Progress of ultrafast terahertz time-domain spectroscopy: Raman inactive soft mode in quantum paraelectric SrTiO$_3$

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Abstract. We have measured the complex dielectric constants of quantum paraelectric SrTiO$_3$ (STO) bulk single crystals by using the ultrafast and broadband terahertz time-domain spectroscopy (THz-TDS) with the reflection configuration. The observed complex dielectric dispersion consists of the Raman inactive TO1 soft mode and is well reproduced by damped harmonic oscillator model where the resonant frequency and the damping constant are 2.75 THz and 0.63 THz, respectively, in good agreement with the previous reports. The ultrafast THz-TDS used in this study employs the technique of high-speed asynchronous optical sampling and Cherenkov type THz generator. The sampling time of one scan is about 10 milliseconds and available frequency of the THz source is from 0.5 to 7 THz. The reflection configuration combined with the ultrafast system enabled to detect the dispersion of a STO bulk sample which has high permittivity and opaque in the THz region.

1. Introduction
Terahertz time-domain spectroscopy (THz-TDS) which is one kind of far-infrared measurement technique is a powerful tool for THz material science [1-4]. THz-TDS records a time-domain waveform of the electric field of the THz electromagnetic wave. Since the measured THz waveforms have information of both amplitude and phase of the electric field, the complex optical constants can be determined directly without the Kramers-Kronig relation.

One of disadvantage of THz-TDS is a long measurement time due to the mechanical delay stage. The measurement time of the THz pulse shape by conventional THz-TDS is about several minutes and this long measurement time causes inaccuracy in experiment. But recently, ultrafast THz-TDS measurement technique has been established using high-speed asynchronous optical sampling (AOS) technique [5]. This technique uses two femtosecond lasers in substitution for mechanical delay stage, and the repetition rates of those lasers are slightly modulated. The AOS technique drastically decreases measurement time down to about 10 milliseconds for one shot of THz pulse. In addition to the ultra-fast scan of THz-TDS, we can use widely tunable monochromatic Cherenkov phase-matched THz wave generator, which was developed using nonlinear optic crystals of ferroelectric MgO doped LiNbO$_3$ [6].

In condensed matter physics, terahertz photon energy (1 THz = 4.14 meV) corresponds to minimal energy comparing to Fermi energy in electronic structure and corresponds to low-frequency optical phonon energy in phonon structure. Therefore, THz light is appropriate for the detection of such
electronic and phonon structure [2, 3]. But THz light is opaque for the metallic and ferroelectric materials due to the high conductivity or high permittivity. So that THz-TDS with reflection configuration having large advantage for conventional FT-IR spectroscopy is strongly required for those materials.

SrTiO₃ (STO) is well known as a quantum paraelectric material, and has perovskite structure (space group: \( \text{Pm\tilde{3}m} \)) at room temperature [4, 7-10]. STO has infrared active but Raman inactive TO1 soft phonon mode in around 3 THz. Due to this soft mode, STO is opaque and has high reflectivity in the THz region. Therefore, the soft mode was studied by Raman scattering by the application of electric or stress fields to suppress the centrosymmetry. While, the study of soft mode without any external fields is very important, because structural phase transitions are very sensitive to external fields.

In this study, we measured TO1 soft mode of a STO bulk single crystal using the ultrafast and broadband THz-TDS with reflection configuration, in addition to the transmission measurement below 2 THz. The combination of two configuration measurements enables the accurate determination of the frequency dependent complex dielectric constant directly without any assumptions.

2. Experimental

The (100) plate of STO single crystal from Furuuchi Chemical, whose size is 10 × 10 × 0.5 mm³ with two optically polished surfaces, was used in this study. The reflectivity spectra were measured by ultrafast THz-TDS (TAS7500SU, Advantest Co.) using a Cherenkov type THz generator and the high-speed AOS technique at room temperature. The reflection configuration is near normal incident and incident angle is about 12º. As a reference, a mirror polished aluminium plate was used. As shown in figure 1, the reflectivity reference THz spectrum has a frequency range of from 0.5 to 7 THz.

![Figure 1](image.jpg)

**Figure 1.** Power spectrum of the broad band THz pulse reflected from an aluminum reference mirror. An available frequency range is from about 0.5 to 7 THz. For convenience, 1 THz = 33.3 cm⁻¹ = 4.14 meV = 48 K.

3. Results and Discussion

Figures 2(a) and (b) show the measured reflectivity and phase shift of a STO single crystal at room temperature. The reflectivity increases toward higher frequency and shows strong increase especially around 2.5 THz. Those reflectivity behaviors are consistent with the reflectivity spectrum of damped harmonic oscillator (DHO) and the observed mode is assigned to TO1 soft mode.

The measured phase shift, which is shown at figure 2(b) by a red solid line, increases toward higher frequency corresponding to reflectivity behavior. In the reflectivity measurement, the reference and
the sample have position discrepancy caused by technical inaccuracy of the sample setting on the sample stage. The discrepancy causes incorrect determination of the complex optical constants. To eliminate the position discrepancy between an aluminium reference and the STO sample, we correct the measured phase shift by the following procedure. First, we measured the STO sample by transmission configuration and extracted the complex dielectric constants. The results of the transmission measurements are shown in figures 3(a) and (b) by open squares. Since the results of transmission THz-TDS measurements for STO bulk sample have high accuracy as shown in figure 3, we fitted the results of the reflectivity measurement by using the transmission data. The measured waveform of the sample is shifted with 6.7 femtoseconds toward the reference peak direction and finally the corrected phase shift is obtained by Fourier transform of the shifted time-domain waveform. Using the reflectivity and the corrected phase shift shown in figure 2(b) by a blue dashed line, we extracted the complex refractive index by the following equation,

$$n = n' + i \cdot n''$$

where $$n = n' + i \cdot n''$$ is the complex refractive index. $$E_{\text{sam}}(\omega)$$ and $$E_{\text{ref}}(\omega)$$ are the complex amplitude spectra of the THz pulse reflected from the sample and the aluminium reference mirror, respectively. The extracted complex refractive index is converted to the complex dielectric constant by the following relation,

$$n = \sqrt{\frac{E_{\text{sam}}(\omega)}{E_{\text{ref}}(\omega)}} \approx \frac{1 - n}{1 + n}$$

Figure 2. (a) Reflectivity and (b) phase shift of STO. Solid lines (red) and a dashed line (blue) are raw and corrected data, respectively.
Figure 3. (a) Real and (b) imaginary parts of complex dielectric constant of STO single crystals at room temperature. Filled circles are the results of the reflectivity measurements. Open squares are extracted from the transmission measurements. Solid lines are the fitting results of a single DHO model.

Table 1. Fitting parameters for TO1 soft mode of STO at room temperature.

| $\varepsilon_{dc}$ | $\omega_1$ (THz) | $S_1$ | $\Gamma_1$ (THz) |
|-------------------|------------------|-------|------------------|
| 331               | 2.75             | 308   | 0.63             |

where $\varepsilon = \varepsilon' + i \varepsilon''$ is the complex dielectric constant.

Figures 3(a) and (b) show the real and imaginary parts of complex dielectric constant, respectively. The entire structure of TO1 soft mode is clearly observed and the behaviour is consistent with frequency dependence of DHO model. The $\varepsilon'$ crosses zero and the $\varepsilon''$ peaks at 2.7 THz indicating the resonant frequency of the soft mode. The experimental results are fitted by a single DHO model as follows.

$$\varepsilon(\omega) = \varepsilon_{dc} + \frac{S_1 \omega_1^2}{\omega_1^2 - \omega^2 - i \omega \Gamma_1},$$

(3)
with \( \varepsilon_r = \varepsilon_{dc} - S_1 \), where \( \varepsilon_{dc} \) is static dielectric constant, \( \omega_1 \), \( S_1 \) and \( \Gamma_1 \) are resonant frequency, oscillator strength and damping constant of TO1 soft phonon mode, respectively. The parameters obtained by the fitting are listed in Table I. The resonant frequency and the damping constant are 2.75 THz and 0.63 THz, respectively and those results are consistent with previous studies [4, 7-10].

4. Conclusion
We successfully obtained the complex dielectric constant of a quantum paraelectric STO single crystal using ultrafast and broadband THz-TDS with reflection configuration. The Raman inactive TO1 soft mode behavior is well reproduced by DHO model and the obtained fitting parameters are consistent with previous studies [4, 7-10]. The measurement of temperature dependence is in progress to clarify the soft mode behavior of quantum paraelectric STO, which can be related to the Barrett’s relation of dielectric permittivity [11]. This ultrafast and reflectivity measurement technique will be applicable to various bulk materials. The combination of reflectivity and transmission configuration measurements enables us to determine directly the reliable complex optical constants of opaque materials in the THz region without any assumptions.

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