range of existing technologies, such as sensors, actuators and transducers, capacitors, pyroelectric detectors, medical ultrasound, and ferroelectric memory. Ultra-fast processes in ferroelectrics are also of direct technological interest for non-linear optics, photonics, telecommunications and optical data storage [2]-[4].

Despite their industrial relevance, it is surprising that very little literature has been published on the dielectric properties of ferroelectric and piezoelectric materials at THz frequencies, with most of the

high frequency work focused on mm wavelength (microwave) applications [5]-[7]. The great majority of the published data has been derived indirectly from THz reflectivity measurements [8]-[16], where the calculations involved are subject to large uncertainties [17]. This is especially relevant in materials with high reflectivity, where both real and imaginary dielectric constants have large values, as is the case in the industry standard piezoelectric family of ceramics known as PZT (i.e. $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ - perovskite solid solutions). Moreover, most of the cited studies were performed using Fourier Transform Spectroscopy (FTS), a technique that offers ultra-broadband measurement over as much as $30\text{-}3000\text{ cm}^{-1}$ (1-100 THz). However, the method does not provide a direct measurement of the *phase*, which therefore makes derivations of optical constants from reflectivity data even more problematic [17], since they must be calculated from the Kramers-Kronig dispersion integrals Chapter 9 in [18].

THz time-domain spectroscopy (TDS) offers a much narrower range of frequencies than FTS, typically 0.1-4 THz, but has the important advantage of yielding a direct measurement of both amplitude and phase shift, making possible a much more accurate determination of the real and imaginary dielectric constants. Chen et al. [7] used reflection THz TDS to measure the refractive index of epitaxial $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ film on SrTiO_3 substrate at 1 THz as a function of applied electric field. Li et al. [6] used the goniometric form of reflection THz TDS to obtain the dielectric constants of a $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$ film on Si substrate at discrete frequencies in the 0.6-1.4 THz range. However, because these studies used reflectivity measurements, the values of the derived optical constants are subject to quite large uncertainties associated with this approach.

In contrast, transmission time-domain spectroscopy provides a direct measurement of the complex dielectric constant with comparatively low uncertainties. Kwak et al. [5] used transmission THz TDS to measure the real and imaginary dielectric constants of sol-gel grown $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ and $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ films in the 0.1-2 THz range, demonstrating the advantages of the technique for these materials. Similarly, Buixaderas et al. [19], [20] included transmission THz TDS in the range 0.15-0.6 THz in their comprehensive study of dielectric properties of PLZT (Pb, La, Zr, Ti) materials at

frequencies between 10^2 - 10^{14} Hz and at temperatures of 20-800 K, as well as in their similar study of PZT materials [21].

With so little data published on the dielectric properties of bulk materials, we present in this paper transmission THz TDS measurements on bulk ceramic $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$ in the range 0.2-2 THz. The dielectric constants are compared with those measured on thin films grown by epitaxial and sol-gel processes.

Experimental techniques

Bulk sintered ceramic plates of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ with nominally tetragonal structure were sourced from a commercial supplier of PZT ceramics. The material composition was measured using energy-dispersive X-ray spectroscopy and confirmed to be Ti-rich, with $x \sim 0.6$. At THz frequencies, PZT has a high refractive index combined with high absorption. In consequence, and in order for transmission measurements to be made possible, the PZT samples must be mechanically thinned to less than about 50 μm . In these experiments, three samples were produced by grinding down and polishing the bulk ceramic to thicknesses between 20-30 μm . Film thickness was measured using the gauge block technique, with an uncertainty of $\pm 1 \mu\text{m}$ [22]. Since these films were too fragile to handle or mount, they were sandwiched between two plates of polymethylpentene (TPX® from Mitsui Chemicals) each 2 mm thick. TPX® was chosen because of its high THz transparency [23] combined with optical transparency and good mechanical stiffness. Two similar plates of TPX® contacted together served for reference measurements.

The THz time-domain spectrometer [24] had a commonly employed configuration with four 90° parabolic mirrors. The pump laser was a mode-locked Ti:Sapphire laser (Femtsource) with a 20 fs pulse length and a centre wavelength of 800 nm, producing an average power of 450 mW. The THz source was a photoconductive emitter fabricated on semi-insulating GaAs biased to 200 V with unipolar square-wave modulation at 10 kHz. The THz signal was detected by monitoring the electro-optic birefringence of a 0.5 mm thick ZnTe crystal using a pair of balanced photodiodes. The dynamic range

of the system was approximately 2000 at 1 THz. For the measurement, the PZT sample was placed approximately 5 mm away from the focal plane of THz beam, in order to minimize wavefront distortion which would be caused by placing the samples at the exact focus [25].

Experimental Results

The refractive indices (n) and absorption coefficients (α) of PZT samples were calculated from the frequency-domain transmission data obtained by Fast Fourier Transform of the THz transients, using the equations [19]:

$$n(\omega) = 1 + \frac{(\phi_{ref} - \phi_{sample})c}{\omega d} \quad (1)$$

$$T(\omega) = 1 - \frac{(n - n_s)^2 + k^2}{(n + n_s)^2 + k^2} \quad (2)$$

$$k(\omega) = \frac{\alpha c}{2\omega} \quad (3)$$

$$\alpha(\omega) = -\frac{2}{d} \ln \left(T \frac{E_{sample}}{E_{ref}} \right) \quad (4)$$

where ϕ and E are respectively the phase and amplitude of the THz signal, ω is its frequency, and c is the speed of light in vacuum; k is the extinction coefficient. The sample thickness is d , and the refractive index of TPX plates is $n_s = 1.45$ [6]. The transmission factor T accounts for losses arising from Fresnel reflections. Note that when k is non-negligible, as it is for PZT, Eqs. 2-4 must be solved iteratively.

Fig. 1 shows the obtained refractive index and absorption coefficient of the PZT samples, and values at selected frequencies are listed in Table 1. Three different samples were measured, with thicknesses of 20, 24 and 29 μm . Each sample was measured at 3 different locations, with 4 scans at each location. The results from all three samples are similar within the measurement uncertainty, indicating consistency of the material properties and the absence of inhomogeneous surface effects arising from sample preparation (e.g. scattering, surface contamination).

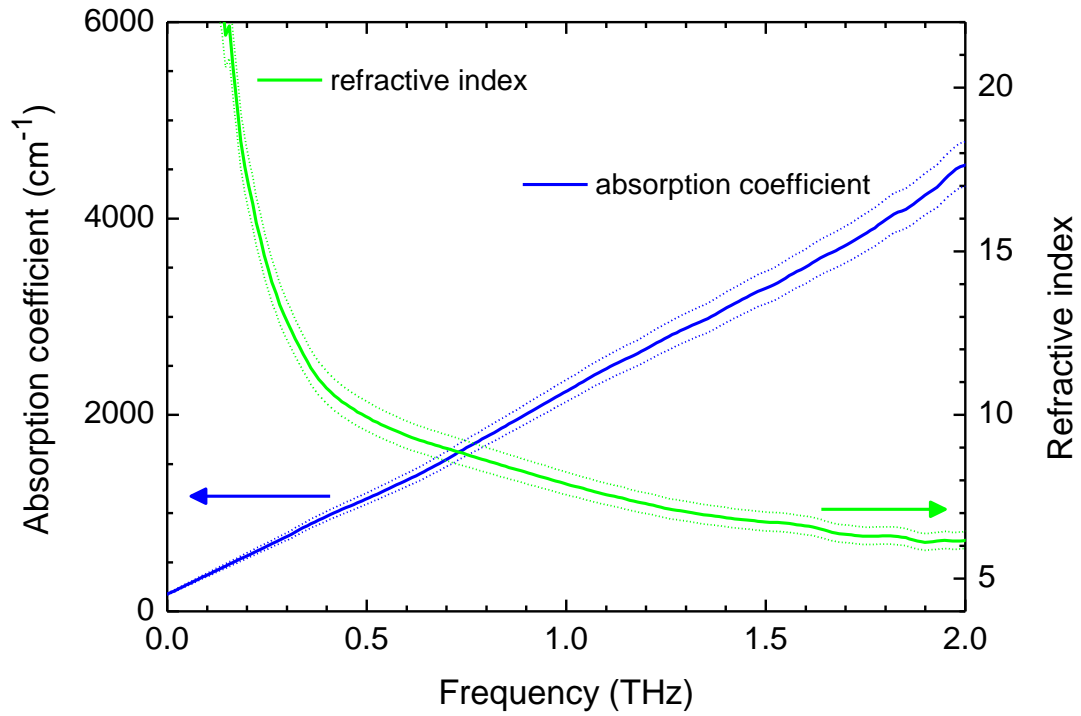


Fig. 1. Refractive index and absorption coefficient of PZT calculated from the transmission data according to Eqs. 1-4. The data represent measurements on 3 samples whose thicknesses were 20, 24 & 29 μm (with an uncertainty of $\pm 1 \mu\text{m}$). The dashed lines represent measurement uncertainty arising from uncertainty in the sample thickness, which accounts for the main contribution to the error in this measurement.

Table 1. Refractive indices, absorption coefficients and real and imaginary permittivity of $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$ at 0.25, 0.5, 1.0 and 1.5 THz.

Frequency (THz)	0.25	0.5	1.0	1.5
Refractive index	14.6 ± 1.4	9.9 ± 0.5	7.9 ± 0.4	6.7 ± 0.3
Absorption coefficient (cm^{-1})	660 ± 30	1150 ± 60	2250 ± 120	3290 ± 160
ϵ'	171 ± 9	69 ± 3	34 ± 1	18 ± 1
ϵ''	184 ± 9	108 ± 5	84 ± 4	70 ± 3

The refractive index has large dispersion, falling from ~ 20 at 0.2 THz to ~ 8 at 2 THz. The absorption coefficient is very large, and increases steeply from $\sim 500 \text{ cm}^{-1}$ at 0.2 THz to $\sim 7000 \text{ cm}^{-1}$ at 2 THz. Both these features are indicative of relaxations on THz timescales [26]. The complex permittivity was calculated from the absorption and refractive index [21] according to:

$$\varepsilon = \varepsilon' + i\varepsilon'' = (n + ik)^2 = (n^2 + k^2) + i(2nk) \quad (5)$$

and is shown in Fig. 2.

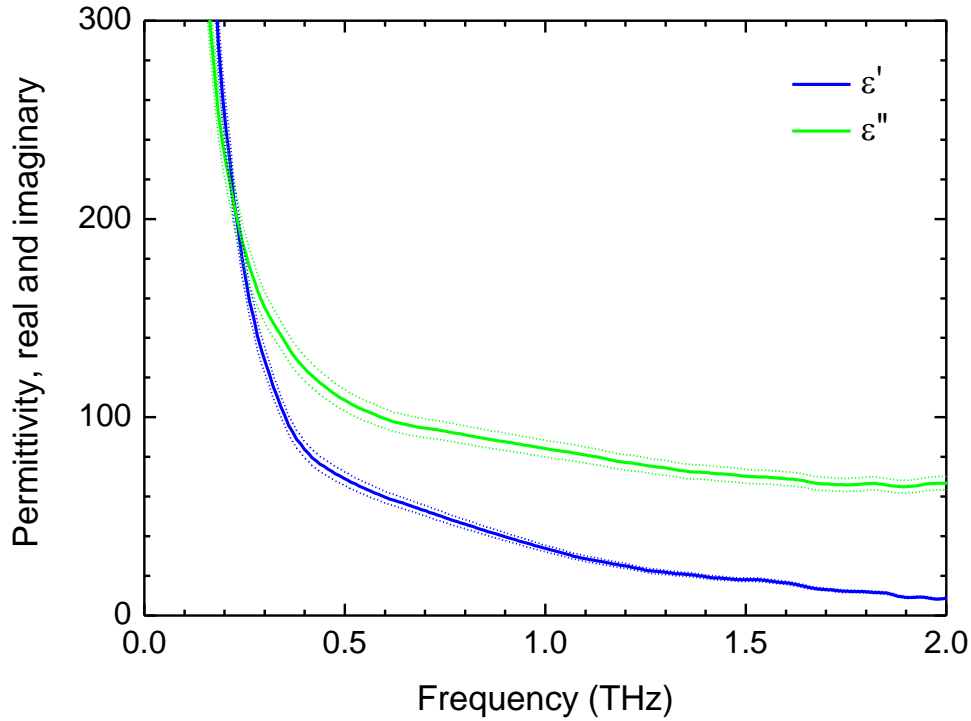


Fig. 2. The calculated permittivity of PZT - dashed lines represent measurement uncertainty. Note the y-axis is the same for real and imaginary permittivity at these frequencies.

Discussion

From our data and calculated values of the real and imaginary values of permittivity we conclude the following:

1. Our polished lamella of PZT exhibit an increase in permittivity with decreasing frequency similar to that observed in the literature. The absolute values differ by a factor of about 2, with our data being approximately half the values reported for similar compositions in the work of Buixaderas, for example [21].
2. Buixaderas et al used TDS to measure PZT ceramics (polished to a similar thickness as our samples in this report) and also noted the increase in permittivity from a high frequency value of approximately 150 at 1 THz to approx. 200 at their lowest measured frequency (6 cm⁻¹ or about 0.2 THz) at room temperature, and for a similar composition [21]. Lower temperature measurements exhibited a flat permittivity, with all measured (calculated) imaginary permittivity passing through a peak before declining at low frequencies. The imaginary permittivity obtained in this work do not show a maximum or peak in response which is observed by Buixaderas and (weakly indicated) by Kwak [5], although an increase in imaginary permittivity with decreasing frequency is characteristic of these materials generally. Our data extends down to approximately 0.2 THz (~6 cm⁻¹), and the peaks reported in [21] occur around this frequency or below, so it is not surprising that this feature was not observed in our study. The discussion in Buixaderas explained the huge peak in imaginary permittivity at low frequency as an indicator of a THz mode contributing significantly to the high permittivity observed in their range of PZT compositions (which is approx. our composition), indicating that the main softening towards the morphotropic phase boundary takes place in this lower frequency range. The permittivity data presented in the literature shows great sensitivity to the chemical composition of the PZT ceramic – especially around the morphotropic phase boundary – and because the exact composition of commercially sourced materials is a closely guarded secret, a direct comparison of the absolute values of permittivity to other published work is not considered scientifically robust.
3. Kwak et al. [5] measured thin films of Pb(Zr_{1-x}Ti_x)O₃ with x=0.3 and x=0.52 grown on MgO single crystal substrates, also using time domain spectroscopy in the range 0.2 – 2 THz. For both compositions they obtain values of ϵ' and ϵ'' at 1 THz roughly 3 times larger than our results. Apart from the different compositions, the most important difference is the use of a

substrate-supported highly textured (oriented) thin PZT film, whilst the material studied in this paper was bulk (polycrystalline) PZT. Significant differences in the real and imaginary permittivity suggest that substrate clamping and degree of polarisation (induced through textured film growth) of the ferroelectric material affect dielectric properties even at these high frequencies. The effect of the substrate on the calculation of ϵ' and ϵ'' has been considered, and it is well known that ferroelectric thin films exhibit much lower polarisation at lower frequencies due to the clamping effect of the substrate at the interface [27], [28]. The clamped dielectric displacement vector due to interfacial strain also results in a modified dielectric polarization compared to bulk, though the changes in permittivity would depend critically on preferred orientation, strain, thickness, depolarising layers, boundary effects and more [2], [29]. The exact effect of the interfacial strain on the electronic and ionic polarisabilities is still under debate, however it does emphasize the need for measurements on bulk samples as well as thin film samples.

4. The THz TDS system used in these measurements was calibrated for frequency and linearity of response [17]. In preparing the samples, particular attention was given to obtaining uniform thickness and near-optical surface finish, and the enclosing TPX plates were likewise tested, thus reducing uncertainties arising from sample quality [17]. The optical constants were calculated from the data by applying Eqs. 1-4 iteratively (unlike, for example in Kwak [5]) to obtain highly accurate parameter values. The PZT material, as mentioned above, is intrinsically highly variable, with its permittivity strongly dependent on the chemical composition and the fabrication process. The great variability of published results emphasises the need for accurate measurements of THz permittivity on a range of compositions and types of material grown under different fabrication conditions.

Conclusions

The dielectric permittivity of an industrially sourced tetragonal (Ti-rich) PZT ceramic has been determined at THz frequencies by transmission time-domain spectroscopy. The measurement uncertainties are reduced with this method compared to others found in the literature, such as reflection

Fourier transform spectroscopy. Both the real and imaginary permittivity differ from reported measurements on bulk ceramic and thin films of similar material compositions. The nature of the THz mode (soft mode) explored by Buixaderas was not observed in our data, most likely because of our composition being far from the MPB and the characteristic peak in their imaginary permittivity data being below our measurement frequency band. The strong dependence of THz permittivity on detailed characteristics of chemical composition, microstructure, manufacturing methods, and form of material (bulk or thin film) demonstrates the need for the accurate measurement of reference and commercial bulk materials, as presented here.

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