Accepted in Ferroelectrics

TIME-RESOLVED AND BACKWARD-WAVE OSCILLATOR SUBMILLIMETRE SPECTROSCOPY OF SOME FERROELECTRIC CERAMICS AND THIN FILMS

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Backward-wave oscillator spectroscopy was applied to the transmission measurements of the complex dielectric spectra in the frequency range 8-33 cm^{-1} at temperatures from 10 K to 300 K. The samples under investigation were relaxor PLZT 9.5/65/35 ceramics, antiferroelectric $PbZrO_3$ ceramics and thin films of $Ba_xSr_{1-x}TiO_3$ (x = 0; 0.1; 1) on sapphire substrates. Room temperature measurements on the same samples were performed using a time-domain terahertz transmission spectroscopy in the range 3-80 cm^{-1}. A good agreement of both data sets is obtained. Temperature behavior of the complex permittivity is discussed; both experimental methods are compared.

Keywords submillimeter spectroscopy; thin film; time-domain spectroscopy

INTRODUCTION

Investigation of dielectric properties in millimeter and submillimeter spectral range is a task of great importance as the low frequency excitations often provide essential information about the dynamical properties of dielectrics [1]. In this paper we use the two major submillimeter techniques: the time-domain terahertz spectroscopy (TDTS) and backward wave oscillator (BWO) spectroscopy, and we investigate the dielectric properties of the following materials:

$Pb_{0.905}La_{0.095}(Zr_{0.65}Ti_{0.35})O_3$ ceramics (PLZT), $PbZrO_3$ (PZ) ceramics, thin films of $Ba_xSr_{1-x}TiO_3$ (x = 0; 0.1; 1) (BST) on sapphire (0001) substrates deposited by injection MOCVD technique as described in [2]. The aim of this paper is to compare the results obtained by both spectroscopic methods for typical ferroelectric ceramics and thin films, and to estimate how precisely the dielectric function can be extracted from the measured data.

Transparent relaxor PLZT ceramics are extensively studied materials owing to their applications in electronic and optoelectronic devices [3]. The spectrum of dielectric dispersion in this material is so broad that it has to be studied starting from very low frequencies (units of Hz) up to far-infrared range [4]. The data in millimeter range are needed for a normalization of far-infrared reflectivity and, moreover, for an estimation of the upper limit of distribution of relaxators.

PZ ceramics show antiferroelectric phase transition of the first order at $T_c \sim 508$ K. The permittivity above T_c in the paraelectric phase is appreciably higher than in the orthorhombic phase below transition and cannot be described only by polar phonons contribution [5, 6]. Far-infrared measurements revealed central-mode type dispersion in the 5–25 cm^{-1} (0.1–1 THz) range which results in an additional contribution to the permittivity [6]. Submillimeter measurements in this case play very important role as far as they can provide quantitative information about the central mode behavior.

The dramatic differences observed in the dielectric properties of various BST thin films and bulk materials is a subject of recent investigations [7, 8]. The permittivity of these films is lower than in single crystals and the losses are higher. Far infrared and Raman measurements have shown an essential difference in the soft-mode behavior in thin $SrTiO_3$ (ST) films comparing to single crystal [9].

EXPERIMENTAL TECHNIQUES

Low temperature measurements of the complex transmittivity of plane parallel samples were performed in BWO setup ‘Epsilon’. Three coherent radiation sources that cover range 8-33 cm^{-1} were used with He-cooled cryostat. Golay cell was used as detector with noise equivalent power (NEP) $10^{-10} – 10^{-11}$ W $Hz^{-1/2}$ [1].

The room temperature measurements were also carried out by TDTS; our experimental setup was described elsewhere [10]. The

typical value of NEP for the coherent detection is ~10^{-16} W $Hz^{-1/2}$ [11]. This system covers the range 3-80 cm^{-1} for the free space propagation. Signal to noise ratio is ~500 within the frequency region that contains 85% of THz pulse power (6–33 cm^{-1}). In the case of samples with low transmission (such as PZ and PLZT), the measured transmission function has acceptable signal to noise ratio only for the above mentioned frequencies.

Spectral resolution of both techniques is approximately 0.1 cm^{-1}. An average power for TDTS is about 0.1 μW that is five orders of magnitude lower than power of BWO sources (1–10 mW). Thus the signal to noise ratio is nearly the same for both spectroscopies.

RESULTS AND DISCUSSION

Let us first discuss the thin films measurements. Room temperature intensity transmission and normalized phase functions of pure ST film (thickness of the film d_f = 300 nm, thickness of sapphire substrate d_s = 0.43 mm) are presented in Fig.1. Good correspondence of BWO and TDTS spectra can be seen. However, numerical calculations of the refraction index based on general equations for complex transmission of

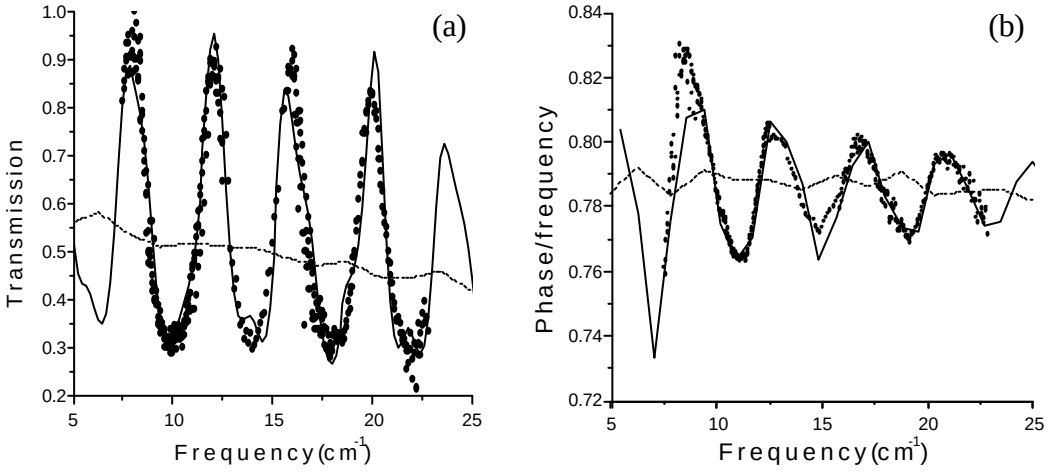

FIGURE 1 Intensity transmission (a) and normalized phase (b) of thin $SrTiO_3$ film on the sapphire substrate measured by BWO (full circles) and TDTS with reflections inside the substrate (solid line) and without them (dotted line)

thin film on substrate [12] do not give acceptably smooth dependence on frequency in the presence of interference fringes from the substrate because even small errors in the values of phase and amplitude of the transmission function lead to huge deviations in refraction index. On the other hand, TDTS technique allows to avoid this problem. As all the Fabry-Perot reflections coming from the substrate are resolved and well separated in time, it is possible to cut the time-domain THz waveform before the first reflected pulse, leaving only the transmitted THz pulse. Then one obtains the transmission function without interferences in the substrate (dotted line in Fig.1). Moreover, in this case a simple explicit formula can be used to calculate the dielectric spectrum of the thin film [13]. Complex permittivity spectra obtained in this way for ST (x = 0) and BST (x = 0.1) are presented in Fig.2 in comparison with a model oscillator fits with parameters taken from [14] on the same samples. TDTS data confirm the soft-mode dispersion in this frequency range. A deviation of TDTS data from the fit values can be explained by uncertainty in the substrate thickness and absorption index.

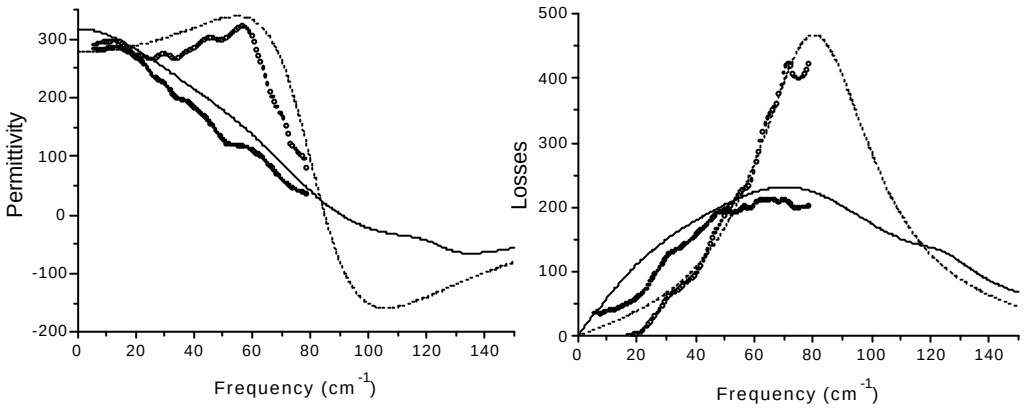

FIGURE 2 Permittivity and losses of BST and ST thin films measured by TDTS (BST: full; ST: open circles) and calculated from the fit of far-infrared transmission (BST: solid; ST: dotted lines)

Results of the measurements of PLZT 9.5/65/35 ceramic by BWO technique and room temperature TDTS data are shown in Fig. 3. Because of high permittivity and losses, the sample had to be polished to the thickness of 17 μm, which is practically the limit for ceramic samples. Intensity transmission was 10^{-3} -10^{-4}, i.e. near the limit where

the noise becomes essential. Therefore the error in the calculated dielectric function was 10–20% for both techniques.

Nevertheless, the result in Fig. 3 together with microwave and lower frequency dielectric data [4, 15] suggests that a loss maximum exists somewhere in the 10^{11} – 10^{12} Hz range which survives down to the liquid He temperatures. This dispersion appears in addition to the frequency independent loss spectrum below 10^{9} Hz [15] (1/f noise) and is not of phononic origin.

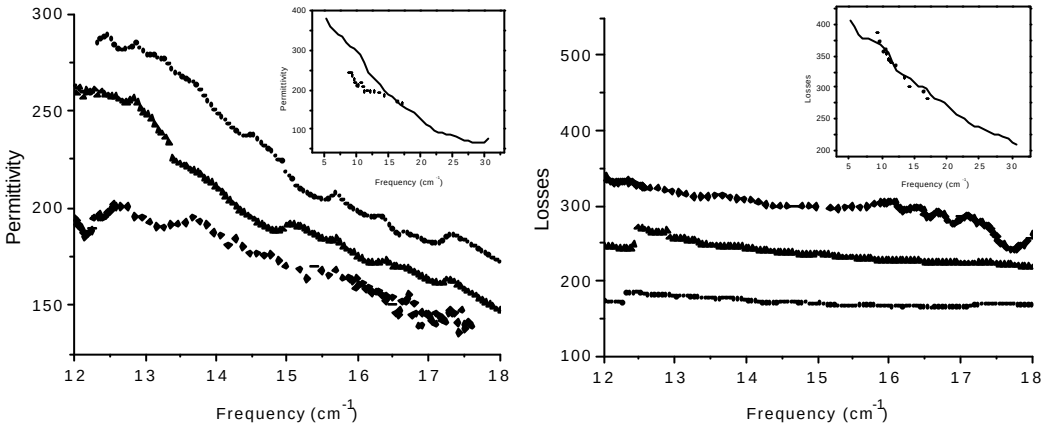

FIGURE 3 Permittivity and losses of PLZT 9.5/65/35 ceramic at 295 K (diamonds), 200 K (triangles), 50 K (circles), inset: comparison between room temperature BWO (circles) and TDTS (line)

Taking into account the estimated errors, we can conclude that, using the transmission spectroscopies in the THz range, losses and/or permittivity up to 500 can be measured. If a He-cooled bolometer is used for detection of the BWO radiation, the measurement sensitivity is increased by one or two orders of magnitude: somewhat higher values of losses and/or permittivity can then be determined.

BWO and TDTS measurements of PZ ceramic sample have shown good correspondence to each other. Low temperature BWO data properly agree with far-infrared fits and have been published in [6].

CONCLUSION

We have performed measurements of different ferroelectric materials in the submillimeter range. Comparison between TDTS and BWO

spectroscopy has revealed approximately the same potential of both for investigation of bulk weakly transparent samples. In the case of thin films TDTS takes an advantage due to its flexibility in processing of measured data.

ACKNOWLEDGMENTS

This work was supported by the Grant Agency of the Czech Rep. (project No.202/01/0612), Grant Agency of AS CR (project No. A1010918) and Deutsche Forschungsgemeinschaft (DFG) via GO 976/1-1.

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