Phase Transition of RDX Under High Pressure Upto 50 GPa

Chan Gao[1], Chuanchao Zhang[2], Zhilei Sui[1], Yanyang Qu[3], Rucheng Dai[4*], Zhongping Wang[4], Xianxu Zheng[5] and Zengming Zhang[4, 6*]

1. Department of Physics, University of Science and Technology of China
Hefei, Anhui, China;

2. Research Center of Laser Fusion, China Academy of Engineering Physics
Mianyang, Sichuan, China;

3. Institute of Chemical Materials, China Academy of Engineering Physics
Mianyang, Sichuan, China;

4. The Centre for Physical Experiments, University of Science and Technology of China
Hefei, Anhui, China;

5. Institute of Fluid Physics, China Academy of Engineering Physics
Mianyang, Sichuan, China;

6. Key Laboratory of Strongly-Coupled Quantum Matter Physics, Chinese Academy of Sciences, School of Physical Sciences, University of Science and Technology of China
Hefei, Anhui, China

Abstract:

Raman spectra of 1, 3, 5-trinitrohexahydro-s-triazine (RDX) are investigated under hydrostatic pressure upto 20 GPa and non-hydrostatic pressure upto 50 GPa. Variations of Raman peaks suggest that α-RDX initially transforms to γ-RDX at 2.5 GPa and completes at 4.3 GPa, further to δ-RDX at 18.6 GPa under the hydrostatic pressure. Unlike hydrostatic condition, α-RDX immediately changes to γ-RDX as soon as the pressure reaches 4.6 GPa under non-hydrostatic pressure. γ-RDX further transforms to δ-RDX at 16.9 GPa, less than the transition pressure of 18.6 GPa for the hydrostatic condition. Continuously loading the non-hydrostatic pressure, a new ζ phase was found at about 27.6 GPa based on the appearance of new ring bending vibrations and the NO_2 stretching modes and ζ phase is stable until 43 GPa. This phase transition is reversible after RDX is released back down to ambient pressure.

Correspondence to: zzm@ustc.edu.cn or dairc@ustc.edu.cn
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1   Introduction

1, 3, 5-trinitrohexahydro-s-triazine (RDX) is widely applied in many fields as an energetic material due to its high energy, fast detonation velocity and better thermostability.α phase RDX is the most stable structure with C_s molecular symmetry at ambient conditions. The molecular conformation of α-RDX is two of the NO_2 groups axial to the triazine ring while the third equatorial, referred to AAE conformer. RDX can exist in another four phases: β, γ, δ and ε [1-7] accompanying with different temperature, pressure and synthesizing method. The β-RDX is a metastable phase which can be prepared either by evaporation of the high-boiling RDX solutions [3] or deposition from RDX solution on a glass substrate [4,7] or by heating α-RDX [5]. β-RDX is denoted as the AAA conformer (with all of the NO_2 groups axial to the triazine ring)[6]. α phase RDX can transform to γ phase at the pressure of ~4.0 GPa and further into δ-RDX at 18.8 GPa. The ε-RDX can be produced at high temperature and high pressure (HT-HP) (489 K, 4.2 GPa) [2].

The pressure induced phase transition of RDX has been studied by using Raman spectroscopy, far-infrared spectroscopy and X-ray diffraction. [1, 8-14] Dreger et.al obtained the HT-HP phase (ε-RDX) at 3.7 GPa and 466 K. This phase is stable in the pressure region from 0.6 to 20 GPa at the room temperature, and transformed back to α-RDX when the pressure is below 0.6 GPa [11]. They obtained the P-T phase diagram of RDX and revealed that the phase transition from α-RDX or γ-RDX to ε-RDX can exist in a narrow range of pressure and temperature（2.8-6.0 GPa, 465-502 K）[2, 13, 14]. The lattice density of ε-RDX is greater than that of α-RDX at 3.6 GPa, and the ε-RDX was predicted to possess a higher detonation velocity [12].

Although some groups had investigated the phase transition of RDX under high pressure, the pressure range is limited. In this paper, a new ζ phase of RDX under higher pressure up to 30 GPa is observed by using diamond anvil cell (DAC) setup. The new structure is important to understand the phase transformation of RDX under high pressure.

2   Experimental section

RDX crystals of 99.9% purity obtained from China academy of engineering physics were used without further purification. A confocal microscope Raman spectrometer system (equipped with Princeton Instruments Acton SP2750 monochromator and Princeton Instruments Pixis 100-BR multichannel CCD) was used to collect signals in situ. Ar^+ laser of 514.5 nm was utilized to excite the sample at a power of 40 mW, and the Raman spectra were detected in the reflection geometry.

A diamond anvil cell (DAC) was used to produce high pressure. RDX powder was packed into a hole with diameter of 150 μm in a stainless-steel gasket. The well-known pressure shift of the Ruby luminescence R_1 line was used as the pressure calibration [15]. The silicon oil were used as pressure medium to provide a hydrostatic pressure environment. While in the non-hydrostatic pressure experiment, only RDX powder and ruby were put into the hole without any pressure medium. And the RDX is soft enough to transmit pressure through itself.

The MIR spectra were collected with a Bruker Tensor 37 Fourier transform infrared spectrometer and Bruker Hyperion 2000 infrared microscope. The RDX and KBr with the ratio of 1 to 100 were carefully grinded together.

3   Results and discussion

3.1 The high pressure Raman spectra of RDX under hydrostatic pressure

Figure 1 shows the Raman spectra of RDX at hydrostatic pressure up to 20 GPa, using the silicone oil as pressure medium. Some remarkable changes of the ring vibration modes of RDX at 2.5 GPa are displayed

in Fig. 1. The new ring bending vibration mode occurs at 649 cm^{-1}. N-N stretching mode at 1272 cm^{-1} is splitting and a new Raman vibration mode at 1016 cm^{-1} also appears. These changes indicate the beginning of the phase transition from α phase to γ phase at 2.5 GPa pressure. The simulated results of Lynn et al. [16] also revealed that the lattice constant and cell volume of α-RDX change in large amount at 2.1 GPa, which indicated the phase transition from α-RDX to γ-RDX.

With the further loading pressure, the phase transition from α-RDX to γ-RDX is completed accompanied with splitting of ring bending vibration mode at 413 cm^{-1} and the appearance of new ring bending vibration mode at 589 cm^{-1},two new ring twisting modes at around 363 cm^{-1} and two new C-H stretching modes at high wavenumber at 4.3 GPa. The major changes are ring vibration modes and C-H vibration modes, while the NO_2 group is remains invariant. That means the crystal conformer of γ-RDX is the same as α-RDX, and which is referred to as AAE. This is consistent with the calculated results reported by Goto et al [8].

Some obvious changes happened among the N-N and C-N stretching modes, and NO_2 group scissoring vibration modes (at 849 cm^{-1},859 cm^{-1},882 cm^{-1}) above 5.9 GPa. A major frequency shift of the breathing vibration centered at 882 cm^{-1} emerges at 13 GPa and a new vibration modes centered at 1614 cm^{-1} appeared among the O-N-O stretching modes. The intensity of N-N stretching mode at 990 cm^{-1} is enhanced significantly, while some stronger ring vibration modes under low pressure wear off under the effect of high pressure. The phase transition from γ-RDX to δ-RDX is completed at 18.7 GPa.

Upon releasing the pressure back down to ambient, the δ-RDX transforms back to α-RDX, which shows that this phase transformation process is reversible. It is worth mentioning that the Raman spectra under 2.9 GPa is almost same as that at 4 GPa. The γ-RDX can exist stable until 2.9 GPa upon releasing the pressure, which is in agreement with the references [16].
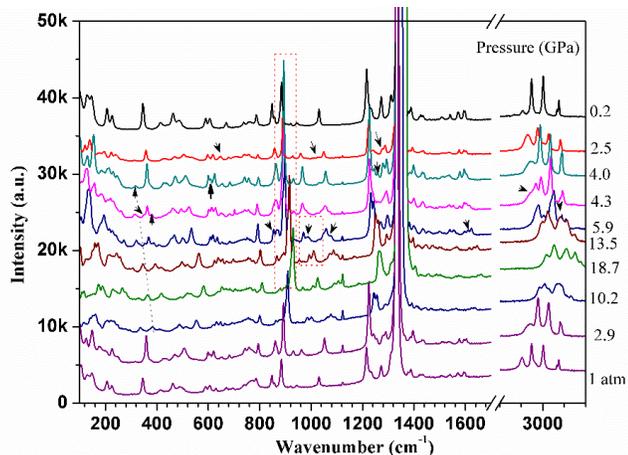

Figure1. The Raman spectra of RDX at hydrostatic compression.

2.2 The high pressure Raman spectra of RDX under non-hydrostatic pressure

Figure 2 is the phase transition behavior of RDX under non-hydrostatic pressure. Unlike the obvious Raman vibration modes changes presented at 2.5 GPa under hydrostatic compression, no obvious changes of the Raman vibration spectra are observed except some increase in the intensity of ring bending modes below 4.6 GPa. The changes of ring vibration modes and C-H stretching modes at 4.6 GPa are the same as the hydrostatic pressure case, which indicate the phase transition from α-RDX to γ-RDX. Moreover, this phase transition is sudden at 4.6 GPa under non-hydrostatic compression.
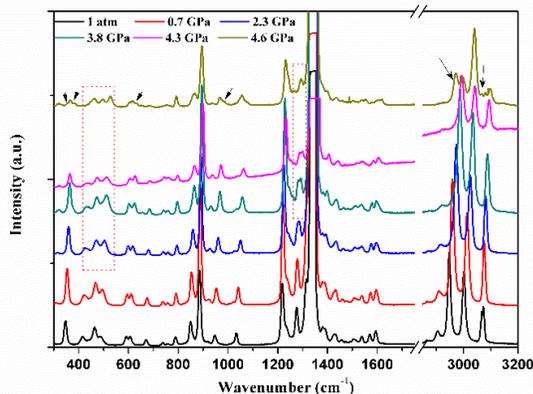
Figure 2. The Raman spectra of RDX at non-hydrostatic compression below 5 GPa.

The structure transformation from γ-RDX to δ-RDX is completed at 16.9 GPa as presented in Fig. 3. It can be observed that the intensity of molecular bending vibration centered at 170 cm^{-1} increased under high pressure; C-N stretching mode and NO$_2$ scissoring vibration are splitting at 7.7 GPa; a new ring twisting mode emerged at 425 cm^{-1}; the intensity of N-N stretching mode at 969 cm^{-1} and 982 cm^{-1} increased with relative intensity inversion. A new ring bending vibration appeared at 417 cm^{-1} at 12 GPa and two new C-H stretching modes emerged at 3023 cm^{-1} (at 12 GPa) and 3138 cm^{-1} (at 16.9GPa). Figure 2 also exhibits a nonlinear frequency shift with increasing pressure. All of these changes indicated the phase transition from γ-RDX to δ-RDX at 16.9 GPa.

With continuously increasing the pressure, some discontinuous shifts of Raman peaks such as in the N-N stretching mode, CH$_2$ rocking vibration and O-N-O stretching mode are observed and marked with the red dotted lines as seen in Fig.3. The ring breathing vibration modes centered at 849 cm^{-1} and 883 cm^{-1} also show a frequency discontinuity for almost 20 cm^{-1} under 27.6 GPa. In addition to this, two new Raman vibration peaks presented at 597 cm^{-1} referred to ring twisting mode and N-N stretching mode and 774 cm^{-1} referred to N-NO$_2$ umbrella mode. Furthermore, C-H stretching mode at the range from 2800 cm^{-1} to 3200 cm^{-1} show some peak broadening and frequency discontinuous at 27.6 GPa. These results reveal the structure transformation from δ-RDX to a new phase notated as ζ phase. This ζ phase can exist stably up to 43 GPa.

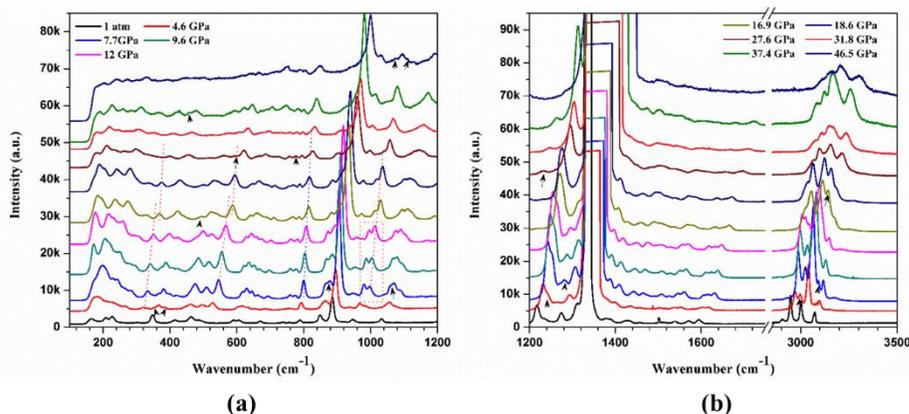(a)   (b)

Figure 3. The Raman spectra of RDX at non-hydrostatic compression above 5 GPa.

Figure 4 displays the Raman shift of RDX along with the pressure at non-hydrostatic compression. We can see clearly the phase transition of RDX under high pressure. Comparing with the hydrostatic

compression, the phase transition from α-RDX to γ-RDX under non-hydrostatic compression happened at 4.6 GPa which is larger than 4.3 GPa under hydrostatic pressure. But the phase transition from γ-RDX to δ-RDX occurs at 16.9 GPa less than 18.6 GPa under hydrostatic condition. Different with the changes of the Raman vibrational spectra at 2.5GPa under hydrostatic compression, there are no obvious changes of Raman spectra at this pressure under non-hydrostatic pressure.
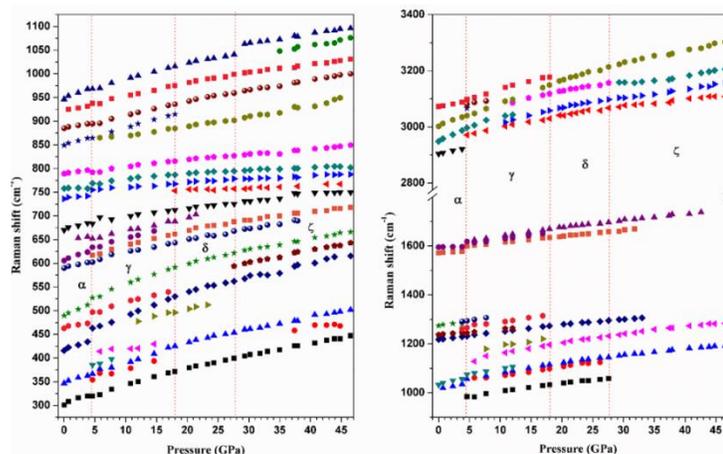

Figure 4. The Raman shift of RDX along with the pressure under non-hydrostatic compression.

4   Conclusion

The phase transition of RDX under hydrostatic compression upto 20 GPa and non-hydrostatic compression upto 47 GPa were studied using a diamond anvil cell and Microscopic confocal Raman spectroscopy. Under the hydrostatic compression, some C-N stretching vibrations and ring bending modes emerged at 2.5 GPa, which indicates the phase transition from α-RDX to γ-RDX, and the phase transition completes at 4.3 GPa. NO_2 group does not change significantly which reveals that γ-RDX have a similar conformation with α-RDX. Some discontinuous Raman shifts and some ring bending modes and NO_2 umbrella modes were observed at 18.5 GPa revealing the phase transition completion from γ-RDX to δ-RDX.

Under non-hydrostatic pressure, the phase transition from α-RDX to γ-RDX and further to δ-RDX occurred at 4.6 GPa and 16.9 GPa, respectively. Moreover, a new ζ phase emerges at about 27.6 GPa, along with the discontinuous Raman shift, new ring bending vibrations and the NO_2 stretching modes. This ζ phase is stable up to 43 GPa. No matter what the condition of pressure, all of the phase transitions in our experiment are reversible when the pressure was subsequently released back down to ambient.

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