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# Energetic materials under high pressures and temperatures: stability, polymorphism and decomposition of RDX

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**Abstract.** A recent progress in understanding the response of energetic crystal of cyclotrimethylene trinitramine (RDX) to high pressures and temperatures is summarized. The optical spectroscopy and imaging studies under static compression and high temperatures provided new insight into phase diagram, polymorphism and decomposition mechanisms at pressures and temperatures relevant to those under shock compression. These results have been used to aid the understanding of processes under shock compression, including the shock-induced phase transition and identification of the crystal phase at decomposition. This work demonstrates that studies under static compression and high temperatures provide important complementary route for elucidating the physical and chemical processes in shocked energetic crystals.

#### **1. Introduction**

Energetic materials (EMs) are a class of materials with a large amount of stored energy in chemical bonding which can potentially be released. Generally stable at ambient conditions, these materials decompose (deflagrate, detonate) with proper stimulus. The practical application of energetic materials often involves exposure to shock waves, therefore of particular interest are their properties and performance at high pressures and temperatures. The fast time scale of processes occurring during shock compression poses significant experimental challenges to fully quantify the molecular mechanisms involved in the energetic materials at these conditions. On the other hand, static compression experiments, despite of differences in rate of loading, states of stress, and thermal conditions can provide critical knowledge to gain insight into processes in shocked energetic materials. In particular, detailed information on polymorphism, chemical stability, and thermal decomposition obtained from static experiments can be useful to understanding the reactive behaviour of energetic crystals over the range of pressures and temperatures relevant to those under shock initiation.

Here, we present recent progress in understanding the response of energetic crystal of cyclotrimethylene trinitramine (RDX) to high pressures and high temperatures [1-3]. RDX is an important EM used extensively in explosives and monopropellants formulations. Despite of these significant applications the fundamental knowledge on this crystal at high pressures and temperatures has been both limited and inconsistent. Two RDX phases,  $\alpha$  and  $\gamma$  have been known for long time [4, 5], but even though the detailed structure of the  $\gamma$ -RDX has been determined recently [6]. The transition between these two phases takes place at ~ 4 GPa. Later on it was demonstrated that both phases transform to the other phase at high temperatures [7, 8]. It was proposed that this new, a HP-HT phase is actually the  $\beta$ -RDX, which was previously observed only at ambient pressure. Furthermore, the same studies provided the phase diagram for three RDX phases:  $\alpha$ ,  $\gamma$  and HP-HT. However, the

results from the two studies were largely inconsistent regarding the phase boundaries and the triple point. For example, the triple point locus differed by more than 100 K in those two studies. Also, it was reported that the HP-HT phase is primarily responsible for RDX decomposition at high pressures and temperatures. Given that the behaviour of RDX at high pressures and temperatures is of primary interest for understanding the shock initiation, the proper characterization of the HP-HT phase is essential. Therefore, in this work we present recent studies on RDX at high pressures and temperature to address the previous inconsistencies and to complement understanding of processes under shock compression [1, 2, 9-12]. In particular, we focus on: (i) determining details of the vibrational structure of the HP-HT phase, (ii) assessing the claimed association of this phase with  $\beta$ -RDX, (iii) providing the refined P-T diagram of RDX, (iv) examining the stability and decomposition of the HP-HT phase, and (v) relating the static compression results to those under shock compression.

### 2. Experimental Approach

All experiments were performed with single crystals. A large oriented crystals used in shock experiments were provided by Dr. D. E. Hooks from Los Alamos National Laboratory. Small crystals for static experiments were grown from acetone solvent. Static high pressure experiments were performed in a heated diamond anvil cell (DAC). Cryogenically loaded argon was used as a pressure transmitting medium. Ruby fluorescence was used to monitor pressure. Temperature of the DAC was controlled using a resistive heater wrapped around the cell. The sample temperature was monitored with iron-constantan thermocouples. A micro-Raman system (T64000, JY-Horiba) equipped with a microscope (Olympus BX-40), utilizing a 532 line from a cw diode-pumped solid-state laser, was used for Raman spectra measurements. Experimental details for static compression measurements can be found elsewhere [1].

For shock experiments, oriented, single crystals of RDX were prepared with dimensions of 7 x 7 x  $0.4 \text{ mm}^3$  and confined between two optical windows. Shock waves were generated by impacting the target assembly with quartz or sapphire crystals launched by a single stage light-gas gun. Because of the impedance mismatch between the optical windows and RDX crystals, the sample was compressed under stepwise loading. Three experimental techniques were used to obtain the Raman and emission spectra. High spectral resolution Raman measurements were performed with a single 20 ns pulse from a Nd:YAG (532 nm) laser. Time-resolved Raman measurements were obtained with a 2  $\mu$ s pulse from a tunable dye (514.5 nm) laser. Raman experiments were performed to stresses up to 10 GPa. In the emission experiments, light produced by the shocked crystal was detected by the spectroscopic system to provide time-resolved emission spectra. Emission experiments were performed for stresses between 7 and 20 GPa. Details of shock experiments and detection techniques can be found elsewhere [10, 11, 13, and 14].

### 3. Results and Discussion

### 3.1. Static compression

### 3.1.1. HP-HT phase

First we addressed issue concerning the proposed association of the HP-HT phase with the  $\beta$ -RDX. Because the HP-HT phase has limited chemical stability under the pressure-temperature conditions where it is produced, the detailed characterization of its structure is rather challenging. However, it turned that this phase can be quenched to room temperature. In Figure 1, we demonstrate that the quenching can preserve both the shape of vibrational spectra and the quality of single crystal of the HP-HT phase. Note the spectrum at high temperature has broader peaks due to the thermal effects. Having the HP-HT phase at room temperature, we found that this phase is stable over the wide range of pressures; however, it transforms to  $\alpha$ -RDX at ~ 0.6 GPa.



**Figure 1.** An example of Raman spectra of the HP-HT phase at high temperature and at room temperature (RT) with corresponding images of RDX crystal in a diamond anvil cell. Spectra were acquired for 10 s. Both spectra and images were obtained at 4.2 GPa.

To examine the association of the HP-HT phase with the  $\beta$ -RDX, we compared the Raman spectra of the stable form of the HP-HT phase with the Raman spectra of  $\beta$ -RDX grown from nitrobenzene solution. The spectra in the low frequency and the CH stretching range are shown in Figure 2. A clear difference can be noticed between two sets of spectra, demonstrating that the HP-HT phase is not the  $\beta$ -RDX as was previously suggested, but it is a new phase [1, 3]. This phase was labeled as  $\epsilon$ -RDX, and its crystal structure was determined as having the same space group as  $\gamma$ -RDX [3].



**Figure 2.** Comparison between Raman spectra of the HP-HT RDX (black lines) and  $\beta$ -RDX (grey lines). The HP-HT spectrum was obtained at 0.8 GPa and the  $\beta$ -RDX at ambient pressure.

#### 3.1.2. New phase diagram and decomposition of $\varepsilon$ -RDX

To determine the pressure and temperature locus for the RDX phases, the Raman and optical imaging measurements were performed at a specific pressure and with gradually increasing temperature. All experiments were carried out at pressures ranging from 0 to ~7 GPa, and at temperatures ranging from ~295 K to 550 K. Identification of characteristic features in Raman spectra permitted determination of the boundaries between three phases. In Figure 3, we show new phase diagram of RDX [2], along with the previously published [7, 8]. The Figure 3a is from this work and the lines represent the best fit to the experimental data; while the Figure 3b is from previous studies. This experiment allowed us to locate the triple point between RDX phases, as being approximately at 3.7 GPa and 466 K. Also, we found that: (i) both the  $\alpha$ - $\varepsilon$  and the  $\gamma$ - $\varepsilon$  transitions are irreversible at the phase boundaries and (ii) the  $\gamma$ -phase can decompose at high temperature without involving the  $\varepsilon$ -RDX. The results presented here

clearly differ from previously reported results [7, 8]. Although it is difficult to determine the source of these discrepancies, we believe that previous results could be affected by: (i) sample morphology; polycrystals or powders, (ii) nonhydrostaticity and pressure gradients, and (iii) interactions between the sample and pressure transmitting media.



Figure 3. Phase diagram of RDX: a) This work, b) Previous works; solid lines [7], dashed lines [8].

As can be noticed from the new phase diagram, the  $\epsilon$ -RDX appears to exist in a limited range of pressure and temperature from 2.8 to 6.0 GPa, and above ~ 465 K. Since this phase has also limited chemical stability we looked into its thermal decomposition kinetics. By relating a decrease in Raman intensity with time to the fractional extent of decomposition (FED), we found that the FED obeys autocatalytic-type reaction. Fitting the data to the Prout-Tompkins model [15] provided the global decomposition rates at several pressures and temperatures. The obtained rates increased with temperature and decreased with pressure. Therefore, the activation volume for  $\epsilon$ -RDX decomposition was found to be positive, in contrast to  $\alpha$ -RDX for which the negative values were reported [8].

#### 3.2. Relevance of static results for shock compression

## 3.2.1. The $\alpha$ - $\gamma$ phase transition under shock compression

The  $\alpha$ - $\gamma$  phase transition is well established under static compression and recognized by characteristic changes in the Raman spectra [9]. However, it was unclear if this phase transition can occur under shock compression conditions. To address this issue we performed shock experiments using the high spectral resolution Raman system for detecting characteristic features in the spectra. As shown in Figure 4a, our experiments to different peak stresses on crystals impacted at (111) plane revealed that changes in Raman spectra occur ~ 4 GPa [10]. Having data under static compression, see Figure 4b, we found that the changes in Raman spectra obtained under shock compression are similar to those under static compression. Therefore, this result demonstrates that the same  $\alpha$ - $\gamma$  phase transition, as observed under static compression, takes place under shock compression on a nanosecond time scale. Furthermore, the shock studies on crystals with different orientation indicated that the  $\alpha$ - $\gamma$  transition occurs regardless of crystal orientation [10].



**Figure 4.** Raman spectra of RDX crystal at several pressures: a) shock compression results for (111) oriented crystal, b) static compression results. Note similar spectra at 4 GPa under shock and static compression. Pressures are given in GPa.

#### 3.2.2. RDX phase at the shock-induced decomposition

The experiments at low stresses (< 5.5 GPa) did not reveal signatures of decomposition. Therefore, to gain insight into the shock-induced decomposition the experiments were performed at higher stresses [11]. At stresses higher than7 GPa, we observed, in addition to changes in the Raman spectra, a gradual raise of light emission from the crystal with time. This shock-induced emission dominated the Raman spectrum at latter times. Because, the emitted light is associated with the chemical decomposition, the presence of Raman and emission signals at the same time can be used to identifying the phase of decomposing crystal under shock compression. In Figure 5, we present an attempt to establish the phase of the shocked-decomposing crystal.



**Figure 5.** Comparison of Raman spectra of the shocked-decomposing crystal with Raman spectra of the  $\gamma$ -and  $\epsilon$ -RDX measured under static compression.

For this purpose we compared the Raman spectra obtained on the shocked-decomposing crystal with the Raman spectra of the  $\varepsilon$ - and  $\gamma$ - phase obtained at static compression. When comparing these spectra one should keep in mind that the spectrum of shocked crystal, in contrast to other spectra, was obtained with single pulse laser and, therefore has much lower signal-to-noise ratio. Nevertheless, we

find several instances: region of 3000 cm<sup>-1</sup>, below 400 cm<sup>-1</sup>, and above 1000 cm<sup>-1</sup> indicating that the spectrum of shocked-decomposing crystal is similar rather to the  $\gamma$ -phase than to  $\varepsilon$ -phase. Therefore, this result implies that the shock-induced decomposition in RDX takes place from the  $\gamma$ -phase. This finding has important implication for the modeling of the shock-induced decomposition of RDX.

# 4. Final Remarks

We summarized recent work on energetic crystal of RDX under high pressures and temperatures.

Using Raman spectroscopy and optical imaging we provided new phase diagram for RDX crystal. In particular, we provided evidence that: (i) the HP-HT phase is a new RDX phase;  $\varepsilon$ -RDX, (ii) the  $\varepsilon$ -RDX exists in a narrow P-T domain and decomposes autocatalytically with the rates decreasing with pressure, and (iii) the  $\gamma$ -RDX decomposes without involving the  $\varepsilon$ -RDX. Finally, we demonstrated the use of static compression results in understanding the phase transition and decomposition under shock compression.

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