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Time-Domain Terahertz Spectroscopy of $SrBi_2Ta_2O_9$*

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Time-domain terahertz transmission and reflection spectroscopies are described and compared. New results obtained in $SrBi_2Ta_2O_9$ ceramics and thin film are presented and discussed. A central-mode type dispersion was detected near 10 cm^{-1} which should be responsible for a strong dielectric anomaly at the ferroelectric phase transition.

Keywords Terahertz time-domain spectroscopy; soft mode; central mode; ferroelectric; strontium bismuth tantalate

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Introduction

Time-domain terahertz spectroscopy (TDTS) is based on emission of picosecond terahertz (THz) pulses and their synchronous phase-sensitive detection, i.e., it can provide the temporal profile of the electric field of a pulse transmitted or reflected by the investigated sample [1]. A determination of the complex sub-mm dielectric response by means of TDTS always requires a reference measurement which ensures the result to be independent of the THz pulse shape as well as of the instrumental functions. The transmission variant of the method is well established, and it has been already successfully applied to ferroelectrics and related materials [2, 3, 4]. A reliable phase-sensitive reflection setup is then needed for investigation of heavily absorbing soft modes in bulk samples (which are consequently not transparent in the sub-mm range) and for characterization of ferroelectric thin films (where the accuracy of the transmission measurement critically depends on the quality of the substrate). However, owing to difficulties with an accurate determination of the reflectance phase, the reflection variant of TDTS could be used only in some very specific cases until recently (see Ref. [5] and references therein).

In this paper we present and discuss sub-mm spectra of a bulk ferroelectric (FE) ceramics and thin film of $SrBi_2Ta_2O_9$ (SBT) as obtained by TDTS in the transmission and, recently, also reflection setup [5]. SBT is a ferroelectric compound with Aurivillius perovskite

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layered structure with an excellent polarization fatigue-free behavior and low coercive field for polarization switching. For this reason SBT is one of the most frequently used materials for non-volatile FE memories. It is known to undergo two structural phase transitions: a proper ferroelectric one at $T_c \approx 600$ K, and an improper ferroelastic one at $T_{c2} \approx 770$ K (see [6] and references therein). An optical soft mode (SM) was found below 30 cm^{-1} at room temperature and it has been shown to soften only partially upon heating. The existence of a relaxation process below phonon frequencies has been proposed [6].

Experimental Setup

Our experimental setups are depicted in Fig. 1. The optical sampling pulse has a variable time delay with respect to the THz pulse and serves for the electro-optic detection of the THz field. The transmission technique consists in a measurement under normal incidence of a reference waveform $E_r(t)$ with an empty diaphragm and a signal waveform $E_s(t)$ with the sample filling the whole aperture. The complex transmission function is defined as the ratio of the Fourier components of the two signals. Knowing the sample thickness, the complex dielectric function can be evaluated [7].

The reflection technique makes use of a reference mirror with a known field reflectance. A classical setup would require a highly precise positioning of the sample with respect to the position of the reference mirror (precision better than 1 μm is usually necessary [8]) in order to obtain accurately the phase of the complex reflection function. Our setup allows to overcome this problem by making the THz beam and the optical sampling beam coincide between the emitter and the sample: both beams then propagate collinearly, reflect off the sample surface and continue to the electro-optic sensor. A misplacement of the sample changes the optical pathlength by precisely the same amount for both beams, and produces no phase change in the measured THz waveform. The angle of incidence can be varied from 12° up to about 55°.

The (0001) sapphire plate in optical contact with the sensor makes the optical path of the THz beam between the sample and the sensor longer than that of the sampling beam (sapphire is transparent for both optical and THz radiation and induces a pulse walk-off of 4.5 ps/mm). This ensures that the sampled part of the THz waveform is reflected off the sample before the sampling pulse arrival: a possible change of the sample reflectance owing to the optical excitation is thus avoided.

The difference in optical reflectance of the reference mirror and of the sample is taken into account through the signal of the reference photodiode. The suitable samples for the measurement must have optically flat front surface allowing a non-diffusive (specular)

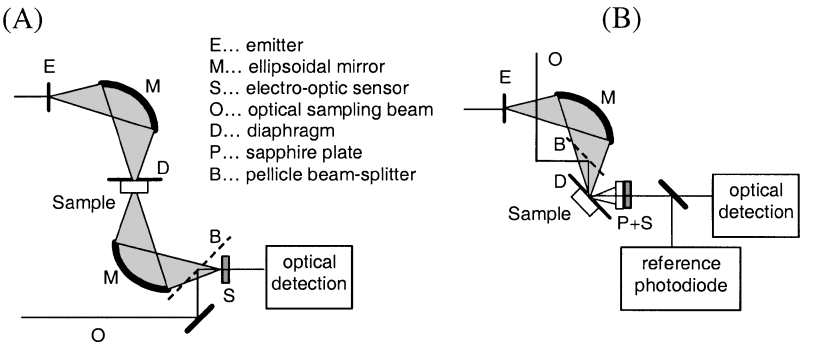

FIGURE 1 TDTS setups: (A) transmission, (B) reflection measurements (see text for the description).

reflection of the sampling beam: according to our experience, the majority of crystalline and ceramic samples can be polished with a sufficient precision to fulfill this condition. More technical details about the reflection setup and the data treatment can be found in [5].

Results and discussion

Figure 2a shows the measured dielectric room temperature sub-mm spectra of SBT ceramics in the reflection setup. The fit of the data based on a sum of harmonic oscillator contributions yields for the SM: frequency $\nu_{SM} = 28$ cm^{-1}, damping $\gamma_{SM} = 12$ cm^{-1}, and dielectric strength $\Delta\varepsilon_{SM} = 81$. These results constitute a direct confirmation of the SM characteristics as measured by Fourier-transform infrared spectroscopy (FTIR) [6] and Raman scattering [9].

In Fig. 2b we present room temperature TDTS spectra of SBT thin film (5.5 μm) deposited on sapphire substrate obtained both in transmission and in reflection geometry.

The phase change that the THz pulse acquires due to the propagation through the (thick) substrate is significantly larger than that due to the propagation through the thin film. The transmission data are then very sensitive to the quality of plane parallelism of the substrate and to the error in its thickness and refractive index determination [10]. In the final evaluation, these errors mainly contribute to the errors in the static value of the permittivity ε_0 and in the oscillator strength of the SM (vertical scaling). On the other hand, the reflectance data are independent of the substrate thickness and depend only weakly on its refractive index: the vertical scaling is thus free of the above described errors.

We adopt the following protocol for the data treatment: for the evaluation of the transmission data we consider the substrate thickness as a variable parameter (typically within 2 μm) which allows to scale vertically the resulting dielectric function in order to find the best match between the dielectric functions from transmission and reflection. After this adjustment the transmission data are found to fulfill slightly better the Kramers-Kronig relations than those obtained from the reflection, they seem to be more accurate namely at low frequencies below 10 cm^{-1}. We then use the transmission data for a detailed analysis of the dielectric spectrum. The SM peak is significantly broadened compared to the ceramics sample: we find at room temperature $\gamma_{SM} \approx 20$ cm^{-1}, and $\Delta\varepsilon_{SM} \approx 42$. This means that the thin film is less homogeneous than the bulk ceramics. Further details about the SM behaviour can be found in [11].

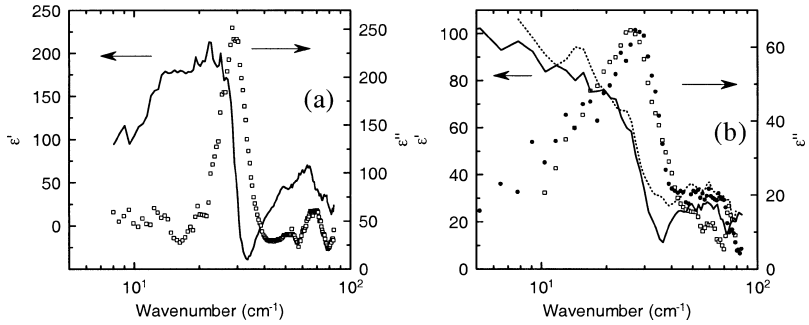

FIGURE 2 Measured dielectric functions of SBT at room temperature. (a) bulk ceramics: reflection setup; (b) 5.5 μm thin film: transmission (closed symbols, solid line) and reflection (open symbols, dotted line) setup.

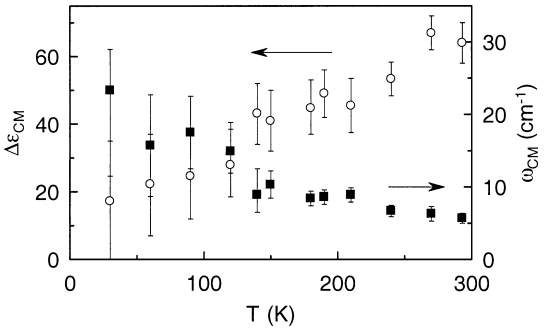

FIGURE 3 Temperature dependence of the CM frequency (ω_{CM}, closed symbols) and dielectrics strength ($\Delta\varepsilon_{CM}$, open symbols).

We have performed a temperature study of the sub-mm properties of SBT thin film: we have found that the spectra exhibit a temperature-dependent and reproducible shoulder at low frequencies. Consequently, we have included a Debye relaxator (central mode—CM) in the fits which significantly improves the accuracy of the fits below 20 cm^{-1}. The temperature dependence of the CM characteristics is shown in Fig. 3. The CM is supposed to be coupled to the SM and should prevent its softening at T_c [6]. Moreover, the contribution to the static permittivity of all polar phonons is about 100 which is substantially less than yield low-frequency permittivity measurements: the contribution of the CM may explain this missing permittivity.

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References

1. M. C. Nuss and J. Orenstein, Terahertz time-domain spectroscopy, In Millimeter and Submillimeter Wave Spectroscopy of Solids (G. Grüner, ed.), Chap. 2, Springer-Verlag Berlin Heidelberg, pp. 7–50 (1998).
2. P. Kužel, and J. Petzelt, Time-resolved terahertz transmission spectroscopy of dielectrics. *Ferroelectrics* **239**, 949–956 (2000).
3. A. Pashkin, P. Kužel, J. Petzelt, B. Gorshunov, and M. Dressel, Time-resolved and backward-wave oscillator submillimetre spectroscopy of some ferroelectric ceramics and thin films. *Ferroelectrics* **272**, 219–224 (2002).
4. S. Kamba, V. Porokhonskyy, A. Pashkin, V. Bovtun, J. Petzelt, J. C. Nino, S. Trolier-McKinstry, M. Lanagan, and C. Randall, Anomalous broad dielectric relaxation in $Bi_{1.5}ZnNb_{1.5}O_7$. *Phys. Rev. B* **66**, 054106 (2002).
5. A. Pashkin, M. Kempa, H. Němec, F. Kadlec, and P. Kužel, Phase-sensitive time-domain terahertz reflection spectroscopy. *Rev. Sci. Instrum.* **74**, 4711–4717 (2003).
6. S. Kamba, J. Pokorný, V. Porokhonskyy, J. Petzelt, M. P. Moret, A. Garg, Z. H. Barber, and R. Zallen, Ferroelastic phase in $SrBi_2Ta_2O_9$ and study of the ferroelectric phase-transition dynamics. *Appl. Phys. Lett.* **81**, 1056–1058 (2002).
7. L. Duvillaret, F. Garet, and J.-L Coutaz, A reliable method for extraction of material parameters in terahertz time-domain spectroscopy. *IEEE J. Select. Topics Quantum Electron.* **2**, 739–746 (1996).
8. D. Hashimshony, I. Geltner, G. Cohen, Y. Avitzour, A. Zigler, and C. Smith, Characterization of the electrical properties and thickness of thin epitaxial semiconductor layers by THz reflection spectroscopy. *J. Appl. Phys.* **90**, 5778–5781 (2001).

9. S. Kojima, Optical mode softening of ferroelectric $SrBi_2Ta_2O_9$ and related bismuth layer-structured oxides. *J. Phys.: Condens. Matter* **10**, L327–L332 (1998).
10. J. Petzelt, P. Kužel, I. Rychetský, A. Pashkin, and T. Ostapchuk, Dielectric response of soft modes in ferroelectric thin films. *Ferroelectrics* **288**, 169–185 (2003).
11. M. Kempa, P. Kužel, S. Kamba, P. Samoukhina, J. Petzelt, A. Garg, and Z. H. Barber, Ferroelectric soft mode and central mode in $SrBi_2Ta_2O_9$ films. *J. Phys.: Condens. Matter* **15**, 8095–8102 (2003).