

Time-resolved terahertz spectroscopy of explosive materials

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We studied terahertz spectra of hexanitrohexaazaisowurtzitane (ϵ -HNIW and γ -HNIW), a kind of explosive materials, using terahertz time-domain spectroscopy (THz-TDS) in the 0.2–2.5 THz region. The experimental results show that explosive samples with different conformations have different intermolecular or phonon bands. For ϵ -HNIW, the observed absorption peaks were located at 0.99, 1.32, 1.43, and 2.08 THz; for γ -HNIW, the absorption peaks were observed at 1.05, 1.52, and 1.90 THz. The frequency dependent refraction index and absorption coefficients of two samples were also extracted.

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Pulsed terahertz (THz) radiation can be used as a new coherent radiation source and it occupies the frequency spectra band between 0.1 and 10 THz. Research in spectroscopy and imaging of explosives and energetic materials has grown significantly. Since part of rotational and vibrational spectra of various explosive molecules lie within the THz frequency band, so time-resolved THz spectroscopy^[1] can be applied to detect and identify explosives.

Many THz spectroscopy researches on some kinds of explosives have been reported in recent years^[2–6], such as 1,3,5 trinitro-s-triazine (RDX), 2,4-dinitrobenzene (2,4-DNT), 2,4,6-trinitrotoluene (TNT) etc.. However, so far there is no report on hexanitrohexaazaisowurtzitane (HNIW) in this range. HNIW (also called CL-20), a caged nitramine, was first synthesized by Nielsen^[7]. Its performances are much better than 1,3,5,7-tetranitro-1,3,5,7-tetraaza-cyclooctane (HMX) which is powerful and commonly used in military explosion^[8]. HNIW has become the new focus of energetic materials. HNIW at ambient pressure and temperature exists in four polymorphic modifications: α , β , γ , and ϵ . Among them ϵ -HNIW possesses the highest crystal density^[9]. The crystal transformation can be carried out under certain conditions. It is important to investigate these polymorphs for qualitative identification, quantitative determination, and the crystal form control in production. In this paper, we present a detailed transmission spectroscopy study of two explosive polymorphs (ϵ -HNIW and γ -HNIW) by terahertz time-domain spectroscopy (THz-TDS). The absorption coefficients of these samples are measured

in the range from 0.2 to 2.5 THz. The characteristics of the spectra are analyzed and compared. The results show that THz-TDS is a powerful tool to detect explosive materials and identify polymorphs.

We measured the THz spectra of HNIW using pump-probe method. A diode-pump mode-locked Ti:sapphire laser (MaiTai, Spectra Physics Laser) with the repetition rate of 82 MHz delivers the femtosecond pulses with duration nearly 100 fs located at 810 nm. A p-type InAs wafer with (100) orientation is used as the THz emitter and a 2.8-mm-thick ZnTe with (110) orientation is employed as sensor. A standard lock-in technology is used in our system.

A THz-TDS setup shown in Fig. 1 is used in experiment. A beam splitter is placed in the optical path to split the femtosecond laser pulses into two separate beams. The stronger pump beam of about 600 mW passes through a delay line then is focused on the p-type InAs by a lens, the incidence angle is 45°. The THz wave, which is generated in the reflection direction, is collimated and focused on the sample by a pair of parabolic mirrors (PMs). After transmitting through the sample, this THz wave which carries information of the sample is collimated and focused again into the sensor. The probe beam of about 360 mW, which is incidence on the sensor, is co-linear with the THz wave. It is modulated by the THz electric field in the sensor. This modified probe beam signal detected by a differential detector, is fed into a lock-in amplifier. A computer is used for the final data processing and analyzing. In order to minimize the absorption of water vapor, the part of THz path is put in a chamber (shown in dashed line) purged with nitrogen. The humidity is less than 2% and temperature is kept at 293 K. The dynamic range is about 4000:1 in this experiment.

THz-TDS can be used to extract optical properties such as absorption coefficient and refractive index of the sample. The transmitted field, $T = E_{\text{sample}}(\nu)/E_{\text{reference}}(\nu)$ is related to the complex refraction index $N = n + i\kappa$ by

$$T = \frac{4N}{(1+N)^2} e^{i2\pi(N-1)d\nu/c} = Ae^{i\phi}, \quad (1)$$

where A is the amplitude, ν is the frequency, ϕ is the phase difference between the sample and reference waveforms, and d is the thickness of sample. Thus, we can obtain the refraction index n and absorption coefficient

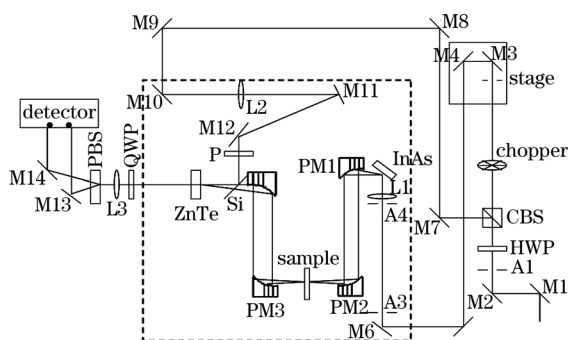


Fig. 1. Schematic diagram of the THz-TDS spectrometer. M: mirror; L: lens; A: apertures; P: polarizer; PBS: polarization beam splitter; PM: parabolic mirror; QWP: quarter-wave plate; HWP: half-wave plate; CBS: cubic beam splitter.

a , respectively,

$$n = \frac{c\phi}{2\pi d\nu} + 1, \tag{2}$$

$$a = \frac{2}{d} \ln\left(\frac{4n}{A \cdot (n+1)^2}\right). \tag{3}$$

Figure 2 shows the time-domain THz waveforms of the reference signal without passing through any sample, signal through a 1.2-mm-thick ϵ -HNIW sample, and signal through a 1-mm-thick γ -HNIW sample, respectively. It can be found that different samples have different time delays in comparison with the reference signal. Corresponding frequency-domain spectra of the THz signals are shown in Fig. 3. The amplitude was attenuated by the absorption; the same phenomena can be observed from the frequency domain spectra in Fig. 3.

Refraction indices and absorption coefficients of ϵ -HNIW and γ -HNIW calculated using Eqs. (2) and (3) are shown in Figs. 4 and 5, respectively.

It is demonstrated that the different polymorphs of HNIW samples have different refraction indices and absorption peaks. Their absorption positions and strength are highly sensitive to the structure of crystals. The refraction index of ϵ -HNIW varies between 1.68 and 1.76 while the refraction index for γ -HNIW varies between 1.60 and 1.66 in the range of 0.2–2.5 THz. The average refraction indices of ϵ - and γ -HNIW samples are 1.71 and 1.63, respectively. The change of refraction

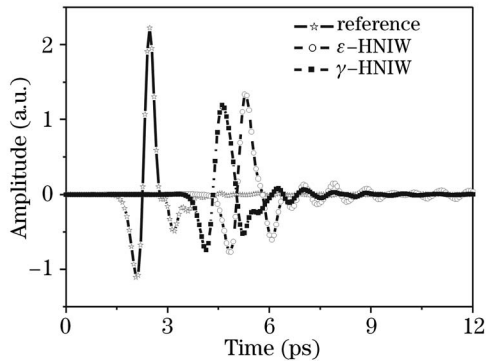


Fig. 2. Time domain spectra of reference, ϵ -HNIW, and γ -HNIW.

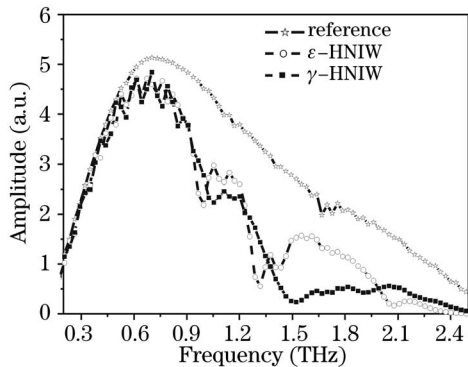


Fig. 3. Frequency domain spectra of reference, ϵ -HNIW, and γ -HNIW.

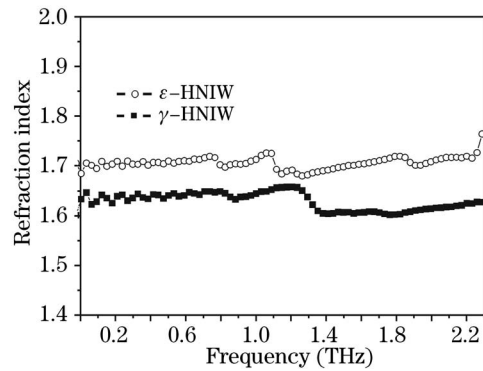


Fig. 4. Refraction indices spectra of ϵ -HNIW and γ -HNIW.

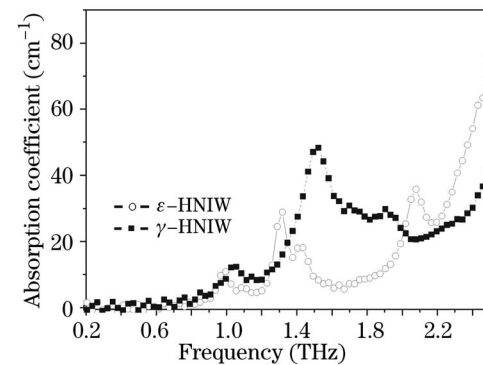


Fig. 5. Absorption spectra of ϵ -HNIW and γ -HNIW.

indices exactly correspond to the absorption peaks, see Fig. 5. The absorption peaks of ϵ -HNIW are located at 0.99, 1.32, 1.43, and 2.08 THz, while those of γ -HNIW at 1.05, 1.52, and 1.90 THz. The absorption peaks possibly correspond to an intermolecular modes or lattice vibrations for their different crystal structures. The absorption spectra differences between the two polymorphs may be caused by their various crystal structures. Further study is needed.

In summary, the THz spectra of ϵ - and γ -HNIW samples were studied by using the THz-TDS in the region of 0.2–2.5 THz. The THz-TDS measurements reveal the frequency dependent absorption. The dispersion of refraction index is in agreement with the absorption. The results show that THz-TDS is sensitive to identify the polymorphs. It is demonstrated that THz spectroscopy is a potentially important scientific tool to detect and identify concealed explosive materials and is useful for the security inspection.

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References

1. L.-L. Zhang, G.-Z. Zhao, H. Zhong, Y. Hu, and C.-L. Zhang, *Chin. Phys. Lett.* **21**, 2295 (2004).
2. F. Huang, B. Schulkin, H. Altan, J. F. Federici, D. Gary, R. Barat, D. Zimdars, M. Chen, and D. B. Tanner, *Appl. Phys. Lett.* **85**, 5535 (2004).
3. Y. Chen, H. Liu, Y. Deng, D. Schauki, M. J. Fitch, R. Osiander, C. Dodson, J. B. Spicer, M. Shur, and X.-C. Zhang, *Chem. Phys. Lett.* **400**, 357 (2004).
4. J. F. Federici, D. Gary, B. Schulkin, F. Huang, H. Altan, R. Barat, and D. Zimdars, *Appl. Phys. Lett.* **83**, 2477 (2003).
5. K. Yamamoto, M. Yamaguchi, F. Miyamaru, M. Tani, M. Hangyo, T. Ikeda, A. Matsushita, K. Koide, M. Tatsuno, and Y. Minami, *Jpn. J. Appl. Phys. Part 2* **43**, L414 (2004).
6. D. J. Funk, F. Calgaro, R. D. Averitt, M. L. T. Asaki, and A. J. Taylor, *Appl. Spectrosc.* **58**, 428 (2004).
7. K. B. Lipkowitz and D. B. Boud, *Review in Computational Chemistry* (VCH Publisher Inc., New York, 1991).
8. J. L. Lyman Y.-C. Liau, and H. V. Brand, *Combustion and Flame* **130**, 185 (2002).
9. X. Zhao and N. Shi, *Chin. Sci. Bulletin* **41**, 574 (1996).