Effect of optical pump on the dielectric properties of $SrTiO_3$ in terahertz range*

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Tuning the dielectric permittivity spectra of strontium titanate ($SrTiO_3$) single crystals in an external optical field is investigated at room temperature by means of terahertz time-domain spectroscopy. The application of the optical field leads to an appreciable tuning of the permittivity, reaching up to 2.8%, with the dielectric loss changing about 3%. The observed behavior is interpreted in terms of soft-mode hardening due to the anharmonic character of its potential. We also find that the change of the refractive index responds linearly to the applied light power. These findings are attributed to a linear electro-optical effect of the internal space charge field of the crystal.

Keywords: THz materials, optical constants, ferroelectrics

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1. Introduction

Strontium titanate ($SrTiO_3$, STO) is an incipient ferroelectric material with the ABO_3 perovskite-type structure. It shows a strong ferroelectric soft mode, which is the fundamental determinant of its dielectric properties. Thus, the dielectric properties of STO can be tuned effectively through the modulation of its soft mode. Together with its remarkably high dielectric permittivity and low microwave loss, STO is very attractive and popular not only for the fundamental research but also for the device applications.

Recently, the properties of STO in the terahertz spectral range have drawn the attention of many researchers.[1–16] Miyamaru *et al* investigated the transmission characteristics of an STO hole array in the THz region and observed a resonant transmission peak.[3] Mechelen *et al* investigated the electron–phonon interaction and the charge carrier mass enhancement in an electron-doped STO and observed an unusually narrow Drude peak.[4] Rubano *et al* proposed a new method measuring the dielectric function of opaque materials such as STO in the frequency range from 8 THz to 30 THz.[5] Han *et al* investigated the low-frequency dielectric and optical properties of powder form ferroelectric STO using terahertz time-domain spectroscopy (TDS).[6] Katayama *et al* reported that the ferroelectric soft mode in an STO thin film can be driven to a large amplitude by monocycle terahertz pulses.[11] The electric-field tunability of STO in terms of soft-mode hardening has been extensively studied.[1,2,13] The temperature dependence of the ferroelectric soft mode in structures such as STO film and $SrTiO_3/DyScO_3$ heterostructure have also been investigated.[7,8,10]

In the above findings, most observations have been carried out by electric-field tuning. The dielectric properties of the soft-mode behavior under an optical field in bulk STO obtained by THz spectroscopy, however, have rarely been reported due to the large forbidden band gap of STO. However, the local defects in the crystal could make the optical tuning possible.[17] Moreover, only a few observations of the STO single crystal tunability at room temperature have been reported.[12,13] For practical applications, it is necessary for the permittivity to be modulated over as wide a range as possible around room temperature. In this paper, we report a study of the dielectric properties and the optical-field-induced tunability of bulk STO at room temperature.

2. Experiment

The investigated STO crystals were purchased from MTI Corp. The dimensions of the studied samples were 10 mm× 10 mm× 0.5 mm and 10 mm× 10 mm× 0.34 mm. The crystal orientations of the samples were ⟨100⟩.

We used a THz time domain spectrum (THz-TDS) system produced by the Zomega Terahertz Corporation of the US to measure the transmittance spectrum at room temperature, as shown in Fig. 1. In this THz-TDS system, a fiber femtosecond laser beam (center wavelength 780 nm, repetition rate 50 MHz, pulse width 90 fs) was divided into two beams (named the pump beam and the probe beam, respectively) by a polarized beam splitter PBS1. A half wave plate HWP was placed to change the ratio between the pump beam and the probe beam. The pump beam was directed though retro-reflector RR1, a quarter wave plate QWP1, and PBS1 to

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lens L1 then focused on a GaAs emitter to generate the THz radiation. The probe beam was directed to PBS2 by mirrors M1 and M2. The reflected beam passed through QWP2 and then was reflected by RR2 and mirror M3. The RR1 and RR2 were attached together on a linear step stage to form a time delay line. After two passes through PBS2, the probe beam was directed to a ZnTe crystal and a balance detector (BD) through two mirrors (M4 and M5), lens L2, and an ITO crystal. Meanwhile, the generated THz radiation was collimated by an off-axis parabolic mirror OAP1, and passed through two confocal polyethylene lenses L3 and L4. The sample was placed at the focus of L3 and L4. At last, the transmitted THz radiation was focused by OAP2 and reflected by the ITO crystal to the ZnTe crystal and BD for coherent detection. The detectable frequency range was from 0.1 THz to 3 THz (3.3 cm^{-1} to 100 cm^{-1}) with a dynamic range of more than 70 dB. The measured frequency resolution was 10 GHz, and the spot size at the focus was 3 mm. An all-solid-state continue-wave (cw) green laser (center wavelength 532 nm) was employed in the experiment to provide external optical pumping. The light was obliquely incident upon the surfaces of the samples at an angle of 45° and the spot size was 5 mm in diameter. Using a temperature control system, the temperature of the system was kept at 24 °C during the measurement.

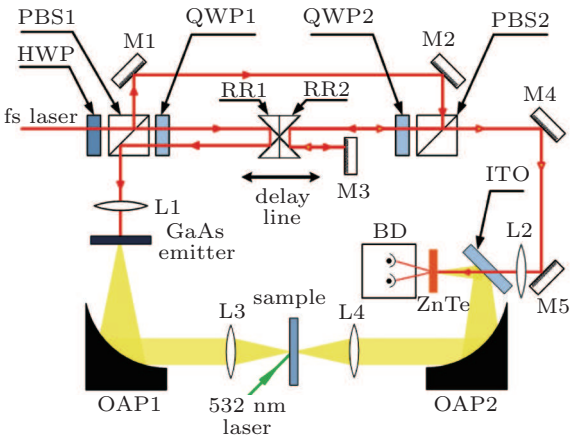


Fig. 1. (color online) Installation diagram of the TDS. A green laser is obliquely incident upon the surface of the sample at an angle of 45° with respect to the polar axis.

3. Results and discussion

Figure 2 shows typical experimental results of the terahertz time domain waveforms passing through the sample. The time lag between the reference and the sample is around 19 ps, as can be seen in Fig. 2(a). The signal waveforms transmitted through the STO samples show little change with increasing optical field amplitude. For example, the transmittance waveform shifts about 0.26 ps when the light pump power is 600 mW, compared to that without light excitation.

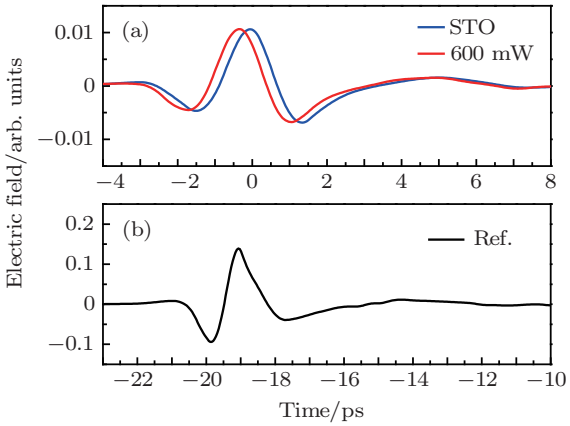


Fig. 2. (color online) (a) Time domain transmittance waveform of STO crystals and its time shift under an external optical field at room temperature. The red line represents the data at $P = 600$ mW; the blue line represents those without an optical pump. (b) The reference waveform.

Through a Fourier transform, we calculated the complex transmittances and the intrinsic phases in the frequency domain from the waveforms in Fig. 2. The complex refractive index $N(f)$ and permittivity $\varepsilon(f)$ were then retrieved from the THz transmittance spectra. Figure 3 shows examples of THz complex dielectric spectra of the samples under different external optical fields. The detectable frequency range is from 0.1 THz to 0.8 THz (3.3 cm^{-1} to 26.6 cm^{-1}), since even the thinnest bulk STO samples are completely opaque above ~ 1 THz.[13] Both the real and the imaginary parts of the permittivity decrease with an increasing pump power.

For the STO samples, the nonlinear response in the THz range can be described by a classical harmonic oscillator model, where the soft-mode frequency is tunable by the external optical field

$$\varepsilon(\omega, I) = \frac{f}{\omega_0^2(I) - \omega^2 - \mathrm{i}\omega\Gamma} + \varepsilon_\infty. \tag{1}$$

Here ω_0 is a bare eigenfrequency, Γ is the damping coefficient, f is the oscillator strength, and ε_∞ is a cumulative contribution to the permittivity caused by higher-frequency excitations such as hard phonons and electrons. In principle, the soft-mode damping Γ can be weakly optical field dependent, although no field dependence of the damping coefficient has been found in the strained STO thin films.[12] As a rule, the oscillator strength f can be considered to be a constant, so the permittivity value in the THz range crucially depends on the soft-mode frequency.

Figure 3(a) shows the frequency dependence of the real part of the dielectric constant $\varepsilon'(f)$ and its variation under different external optical fields of STO (the oscillation in the low frequency range is supposed to be the influence of noise). In Fig. 3(a), the lines represent the fits of the experimental data by an underdamped harmonic oscillator model given by Eq. (1). The oscillator strength f and the high-frequency permittivity

ε_∞ do not change with the optical field; their values are obtained from Ref. [12] and are fixed for all our fits in this paper. In the frequency range of 0.1–0.8 THz, the dielectric constant of STO is about 300–310. The measured permittivity is found to be tunable by up to 2.8% via the application of an external optical field, and the dielectric constant nonlinearly decreases with the power of the green laser increasing. The $\omega_0(I)$ shifts from 88.97 cm^{-1} to 90.25 cm^{-1}, which indicates soft-mode hardening due to the anharmonic character of its potential. When the light power is 600 mW, the largest field-induced change in the soft mode frequency reaches 1.28 cm^{-1}, which is $\sim 1.4\%$ of the frequency of the soft mode. Figure 3(b) demonstrates that the imaginary part of the dielectric constant also shows some differences, indicating that the dielectric loss changes appreciably ($\sim 3\%$) with the external optical field.

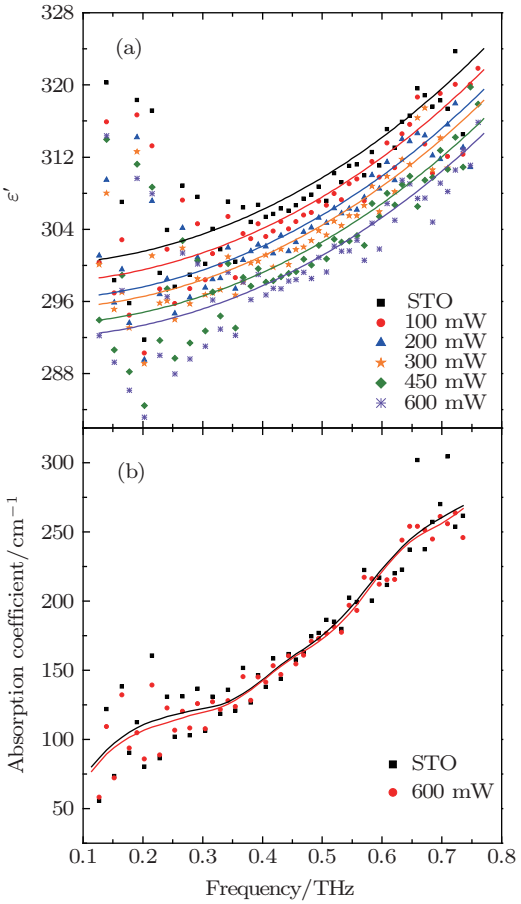


Fig. 3. (color online) Frequency dependences of (a) the real part and (b) the imaginary part of the complex dielectric constant of STO with different external optical fields at room temperature.

In order to illustrate the photo-ferroelectric properties in STO, it is worthwhile studying the variation of its refractive index. Figure 4 shows the modulation of the refractive index as a function of the applied light power and its linear fit. The variation of refractive index $|\Delta n|$ is found to be linearly proportional to the intensity of the applied light. The results can be described using the following relationship proposed by Chen:[17]

$$\Delta n = \frac{1}{2}(n_o^3\gamma_{13} - n_e^3\gamma_{33})E \propto I, \tag{2}$$

where n_o and n_e are the refractive index of the ordinary light and that of the extraordinary light, respectively, γ_{ij} is the linear optoelectronic coefficient, and E is the internal space charge field. This result indicates that the variation of the refractive index dispersion for STO may be attributed to the internal space charge field of the crystal that is caused by excited free carriers.

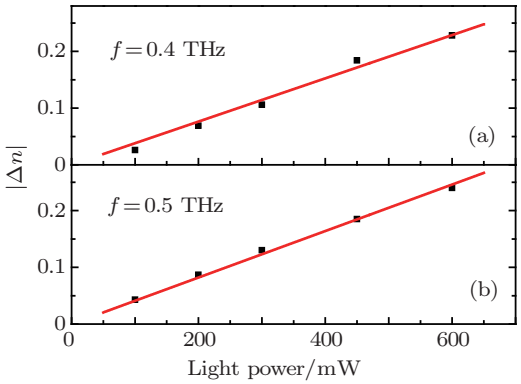


Fig. 4. (color online) Light power dependence of variation of refractive index at (a) 0.4 THz and (b) 0.5 THz for STO samples. The data points are our measured values, and the solid lines are the fits using Eq. (2).

The micro mechanisms behind the observed effect here are discussed as follows. Generally, there are only Ti^{4+} ions in STO single crystals; the local defects could also result in the presence of Ti^{3+} ions at the surfaces of the specimens.[18] Titanium has a deep center, and thermal excitations are negligible here. When applying an external optical field, there could be an exchange of electrons between Ti^{3+} and Ti^{4+} ions. The Ti-3d electrons in Ti^{3+} ions can hop to the conduction band; they migrate in a preferred direction and then are captured by the trap level of Ti^{4+}. The dominant charge driving force is supposed to be the photovoltaic effect. Drift and diffusion could also contribute to the movement of the electrons. The migration process would lead to a redistribution of carriers. The space displacements of carriers lead to an internal space charge field shielding the external field. The internal space charge field changes the refractive index of the sample through the linear electro-optic effect,[17] as shown in Fig. 4.

In most conditions, both the photovoltaic effect and the shielding mechanism induced by photocarriers play roles in the dielectric response of the compounds. The two mechanisms complement each other, resulting in the observed properties of the specimens. Such a variation in the dielectric response could be used in an amplitude modulator in the terahertz range. We can also see great potential for applications of active strontium titanate in the design and fabrication of active metamaterials for the terahertz regime.[19–22]

4. Conclusion

In summary, we have investigated the optical-field-induced tunability of the dielectric properties of bulk strontium titanate single crystals using terahertz time-domain spectroscopy at room temperature. A hardening of the soft mode under the external optical field fully accounts for the variation of the dielectric properties. An appreciable variation of the refractive index in STO with different levels of external optical fields is also demonstrated. This property originates from the photovoltaic effect caused by photo-induced carriers apart from their shielding effect, leading to an internal space charge field. Thus it is presumed that these two mechanisms complement each other, resulting in the observed photo-ferroelectric behaviors of STO. The results of this paper provide a reference point for further development of tunable structures (such as photonic crystals and/or metamaterials) that can be controlled by an external field.

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