

Dielectric constants of ferroelectric PZT at THz frequencies

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Abstract—The complex dielectric constant of bulk ceramic ferroelectric $\text{PbZr}_{0.4}\text{Ti}_{0.6}\text{O}_3$ was measured in the range 0.2-2 THz using transmission time-domain spectroscopy. The material shows strong absorption and high refractive index with large dispersion. The results are compared to equivalent thin film data in the literature.

I. INTRODUCTION

WIRELESS communications technologies are rapidly expanding to ever higher frequencies, with wireless links up to 300 GHz already demonstrated. 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. Ultra-fast processes in ferroelectrics are also of direct interest for a range of technologies.

Despite their industrial relevance, very little literature has been published on the behavior of ferroelectric and piezoelectric materials at THz frequencies. The great majority of the published data has been derived indirectly from THz reflectivity measurements using Fourier Transform spectroscopy [8-16], where the calculations involved in deriving optical constants are subject to large uncertainties. This is especially the case in materials 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 ($\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ - perovskite solid solutions). In contrast, THz time-domain spectroscopy (TDS) makes possible a much more accurate determination of the real and imaginary dielectric constants [1-4].

In this paper we present transmission 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.

II. RESULTS

Bulk sintered ceramic plates of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ were studied. At THz frequencies PZT has high refractive index combined with high absorption; to allow transmission measurements, sample thickness was 20-30 μm . Since samples were too fragile to handle or mount, they were sandwiched between two plates of TPX (Polymethylpentene)

The refractive indices (n) and absorption coefficients (α) of PZT samples were calculated from the frequency-domain data obtained by FFT (Fast Fourier Transform) using the equations:

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

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

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

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

where ϕ and E are the phase and amplitude of the THz signal, ω is its frequency, and c is the speed of light. The sample thickness is d , and the refractive index of TPX plates is $n_s = 1.45$. The transmission factor T accounts for losses arising from Fresnel reflections. When k is non-negligible, as it is for

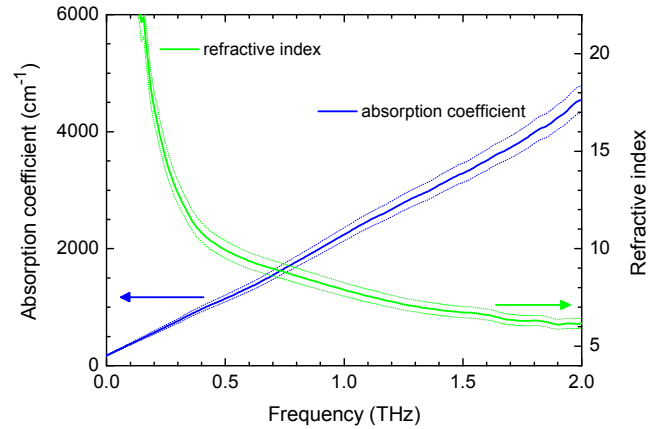


Fig. 1. Refractive index and absorption coefficient of PZT measured on 3 samples. The dashed lines represent measurement uncertainty.

PZT, Eqs. 2-4 must be calculated iteratively.

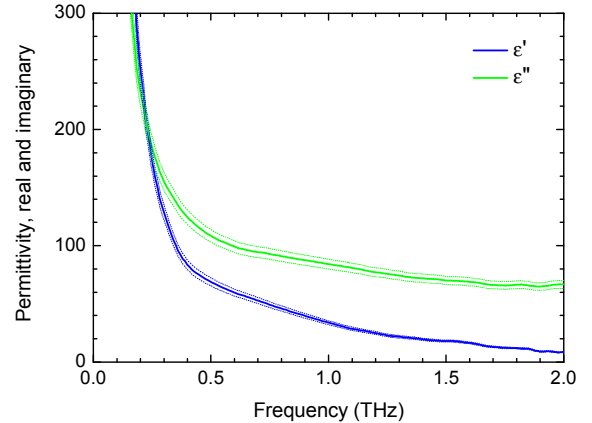


Fig. 2. The calculated permittivity of PZT - dashed lines represent measurement uncertainty. Note that the y-axis is the same for real and imaginary permittivity at these frequencies.

Fig. 1 shows the measured refractive index and absorption coefficient of the PZT samples. 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.

In comparing these results to equivalent thin film data in the literature [1-4], significant differences are observed, suggesting that substrate clamping and degree of polarisation of the ferroelectric material affect dielectric properties even at these high frequencies. The complex permittivity was calculated from the absorption and refractive index and is shown in Fig. 2.

III. DISCUSSION

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 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.

Our polished lamella of PZT exhibits a strong increase in the real and imaginary permittivity at frequencies below about 400 GHz. Buixaderas et al. used TDS to measure undoped PZT ceramics over a range of compositions and temperatures [1]. For samples of similar composition to those reported here (polished to a similar thickness and measured at room temperature), the real permittivity also increased as the frequency decreased from ~ 600 to ~ 200 GHz. However, the absolute value of our data (at 0.5 GHz) is approximately a factor of two smaller than that of Buixaderas et al., and the increasing imaginary permittivity that they report in this frequency range was not observed. 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.

Kwak et al. [4] measured thin films of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ 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. 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.

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