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RESEARCH ARTICLE

Terahertz frequency characterization of anisotropic structure of tourmaline

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Abstract The absorption coefficient and refractive index of tourmaline in different directions were characterized for the first time using terahertz time-domain spectroscopy. Results show that the absorption and refractive index of terahertz frequency are related to the structure of tourmaline. Absorption along the optical axis direction is more sensitive than that along the vertical direction. This result indicates that the identification and characterization of crystals as well as minerals can be realized by the terahertz method.

Keywords tourmaline, optical properties, terahertz spectroscopy

1 Introduction

Terahertz time-domain spectroscopy (THz-TDS) is a method used for the measurement of the real and imaginary parts of the complex index of refraction, complex dielectric constant, and complex conductivity of materials in the 0.1 to 10 THz frequency band [1,2]. This method was invented and developed in the last two decades by researchers in the fields of optics and semiconductor physics. Spectroscopy permits the measurement of the absolute values of the real and imaginary parts of the complex index of refraction with a well signal-to-noise ratio [3]. Based on measurements of the time dependence of the electric field of a short electromagnetic pulse transmitted through a sample, the ratio of the Fourier transforms of measured data with and without the sample yields a complex spectroscopy of the sample in the frequency domain. The major advantages of this method are its high potential for material characterization and nondestructive testing, which have been demonstrated for numerous applications, such as the characterization of anisotropic crystal structures [4], characterization of diesel fuel oil, biological macromolecules [5,6], biomedical and pharmaceutical applications [7,8], and the detection of hazardous or illicit substances [9,10]. Tourmaline, as an anisotropic and natural crystal, has had its optical constants characterized by terahertz frequency spectroscopy in previous research. One purpose of our work is the further application of THz technology in geosciences, and in particular, research into mineral structure.

Tourmaline is a complex borosilicate, its crystal structure is a trigonal system and often has three or hexagonal columnar [11,12] shape. It has been reported that tourmaline can be used for purifying the environment and other applications related to the health of the human body [13]. As a special mineral, the characterization of the dielectric and optical properties of tourmaline crystal in the terahertz band is essential, as it can be used to guide tourmaline modification, processing, and application development.

This paper reports on an experimental study of the optical properties of tourmaline in the wide frequency band of 0.3–2.2 THz (10–73 cm^{-1}) using THz-TDS. The results presented here for the first time demonstrate how THz-TDS can be used to characterize the dielectric properties of tourmaline. Furthermore, by using the optical constants of tourmaline as a reference you can use THz-TDS to identify other crystals and minerals.

2 Experimental

The spectrometer used in the experiment consisted of two parts, a typical transmission THz-TDS system from Daheng New Epoch Technology Inc, and a mode-locked femtosecond Ti sapphire laser. The Ti sapphire laser delivers 100 fs laser pulses with 800 nm wavelength at a pulse repetition rate of 80 MHz. The THz-emitter was a photoconductive antenna, and the THz-radiation pulses

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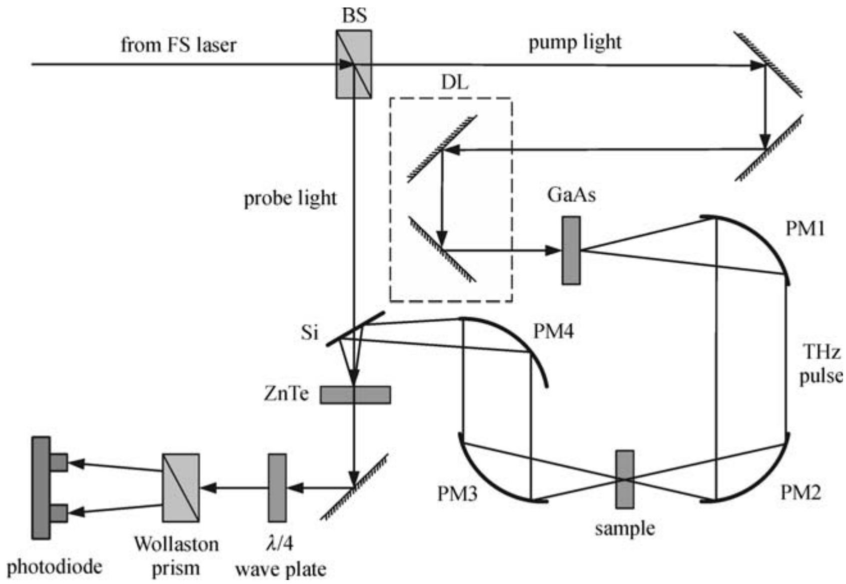

Fig. 1 Schematic diagram of the THz-TDS setup based on femtosecond-laser driven photoconductive emitter and electro-optic crystal detector (FS-femtosecond, BS-beam splitter, DL-delay line, PM-parabolic mirror)

were detected by electro-optic sampling using a ZnTe crystal and lock-in detection as shown in Fig. 1. The polarization direction of the terahertz pulse was horizontal. The spectrometer was purged with nitrogen gas. Measurements were conducted at the air-conditioned temperature of the laboratory, equivalent to (22.0±1.0)°C.

Two samples with dimensions of 1 mm × 10 mm × 10 mm were cut directly from one original crystal, which was black and mined from Brazil. As shown in Fig. 2, the cutting direction is perpendicular to the optical axis (*C* axis) for sample 1, while the cutting is along the *C* axis for sample 2. During measurements, sample 1 and sample 2 were perpendicular to the THz wave as shown in Fig. 3. Furthermore, different orientations of sample 1 along the THz horizontal polarization direction were measured; the angles were 0°, 30°, 60°, 90°, and the initial angle was randomly defined. For sample 2, two different orientations, perpendicular and parallel to the polarization direction of the THz pulse, were measured.

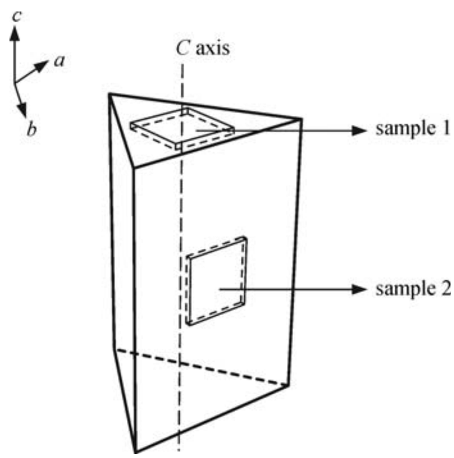

Fig. 2 Schematic diagram of sample cutting. For sample 1, the cutting direction is perpendicular to the *C* axis; for sample 2, the cutting is along the *C* axis direction

3 Results and discussion

Using the physical model of THz optical parameters [14,15], the frequency dependencies of the index of refraction and absorption coefficient were calculated from the time-domain THz transmission data. The absorption and the index of refraction versus frequency, for sample 1, are shown in Fig. 4. The data was considered accurate only up to 1.8 THz. Above this frequency, the absorption of the weak higher frequency components is so strong that the attenuated, transmitted spectral components became obscured by the detected system noise. The terahertz pulse vibration direction is vertical with respect to the *C* axis. Under this case, this pulse is an ordinary pulse. The dispersion of tourmaline in this band can be characterized by the index of refraction and the frequency. Based on the ordinary ray refractive index of 2.717 at 1 THz, and 2.737 at 1.8 THz, a quadratic relationship between the refraction index and the frequency was found. These results indicate that the variation of the refractive index with frequency is in agreement with the normal dispersion relation.

There is a relationship between vibration absorption and the tourmaline structure. In this experiment, the structure perpendicular to the *C* axis can be characterized by the absorption coefficient at different angles as shown in

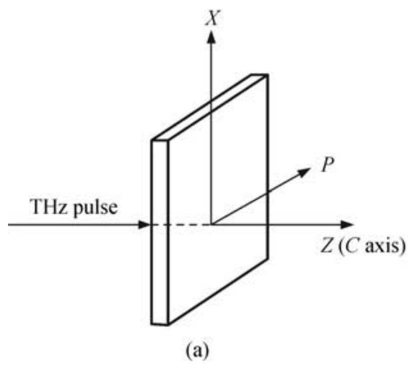

Fig. 3 Experimental schematic diagram of (a) sample 1 and (b) sample 2. The *Z* axis is the direction of propagation of the THz pulse, and the *P* axis is the polarization direction of the THz pulse. When rotating the sample 1, the polarization direction of the THz pulse is always perpendicular to the *C* axis of tourmaline. For sample 2, the polarization direction of the THz pulse is perpendicular to the *C* axis of tourmaline. When sample 2 is rotated by 90°, the polarization direction of the THz pulse is parallel to the *C* axis

Fig. 4(b). It can be seen that the absorption coefficients between the 0° and 60° plots, as well as between the 30° and 60° plots, present similar values. This is consistent with the triangular structure of the tourmaline.

According to the characteristics of terahertz waves, as well as the position of the resonance energy level of molecules, the transmission spectrum will exhibit absorption characteristics. The reason for this resonance absorption is generally the intermolecular rotation and vibration, weak molecular interactions, and the molecular group overall vibration mode [16].

For sample 2, the index of refraction and absorption versus frequency for the ordinary ray and extraordinary ray are presented in Fig. 5. The index of refractions for the ordinary ray and extraordinary ray were $n_o = 2.677$ and $n_e = 2.443$ at 1 THz, respectively, and $n_o = 2.702$ and $n_e = 2.466$ at 1.8 THz, respectively. It should be noted that the dispersion for the extraordinary ray is the same as that for the ordinary ray. The index of refraction between the extraordinary and ordinary ray at 1 and 1.8 THz have almost the same difference values of approximately 0.23, which results in the birefringence of tourmaline being

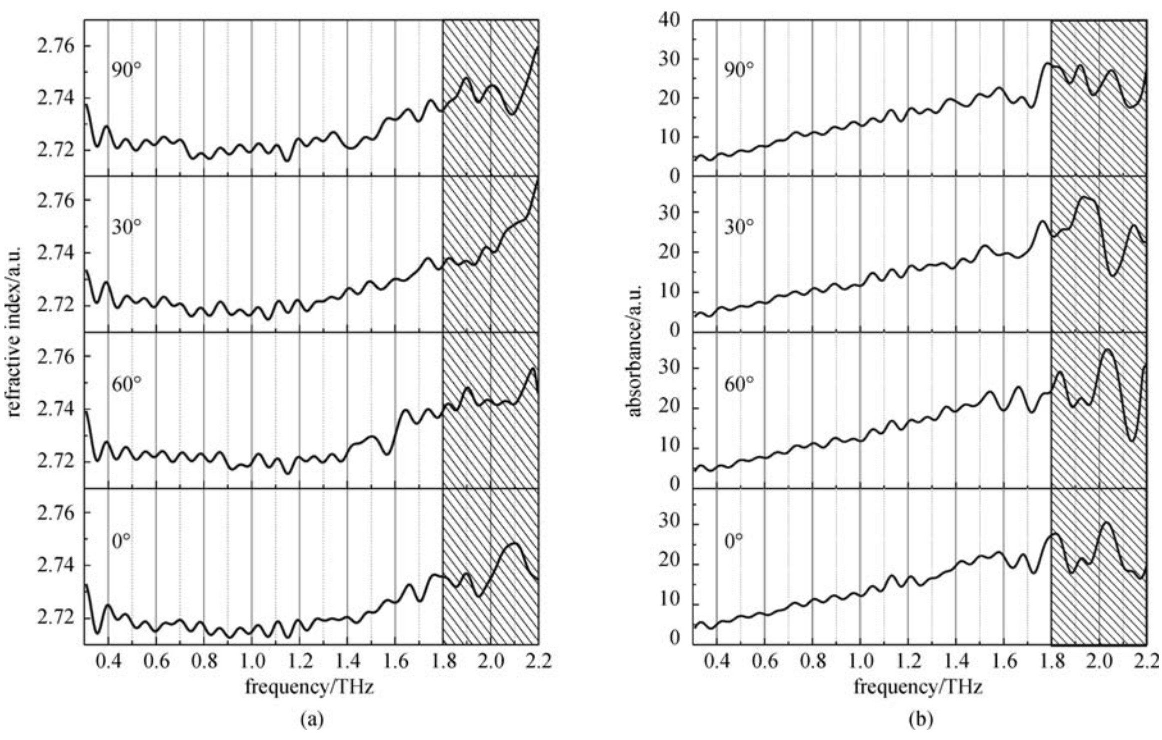

Fig. 4 Frequency dependencies of (a) refractive index and (b) absorption coefficient for sample 1. Replica measurements on four different sample orientations with different angles of 0°, 30°, 60°, 90°

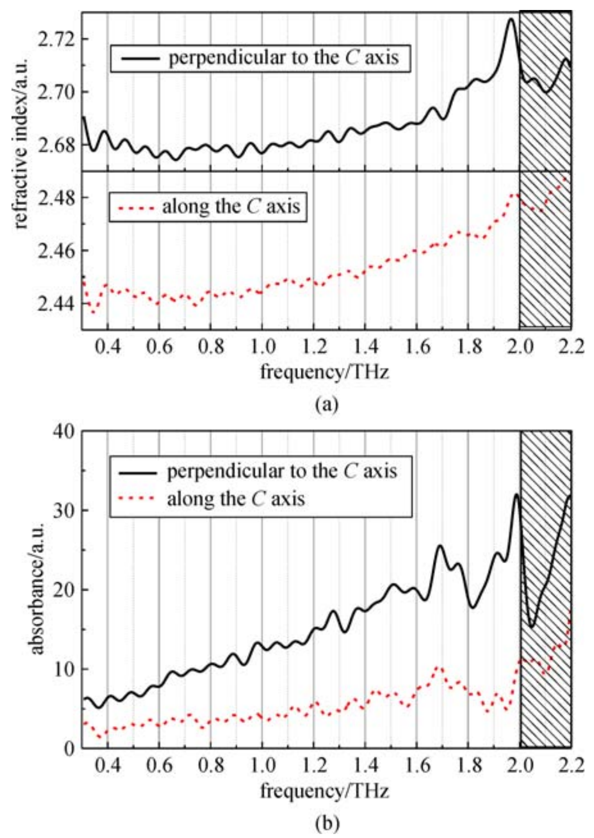

Fig. 5 Frequency dependencies of the refractive index and absorption coefficient for sample 2. Replica measurements of (a) ordinary ray and (b) extraordinary ray

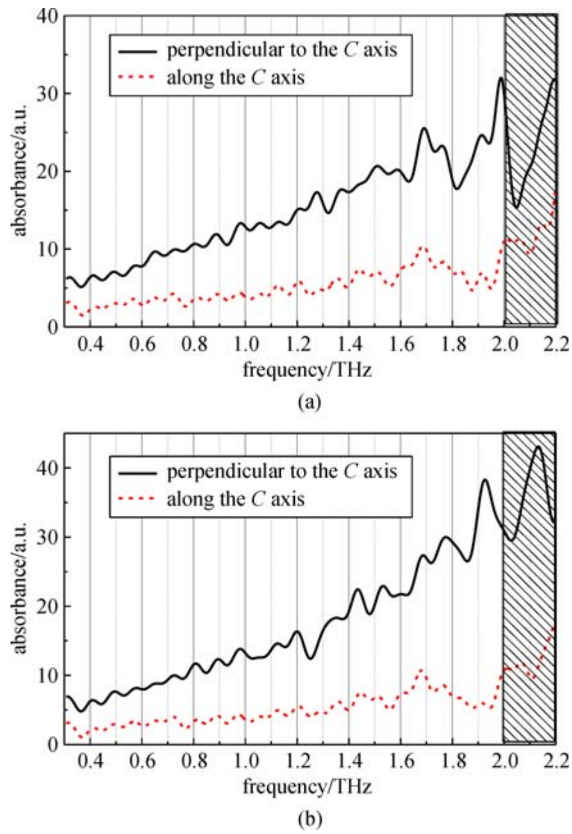

Fig. 6 Frequency dependencies of absorption coefficient for (a) sample 2 and (b) sample 3, respectively. Replica measurements of the ordinary ray and the extraordinary ray; the polarization direction of the terahertz pulse is along the *C* axis and perpendicular to the *C* axis

much more evident in the terahertz band compared to the optical frequency band. The results in Fig. 5(a) are also fitted well by a simple quadratic dependence.

Here, two absorption coefficients α_o and α_e were defined; α_o was defined as the absorption coefficient of terahertz vibration perpendicular to the tourmaline optical axis direction, while α_e was defined as the absorption coefficient of terahertz vibration along the tourmaline optical axis direction. In Fig. 5(b), the absorption of the extraordinary ray is significantly less than that of the ordinary ray; data for the extraordinary ray was considered accurate up to 2 THz. Different absorption coefficients in both directions of tourmaline demonstrate its dichroism. It shows that THz-TDS has the potential to identify aspects of the tourmaline crystal. Although the intensities of the absorption in different vibration directions were different, a similar tendency is presented. This suggests that it is feasible to characterize the tourmaline structure using THz-TDS technology.

To verify the above results for another sample, sample 3 was prepared to determine the corresponding index of refraction and absorption coefficient spectra. Sample 3 and sample 2 were cut from the same crystal and both are parallel to the *C* axis. Results show that the index of refraction of sample 3 and sample 2 exhibit the same properties. The absorption coefficients of the two samples are compared in Fig. 6. The absorption coefficients of the two samples are consistent for terahertz pulse vibration along the *C* axis. When the terahertz vibration direction is perpendicular to the *C* axis, there is a slight divergence in the absorption coefficient. These results indicate that in the tourmaline structure the terahertz absorption spectra of the three anionic groups is more sensitive along the *C* axis than in the vertical direction of the *C* axis.

4 Conclusions

In conclusion, the optical constants of tourmaline between 0.3 and 2.2 THz have been measured by terahertz time-domain spectroscopy. The index of refraction and absorption coefficient of the tourmaline crystals in different directions were determined. The differences in the presentation of the tourmaline refractive index and absorption spectra in different directions indicate that a method for analyzing the structure of tourmaline, as well as other crystals and minerals, can be realized by the THz technology.

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References

1. Grischkowsky D, Keiding S, Van Exter M, Fattinger C. Far-infrared time-domain spectroscopy with terahertz beams of dielectrics and semiconductors. JOSA B, 1990, 7(10): 2006–2015
2. Smith P R, Auston D H, Nuss M C. Subpicosecond photoconducting dipole antennas. IEEE Journal of Quantum Electronics, 1988, 24 (2): 255–260
3. Wilke I, Ramanathan V, LaChance J, Tamalonis A, Aldersley M, Joshi P C, Ferris J. Characterization of the terahertz frequency optical constants of montmorillonite. Applied Clay Science, 2014, 87(61–65)
4. Kim Y, Yi M, Kim B G, Ahn J. Investigation of THz birefringence measurement and calculation in Al_2O_3 and $LiNbO_3$. Applied Optics, 2011, 50(18): 2906–2910
5. Zhao H, Zhao K, Tian L, Zhao S Q, Zhou Q L, Shi Y L, Zhao D M, Zhang C L. Spectrum features of commercial derv fuel oils in the terahertz region. Science China, Physics, Mechanics & Astronomy, 2012, 55(2): 195–198
6. Wang W, Yue W, Yan H, Zhang C, Zhao G. Thz time-domain spectroscopy of amino acids. Chinese Science Bulletin, 2005, 50 (15): 1561–1565
7. Woodward R M, Cole B E, Wallace V P, Pye R J, Arnone D D, Linfield E H, Pepper M. Terahertz pulse imaging in reflection geometry of human skin cancer and skin tissue. Physics in Medicine and Biology, 2002, 47(21): 3853–3863
8. Shen Y C. Terahertz pulsed spectroscopy and imaging for pharmaceutical applications: a review. International Journal of Pharmaceutics, 2011, 417(1–2): 48–60
9. Shen Y, Lo T, Taday P, Cole B E, Tribe W R, Kemp M C. Detection and identification of explosives using terahertz pulsed spectroscopic imaging. Applied Physics Letters, 2005, 86(24): 241116
10. Kawase K, Ogawa Y, Watanabe Y, Inoue H. Non-destructive terahertz imaging of illicit drugs using spectral fingerprints. Optics Express, 2003, 11(20): 2549–2554
11. Bosi F, Andreozzi G B, Agrosì G, Scandale E. Fluor-tsilaisite, $NaMn_3Al_6(Si_6O_{18})(BO_3)_3(OH)_3F$, a new tourmaline from San Piero in Campo (Elba, Italy) and new data on tsilaisitic tourmaline from the holotype specimen locality. Mineralogical Magazine, 2015, 79 (1): 89–101
12. Lin S Y, Cai K Q, Cai X H, Ge W S. The new progress of mineralogical research on tourmaline group. China Non-metallic Mining Industry Herald, 2005, (1): 20–23
13. Xu W H, Lv Y P, Zhao G F, Xu Z J, Wang A J, Xiao G Y. Tourmaline structure, properties and applications. Materials Review, 2008, 3(2): 22–26
14. Dorney T D, Baraniuk R G, Mittleman D M. Material parameter estimation with terahertz time-domain spectroscopy. JOSA A, 2001, 18(7): 1562–1571
15. Duvillaret L, Garet F, Coutaz J L. Highly precise determination of optical constants and sample thickness in terahertz time-domain spectroscopy. Applied Optics, 1999, 38(2): 409–415
16. Bao R M, Zhao K, Zhao H. Terahertz spectroscopic properties of rocks. Modern Scientific Instruments, 2013, (1): 115–117

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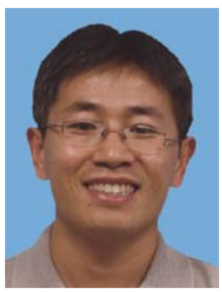

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