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Citation: *Appl. Phys. Lett.* **90**, 031104 (2007); doi: 10.1063/1.2431448

View online: <http://dx.doi.org/10.1063/1.2431448>

View Table of Contents: <http://aip.scitation.org/toc/apl/90/3>

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Dielectric response of soft mode in ferroelectric SrTiO₃

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(Received 6 September 2006; accepted 7 December 2006; published online 16 January 2007)

The authors report far-infrared dielectric properties of powder form ferroelectric SrTiO₃. Terahertz time-domain spectroscopy (TDS) measurement reveals that the low-frequency dielectric response of SrTiO₃ is a consequence of the lowest transverse optical (TO) soft mode TO1 at 2.70 THz (90.0 cm⁻¹), which is directly verified by Raman spectroscopy. This result provides a better understanding of the relation of low-frequency dielectric function with the optical phonon soft mode for ferroelectric materials. Combining terahertz TDS with Raman spectra, the overall low-frequency optical phonon response of SrTiO₃ is presented in an extended spectral range from 6.7 to 1000.0 cm⁻¹. © 2007 American Institute of Physics. [DOI: 10.1063/1.2431448]

Since the discovery of the polar soft mode in strontium titanate (SrTiO₃) crystals, there has been a great interest and challenge to understand the behaviors of dielectric properties of ferroelectric materials, particularly to explore the relationship between the dielectric properties and the optical phonon responses.¹⁻³ As an incipient ferroelectric material SrTiO₃ of the perovskite structure plays a very important role among the ferroelectrics family, ABO₃ compounds. Because of the remarkably high dielectric permittivity, tunability, and low microwave loss, SrTiO₃ becomes very attractive and popular not only for fundamental research but also for device applications. It is an important material in high-storage-density capacitor structures, such as dynamic random access memory, because of high static dielectric constant.⁴ SrTiO₃ has also been utilized in various tunable microwave devices.^{5,6} In addition, the unique characteristics of SrTiO₃ make it a material of choice for applications in terahertz devices, particularly for controlling terahertz radiation and devices.⁷ The dielectric properties of SrTiO₃ are closely related to its low-frequency optical phonon modes.

In this letter, we study the dielectric response of powder form SrTiO₃ in the frequency range from 0.2 THz (6.7 cm⁻¹) to 2.0 THz (66.7 cm⁻¹) by use of terahertz time-domain spectroscopy (TDS).⁸⁻¹² The experimental results are well fit by the classical pseudoharmonic model. To verify the terahertz TDS measurements, the optical phonon resonance of SrTiO₃ is also characterized by Raman light scattering. Our results reveal that the dielectric response of SrTiO₃ in the terahertz region is dominated by the lowest transverse optical (TO) soft mode TO1 at frequency ($\omega_{\text{TO}}/2\pi$) 2.70 THz (90.0 cm⁻¹). The complex low-frequency optical phonon response processes of SrTiO₃ are depicted in a broad spectral range (6.7–1000.0 cm⁻¹) by combining terahertz TDS with Raman spectroscopy. The terahertz TDS results of powder form SrTiO₃ are compared

with those of different forms of SrTiO₃, demonstrating that the powder form SrTiO₃ shows similar dielectric response behaviors of single-crystalline and thin-film SrTiO₃.

The SrTiO₃ sample (Sigma-Aldrich) has a purity of higher than 99%, a room-temperature density of 4.81 g/ml, and an average grain size of less than 5 μm . The sample for analysis was prepared by milling the powder carefully and then placed in a cell with two parallel windows made from 636- μm -thick, *p*-type 20 $\Omega\text{ cm}$ silicon slabs.¹¹ An identical empty cell was used as a reference. The photoconductive switch-based terahertz TDS system employed here has a useful bandwidth of 0.1–4.5 THz and a signal-to-noise ratio (S/N) > 10 000:1 as described previously.^{11,12}

Figure 1 shows the terahertz TDS transmission spectra of powder absorption $\alpha(\omega)$ and refractive index $n(\omega)$ of the

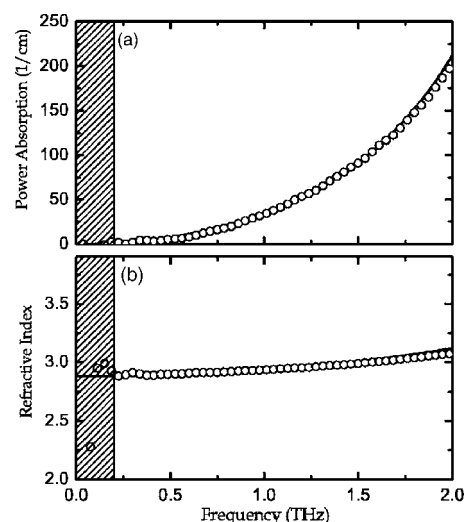


FIG. 1. (a) Terahertz-TDS measured power absorption α (open circles) and the theoretical fitting through the classical pseudoharmonic model and the Bruggeman effective medium approximation (solid curve); (b) measured refractive index (open circles) and the theoretical fitting (solid curve).

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SrTiO₃ sample. In order to increase the S/N, the experimental data are averaged on seven individual measurements. The power absorption is enhanced with increasing frequency; no prominent absorption peaks are observed below 2.0 THz as confirmed by the refractive index that shows no prominent changes. The frequency-dependent complex dielectric function of SrTiO₃ is determined by the recorded data of the power absorption and the refractive index through the relationship $\varepsilon(\omega) = (n_r + in_i)^2$, where the imaginary part of the refractive index n_i is related to the power absorption as $n_i = \alpha\lambda/4\pi$. Hence the real and imaginary dielectric constants are determined as $\varepsilon_r = n_r^2 - (\alpha\lambda_0/4\pi)^2$ and $\varepsilon_i = \alpha n_r \lambda_0/2\pi$, respectively.¹² The observed real and imaginary parts of the complex dielectric function are shown by open circles in Fig. 2.

Since the measured sample is a composite medium of SrTiO₃ and air, the dielectric constant shown in Fig. 2 is an effective quantity ε_{eff} . Hence, the dispersion of the dielectric constant in the terahertz region is analyzed by the use of the Bruggeman theory, one of the most commonly used effective medium approximation (EMA). The Bruggeman EMA is given by¹³

$$f \left(\frac{\varepsilon_m - \varepsilon_{\text{eff}}}{\varepsilon_m + 2\varepsilon_{\text{eff}}} \right) + (1-f) \left(\frac{\varepsilon_h - \varepsilon_{\text{eff}}}{\varepsilon_h + 2\varepsilon_{\text{eff}}} \right) = 0, \quad (1)$$

where f is the filling factor that defines the volume fraction of SrTiO₃. ε_h and ε_m are the dielectric constants of the host medium and the pure SrTiO₃, respectively. In this case, the host medium is air, giving $\varepsilon_h = \varepsilon_{\text{air}} = 1.0$. The dielectric function ε_m for pure SrTiO₃ can be calculated by the simple classical pseudoharmonic model, where the interaction of a radiation field with the fundamental lattice vibration results in absorption of electromagnetic wave due to the creation or annihilation of lattice vibration. In the frame of the classical pseudoharmonic model, the complex dielectric function can be expressed as¹⁴

$$\varepsilon_m(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)\omega_{\text{TO}}^2}{\omega_{\text{TO}}^2 - \omega^2 - i\gamma\omega} = \varepsilon_{mr} + i\varepsilon_{mi}, \quad (2)$$

where ε_∞ is high-frequency dielectric constant, ε_0 is low-frequency dielectric constant, ω_{TO} is the angular frequency of the transverse optical phonon mode, and γ is the damping constant.

The solid curves in Figs. 1 and 2 represent the theoretical fitting to the measured power absorption, refractive index, and complex dielectric function with the lowest transverse optical soft phonon mode centered at $\omega_{\text{TO}}/2\pi = 2.70 \pm 0.10$ THz and with a linewidth $\gamma/2\pi = 1.30 \pm 0.10$ THz. The optical constants used in the fitting are $\varepsilon_\infty = 5.20$ and $\varepsilon_0 = 310$,² and the filling factor f is estimated to be 0.31. The parameters are determined with good accuracy by the fitting on the real and imaginary parts of the dielectric function simultaneously. The determined eigenfrequency of the soft mode 2.70 THz is quite consistent with that observed in the bulk crystals and thin films.^{2,4,5,15} The good agreement between the experimental data and the theoretical fitting shown in Figs. 1 and 2 indicates that the low-frequency terahertz response of SrTiO₃ is mainly attributed to the lowest soft phonon mode TO1 located at 2.70 THz.

Generally, the phonons of SrTiO₃ are triply degenerate F_{1u} modes, and the dielectric response is mainly ascribed to

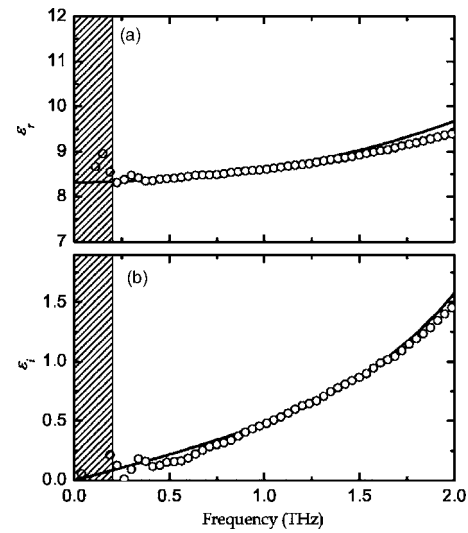


FIG. 2. Complex dielectric constant of SrTiO₃: (a) measured real part of dielectric constant ε_r (open circles) and the theoretical fitting (solid curve); (b) measured imaginary dielectric constant ε_i (open circles) and the theoretical fitting (solid curve).

the contribution of three ferroelectric TO modes. The lowest ferroelectric optical soft mode TO1 is induced predominantly by Ti–O–Ti bending; TO2 is mainly due to Sr against TiO₆ octahedra translations; TO4 includes Ti–O stretching; and TO3 (F_{2u}) is a silent mode and optical inactive.^{3,16,17} Both TO2 and TO4 are temperature independent and have a very slight variation in the magnitude of dielectric strengths and eigenfrequencies when temperature varies. According to the previous experimental reports, the typical eigenfrequencies of TO2 and TO4 modes are located at 178.0 and 546.0 cm⁻¹, respectively. The eigenfrequency of soft mode TO1 depends mostly on temperature and both its strength and eigenfrequency have distinct changes with temperature. Its frequency decreases drastically at lower temperatures, while the magnitude of dielectric constant increases at the mean time. In fact, TO1 is both Raman and IR active; however, it is difficult for conventional IR reflection and Raman techniques to resolve the lowest soft mode, especially at low temperatures. This is because the frequency value of TO1 mode is beyond the reliable measurement range. The previous fit to the infrared and Raman measurements showed that the eigenfrequency of optical soft mode TO1 was near 90.0 cm⁻¹ at room temperature,^{3,4} which agrees well with our extrapolated results based on the fitting to the terahertz TDS data. A further obvious understanding of such phonon features requires direct measurement of the soft TO1 mode. However, terahertz TDS does not cover up to 90.0 cm⁻¹ due to the fact that the SrTiO₃ sample is highly absorptive at frequencies above 2.0 THz (66.7 cm⁻¹). Therefore, Raman light scattering is utilized as a complement of terahertz TDS to extend the spectral range to higher frequencies.

The Raman spectrum was excited with the 514.5 nm line of an argon ion laser with a beam spot focused down to 5 μm in diameter. Figure 3 shows completed optical response processes over a frequency range from 6.7 to 1000.0 cm⁻¹ by combining terahertz TDS and Raman spectroscopy. The solid curve illustrates the Raman spectrum of the SrTiO₃ beginning from 67.0 cm⁻¹, while the open circles represent the recorded data by terahertz TDS at lower frequencies. The Raman spectrum reveals four broad optical phonon bands that correspond to the active vibrational

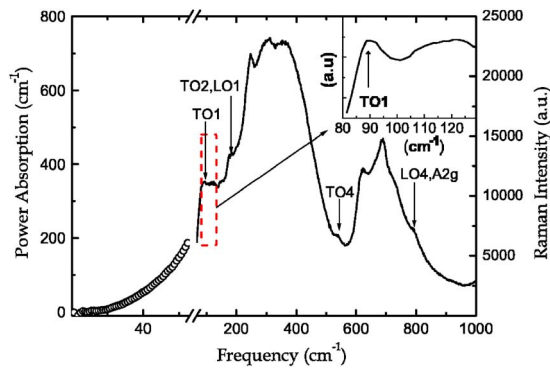


FIG. 3. (Color online) Completed low-frequency optical response of SrTiO_3 : the open circles are measured by terahertz-TDS in the frequency region of 6.7–66.7 cm^{-1} , and the solid curve is the Raman spectrum recorded from 67.0 to 1000.0 cm^{-1} . The inset shows the detailed feature of the measured TO1 mode.

modes of F_{1u} symmetry: the lowest optical soft mode TO1 at 90.0 cm^{-1} , the TO2-LO1 band near 170.0 cm^{-1} , the TO4 mode at 539.0 cm^{-1} , and the LO4-A2g band at 793.0 cm^{-1} . The other abundantly observed features are related to the additional active modes. These optical responses show good consistency with the previous work on SrTiO_3 thin-film and ceramic samples.^{3,7,18,19} The inset of Fig. 3 shows the magnified features of the TO1 mode at frequencies between 80.0 and 130.0 cm^{-1} . The Raman spectrum has confirmed that the dielectric properties of SrTiO_3 characterized by terahertz TDS is indeed dominated by the soft TO1 mode at 90.0 cm^{-1} .

Additionally, the terahertz TDS results of powder SrTiO_3 are compared with that of single-crystalline and thin-film SrTiO_3 . The $\langle 100 \rangle$ oriented single-crystalline SrTiO_3 is undoped, with dimensions of $10 \times 10 \times 0.5 \text{ mm}^3$ and high dielectric constant of ~ 300 (MTI Corporation). Figure 4 illustrates a comparison of power absorption and refractive index between different forms of SrTiO_3 . The measured results of single-crystalline SrTiO_3 are well fit by the classical pseudoharmonic model in Eq. (2), while the data of pure powder are extracted through EMA of Eq. (1) and are fit with

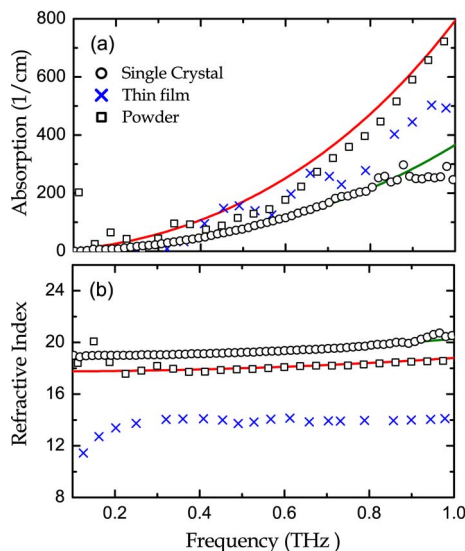


FIG. 4. (Color online) Comparison of terahertz-TDS results of (a) power absorption and (b) refractive index of pure powder SrTiO_3 (squares) with that of single-crystalline (circles) and thin-film (crosses, obtained from Ref. 7) SrTiO_3 . The solid lines represent theoretical fit.

Eq. (2). The theoretical fitting indicates that the terahertz response of single-crystalline SrTiO_3 is also dominated by the soft mode TO1 at 90.0 cm^{-1} . The data of thin film for comparison are obtained from Ref. 7. Compared to single-crystalline and thin-film SrTiO_3 , the powder form shows slightly higher absorption, but all these samples have similar frequency-dependent behaviors. At 0.5 THz, the refractive index of thin film (13.9) and pure powder (18.0) are close to the value 19.2 of single-crystalline SrTiO_3 , but much higher than 3.0 for the composites [Fig. 1(b)] due to inclusion of air in the latter. The above comparison has shown that the powder form SrTiO_3 has similar dielectric properties and low-frequency optical response with that of single-crystalline and thin-film SrTiO_3 .

In summary, we have investigated the low-frequency dielectric and optical properties of powder form ferroelectric SrTiO_3 . The terahertz TDS study implicates that the dielectric constant of SrTiO_3 is highly correlated with the lowest optical soft phonon mode at 90.0 cm^{-1} . The combination of terahertz TDS and Raman light scattering is demonstrated as a powerful approach to explore the low-frequency dielectric properties associated with optical phonon resonances in semiconductors and composite materials. The comparison among different forms of SrTiO_3 reveals that the powder form SrTiO_3 exhibits similar low-frequency dielectric properties with that of single-crystalline and thin-film SrTiO_3 .

The authors acknowledge the efforts of A. K. Azad. This work was partially supported by the National Science Foundation and the Oklahoma EPSCoR for the National Science Foundation.

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