High-Pressure Synchrotron Radiation X-Ray Diffraction Studies of Pentaerythritol Tetranitrate C(CH₂ONO₂)₄

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A high-pressure x-ray diffraction study of nanocrystalline pentaerythritol tetranitrate, $C(CH_2ONO_2)_4$, (PETN), has been performed in a diamond-anvil cell at ambient temperature using synchrotron radiation. Pressure-induced alterations in the profiles of the diffraction lines, including their positions, widths and intensities were followed up to 30 GPa in a compression cycle. The spectral changes in the diffraction patterns at low pressures indicated continuous densification of the tetragonal structure (space group $P\overline{4}2_1c$). The diffraction patterns confirmed that PETN compressed from ambient pressure to 7.4 GPa by 17 %. At 8.2 GPa and above, several new diffraction lines appeared in the patterns. These lines suggest that the lattice undergoes an incomplete stress-induced structural transformation from the tetragonal to an orthorhombic structure (most probably space group $P2_122_1$). The mixture of both structures appeared to persist to 30 GPa. The progressive broadening of the diffraction lines as the pressure increased beyond 10 GPa is attributed to the combined diffraction lines of a mixture of two coexisting PETN phases and inhomogeneous pressure distribution within the sample.

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INTRODUCTION

Pentaerythritol tetranitrate, C(CH₂ONO₂)₄ (PETN), is a well-known energetic material, widely used as a secondary high explosive. At ambient pressure and temperature, PETN crystallizes in a tetragonal space group $P\overline{4}21c$, with two molecules per unit cell [Trotter 1963]. Numerous studies have attempted to understand the structural, electronic [Kuklja 2001, Bunte 2000], mechanical [Bunte 2000], thermal expansion [Sorescu 1999], vibrational [Gruzdkov 2001, Park 2004] and elastic [Bunte 2000] properties of the PETN as well as to evaluate the effects of pressure on its molecular conformation [Gruzdkov 2004]. The observed anisotropy in shock sensitivity of solid PETN has also been subject of much research [Dick 1984; Dick 1991; Yoo 2000; Dick 1994]. In theoretical studies of hydrostatic compression based on the rigid-molecule approximation, the calculated linear compressibilities of PETN crystals [Sorescu 1999; Sorescu 1999] were found to be in reasonable agreement with experiment to about 5 GPa; significant discrepancies occur at higher pressures. Quantum mechanical calculations of the effects of shock impact on PETN have been reported and explain the chemical mechanism and observed anisotropy of shock wave initiation [Gruzdkov 2000]. High-pressure experiments with PETN have estimated the

linear and volumetric hydrostatic compressions by x-ray diffraction or neutron scattering techniques for pressures up to 4.3 GPa and 10.5 GPa, respectively [Ollinger 1975; Dick. 1997]. However, the results of these studies are inconsistent and show a discrepancy either in the linear compressibilities or in the volumetric compression which increases at higher pressures.

A comprehensive understanding of the properties of PETN, especially its highpressure behavior, is of great importance for applied chemistry and materials science and future applications of this material. Despite considerable theoretical and experimental efforts to evaluate the effects of high-pressures on the structure of PETN, detailed experimental data, particularly in the high-pressure range, are still lacking. The present work was undertaken in order to determine the range of pressure-induced structural modifications that may occur for this compound.

EXPERIMENTAL

Polycrystalline PETN was obtained from Los Alamos National Laboratory. For in-situ xray diffraction studies a polycrystalline powder of PETN was compressed in a Mao-Bell-type diamond anvil cell (DAC). A rhenium gasket was pre-indented to a thickness of 45µm between two diamonds with 300 µm diameter culets. The sample chamber consisted of a 150 µm diameter hole drilled in the preindented rhenium gasket. A few 10 µm grains of ruby powder were included and used to measure the pressure. No pressure-transmitting medium was used in this experiment. The time gap between each increment of pressure and subsequent x-ray measurement was about 2 minutes. All x-ray diffraction patterns were collected at the 16-ID-B undulator beamline at the High Pressure Collaborative Access Team (HPCAT) of the Advanced Proton Source at Argonne National Laboratory, using a monochromatic beam of 0.3699 Å wavelength. The diffracted x-rays were collected with an image plate (MAR-345) detector placed 353 mm from the samples. The collected diffraction patterns were analyzed by integrating images as a function of 2 theta using the program FIT2D [Hammersley 1998] to obtain a conventional, one dimensional diffraction profile. The diffraction patterns were processed with programs such as Powder Cell 2.4 [Kraus 2000], Jade 6.5 [2004], and General Structure Analysis System-GSAS [Larson 1988; Toby 2001].

RESULTS AND DISCUSSION

In situ high-pressure x-ray diffraction patterns collected in one compression sequence are shown in Figure 1. The powder patterns at low-pressures can be indexed using the tetragonal unit cell previously reported for the ambient PETN structure [Trotter 1963]. The space group is $P\overline{4} 2_1 c$; the refined unit cell constants for the ambient phase of PETN are: a = 9.42 Å, b = 9.42 c = 6.71 Å; the cell volume is 595 Å³; and the density is 1.72 g/cm³.



Figure 1 (a). Pressure evolution of the *in-situ* (DAC) X-ray diffraction patterns of PETN and **(b)** magnification of the low angle range at ambient temperature at pressures from ambient to 30 GPa. Background due to the DAC has been subtracted. Emerging lines of the new phase are marked with asterisks. Miller indices of the tetragonal ($P\overline{4}2_1c$) and the proposed orthorhombic ($P2_122_1$) phase corresponding with observed diffraction peaks are indicated.

Figure 2 shows a Rietveld profile refinement [Larson 1988; Toby 2001] of a diffraction pattern collected from a sample in a DAC at ambient pressure. The full-profile fit is excellent and explains all of the observed diffraction lines. The tetragonal structure can be fit to all diffraction data collected from ambient pressure to about 7 GPa. New diffraction lines almost overlapping the lines of the tetragonal phase of PETN were first observed between 7.4 and 8.2 GPa (Figures 3a, b, c and d) and are interpreted in terms of an incomplete transformation to a new orthorhombic phase. At pressures above 8.2 GPa, the diffraction patterns can be indexed as a mixture of a tetragonal and an orthorhombic structure with $P2_122_1$ as the trial space group. The new lines appearing in the diffractograms and tentatively ascribed to the orthorhombic phase are: 002, 102, 012, 112, 211, 221 and 311.



Figure 2. Typical Rietveld full-profile refinement preformed using the GSAS program [Larson 1988; Toby 2001] of the X-ray diffraction pattern of PETN collected in a DAC at ambient pressure. The refinement was done for the tetragonal space group $P\overline{4}2_1c$. The solid red line and black stars represent modeled and experimental spectra, respectively. The dotted line represents the difference between the measured data and the refined profile.

The present diffraction data are not of sufficient quality to allow a full refinement of the structure of the proposed orthorhombic phase of PETN or calculations of the molecular orientations, bond lengths, and bond angles. The diffraction lines attributed to the new orthorhombic structure also are not well isolated, but their presence is indicated by an enhanced intensities and profile broadening of lines assigned to the tetragonal phase (Figure 3). The profiles of the diffraction patterns appear composed of a mixture of both the lines of the tetragonal as well as of the emerging orthorhombic phase (Figures 1 and 3). A few diffraction lines of the tetragonal phase mixture lingers up to 30 GPa. That is, we suggest that, under the conditions of these experiments, the transition to the orthorhombic phase (and the proposed space group $P2_122_1$) is initiated but not completed in the pressure range investigated. The existence of the orthorhombic-type structure of PETN has been recently suggested [Gruzdkov, 2004] in a study of single-crystal PETN compressed under silicone oil, although the predicted transition pressure, about 5 GPa, varies somewhat from that seen by our experimental results.



Figure 3. Details of the diffraction patterns of PETN at high pressures taken from Figure 1 which show areas where features attributed to the new orthorhombic phase occur. The new diffraction lines appear beyond 6 GPa and are marked with asterisks. Miller indices of the tetragonal ($P\overline{4} 2_1 c$) and the proposed orthorhombic ($P2_1 22_1$) phase, corresponding with observed diffraction peaks, are indicated in blue and red, respectively.

Figure 4 shows the pressure dependence of the unit cell *d* spacings and illustrates the appearance of new lines assigned to orthorhombic PETN. The figure includes only diffraction lines whose positions were clearly discerned. Some diffraction lines assigned to the high-pressure phase of PETN were first noticed at 7.4 GPa as broad bumps, overlapping lines of the tetragonal phase (Figures 3 and 4). At consecutively higher pressures, the combination of these new diffraction lines with the lines of the persistent

tetragonal phase, cause significant spectral broadening. At pressures above 10 GPa, the diffraction patterns are dominated by broad bands made up of two or more overlapping lines. The angular positions of such lines had to be estimated using a whole profile fitting procedure [Jade, 2004] that involved multiple deconvolutions of the broad bands.



Figure 4. Pressure dependence of the interplanar *d* spacings of PETN for only diffraction lines whose positions were clearly discerned. The solid circles and the open circles indicate the features attributed to the tetragonal and the new orthorhombic phase, respectively. Dotted lines are guides for the eye.

In this experiment, strongly nonhydrostatic stresses and the proposed mixture of two PETN phases can broaden the diffraction lines in the pattern. Furthermore, a highly disordered material could be produced by fine intergrowth of the two low- and high-pressure phases, possibly as defective crystals, and further broaden the diffraction lines. Although the structures of the tetragonal and the proposed orthorhombic phase of PETN are different, several diffraction lines of both phases nearly match. This, combined with line broadening, makes the conversion from tetragonal to orthorhombic phase difficult to monitor precisely in these experiments.

The decrease of the unit cell volume of the tetragonal phase with increasing pressure is illustrated in Figure 5. For this phase, the unit cell volume decreases by about 19% $(V/V_o=0.81, where V_o$ is initial cell volume and V is the volume at a given pressure) on compression to about 7.5 GPa. This decrease is in a good agreement with values obtained from theoretical calculations for low-pressure compression of PETN [Sorescu 1999; Ollinger 1975].



Figure 5. Evolution of the computed PETN unit cell volume with pressure during compression from ambient pressure to 7.5 GPa. These computations assume a tetragonal unit cell with space group $P\overline{4}2_1c$. The dotted line represents a least-squares weighted fit.

Even though the precise sequence of events during compression of PETN cannot be completely specified by our studies, we may draw upon the basis of our results the following microstructural picture. At ambient pressure, the covalently bonded PETN molecules are drawn to one another by weak van der Waals forces of attraction and so the initial compression of PETN is almost entirely due to a decrease of intermolecular distances. At extremely high pressures (i.e. smaller intermolecular distances), repulsive intermolecular forces become comparable to the intramolecular repulsions along the covalent bonds [Ollinger 1975; Pastine 1974]. At intermediate pressures, the energetic cost of further reducing intermolecular distances becomes comparable to that associated with distorting the intramolecular degrees of freedom. In this range of pressures, these repulsive forces may be relieved by altering the arrangement of the molecules in the crystals (the crystal structure) and/or molecular conformations. Thus, we can expect that in the first stage of compression, the unit cell compresses rapidly; and, in a later stage, that is at higher pressures, the rate of change of the cell's compressibility decreases gradually (Figure 5) as all types of repulsive interactions increase. This interpretation provides a satisfactory explanation of our experimental results and was very recently confirmed by theoretical studies [Gan 2004]. In fact, all-electron calculations of the PETN compression [Gan 2004] indicated that the bond lengths and bond angles remain almost constant for $0.8 \le V/Vo \le 1$, with the onset of significant intramolecular distortions for higher compressions..

CONCLUSIONS

High-pressure x-ray diffraction studies of pure polycrystalline PETN compound were performed during compression in a diamond-anvil cell at pressures varying from ambient to 30 GPa. The pressure-driven evolution of the diffraction lines assigned to the ambient, tetragonal structure (space group $P \mathbf{4} 2_1 c$) indicated a progressive densification of the studied material. In particular, in the low-pressure range, a gradual decrease of the volume of the unit cell was calculated to be 19% at about 7.5 GPa and was explained by intermolecular compaction. The calculated volume decrease was in good agreement with the values obtained from theoretical calculations for low-pressure compression of PETN reported in the literature. Our studies indicate essentially steady molecular compression up to about 7.4 GPa, where $V/V_0 = 0.81$, with the onset of significant structural modifications occurring for higher compressions that we assign to the appearance of a second phase. The transition from the ambient, tetragonal structure to the postulated orthorhombic phase was evidenced by the appearance of new diffraction lines. At 8 GPa and higher pressures, the diffraction patterns were indexed using a combination of the tetragonal and an orthorhombic structure with $P2_122_1$ as a trial space group. The pressure-driven phase transition, initiated between 7 and 8 GPa, appeared to be incomplete even to 30 GPa, the highest pressure achieved in this study. To investigate PETN further under high pressures, we recently performed Raman scattering experiments to 32 GPa with nitrogen as a quasi hydrostatic pressure transmitting medium. Analysis of the Raman spectra show no evidence for a phase transition in the 5 to 8 GPa pressure range, strongly implying that the anisotropic stresses are significant in initiating the phase transition detected in neat PETN. The results of the Raman study have been submitted for publication [Lipinska-Kalita 2005]. Our future work will endeavor to further elucidate the potential mechanism of shear stress-induced structural transformations in PETN by varying experimental conditions.

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