Uniaxial compression behavior and spectroscopic properties of the explosive pentaerythritol tetranitrate from first-principles calculations

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ABSTRACT

Using dispersion corrected density functional theory, we have investigated the uniaxial compression effect on pentaerythritol tetranitrate (PETN) crystal, which is an secondary high explosive. The principal stresses and shear stresses along different orientations exhibit considerable anisotropy. The Raman spectroscopy is used to explore the pressure effects on the vibrational properties of PETN. Several features are observed in selected Raman vibrational modes along different orientations. Especially, compression along the [0 0 1] orientation induces some anomalous changes of some vibrational modes. Through analyzing intermolecular hydrogen bonds, vibrational mode assignments and variation of the corresponding peak positions of PETN crystal, we propose that the changes between 15.8 and 17.6 GPa may be associated with a phase transformation. This present study has shed light on the anisotropic impact sensitivity and phase change of PETN under compression at atomistic scale.

1. Introduction

Pentaerythritol tetranitrate (PETN, $C_5H_8N_4O_{12}$) is a secondary high explosive material for civilian and military applications [1,2]. Under ambient conditions, PETN molecules crystallize with tetragonal symmetry in $P\bar{4}2_1c$ space group, namely PETN-I [3–5]. At high temperatures, the ambient PETN-I phase transforms to PETN-II phase with $Pcnb$ space group, while the geometries of PETN molecules in PETN I and II are nearly identical [5]. Subsequently, three crystalline phases, i.e., PETN-I, PETN-III, and PETN-IV, exist in (hydrostatic) high-pressure and high-temperature conditions. Heating PETN-I shows no transition to PETN-II and the PETN-I to PETN-III transition takes place above 8.5 GPa [6].

The high-pressure and high-temperature behavior of PETN crystal under shock wave loading is important for its applications as an explosive, especially for understanding the sensitivity. PETN exhibits a highly anisotropic sensitivity to shock wave initiation, in which the shock initiation of PETN markedly depends on the orientation of the crystal axes relative to the shock propagation vector [7–11]. Thus, the anisotropic behavior and the underlying microscopic mechanism for PETN have been extensively investigated from both theoretical and experimental points of view.

In 1976, Halleck et al. firstly measured shock compressions of mean stress from 0.6 to 4.0 GPa in PETN single crystal with planes cut

perpendicular to the [1 1 0] and [0 0 1] directions [7]. Afterwards, Dick et al. unambiguously demonstrated strong orientation dependence of shock sensitivity of PETN single crystals [8–11]. They established that the [1 1 0] and [0 0 1] orientations were highly sensitive while [1 0 1] and [1 0 0] orientations were insensitive and explained the observed anisotropy in terms of a steric hindrance model. Dlott et al. proposed that the orientation dependence of shock sensitivity was possibly attributed to anisotropic shock-induced heating [12]. By means of shock compression of PETN crystal along different orientations, Gupta et al. suggested that the molecular mechanics of shear deformation at the lattice level was correlated with rotational conformations of PETN, further indicating that the chemical anisotropy of PETN was due to local lattice polarization [13]. From time-resolved emission spectroscopy, nitronium ion NO_2^+ was observed when the PETN crystal was shocked along the [1 1 0] and [0 0 1] orientations [14]. Furthermore, they developed an isotropic continuum model to describe the thermo-mechanical response of unreacted PETN single crystals subjected to shock wave loading [15].

Atomistic simulations, based on either density functional theory (DFT) or empirical force field, are effective ways to understand the detonation mechanism under high pressure and/or high temperature and have been employed to characterize the behavior of PTEN under hydrostatic compression and uniaxial compression in the different directions [16–28]. Conroy et al. performed first-principles simulation for

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hydrostatically and uniaxially compressed PETN to explore the relationship between shear stress and anisotropic sensitivity, in which the maximum shear stresses in the sensitive [1 1 0] and [0 0 1] directions are greater than for the insensitive [1 0 0] direction at longitudinal stresses above 4 GPa [16]. Using molecular dynamics simulations with a nonreactive force field, Eason and Sewell also characterized the mechanical deformation processes of PETN single crystals for shocks along the relatively sensitive [0 0 1] and the insensitive [1 0 0] directions [17]. Additionally, utilizing nonequilibrium molecular dynamics (NEMD) simulations with the ReaxFF reactive force field, Zybin et al. investigated the primary initiation pathway of PETN under shock compression and rapid compression and shear loading, in which NO_2 was the primary product when strongly shocked along the [1 0 0] direction [18] and the considerably larger jumps in stress and temperature of the sensitive direction were attributed to the close intermolecular contacts [19].

Infrared and Raman spectroscopies are useful tools to characterize conformational changes and bonding features and to disclose the initiation mechanism of shock-compressed energetic materials, especially the anisotropic sensitivity. For instance, using single-pulse Raman spectroscopy, Gupta and co-workers examined selected vibrational modes to investigate the molecule-level response of PETN single crystals shocked along the [1 1 0] and the [1 0 0] orientations. They found that the Raman shift as a function of shock stress for the CH_2 and NO_2 stretching modes is substantially different for the [1 1 0] and [1 0 0] orientations, and a discontinuous change for [1 1 0] orientation originating from the conformational changes of PETN was observed between 4 and 5.5 GPa [20]. Subsequently, molecular and reactive behavior of PETN at high pressures and high temperatures relevant to shock wave induced decomposition were analyzed by the changes in Raman spectra [6]. Additionally, there have been substantial studies on the changes of conformation or symmetry of PETN molecules or crystal via examining the vibrational spectra [21–25]. In particular, the propensity of PETN molecules to conformational changes were evaluated based on the Raman measurements and DFT calculations. It was pointed out that change of conformation/symmetry can be readily observed through changes in the vibrational spectrum owing to the extreme flexibility of PETN molecule [22]. However, the Raman spectra of PETN have also been measured in a compression sequence up to about 31.3 GPa, in which no pressure-induced phase transformation occurred. It was believed that the experimentally observed pressure-driven phase transition is strongly influenced by the nonhydrostatic conditions and that such transition is shear-driven [23].

Despite the extensive theoretical efforts devoted to the anisotropic sensitivity of PETN, most of them focused on mechanical deformation, decomposition mechanism and conformational changes along different orientations [13–17,21–25]. However, the detailed changes in spectroscopic characteristics, possible phase transformations, and energy transfer mechanism of PETN under uniaxial compression are still insufficiently investigated. These goals motivate the present DFT calculations to shed light on the anisotropic response and vibrational modes of PETN under uniaxial compressions along two major crystalline directions. The calculated principal stresses, shear stresses and band gap exhibit considerable anisotropy. Significant changes in Raman spectra along the [0 0 1] orientation compression provide evidence for a possible pressure-induced phase transition in the range of from 15.8 to 17.6 GPa.

2. Computational methods

The polymorph of PETN crystal at ambient conditions is the PETN-I phase, with a tetragonal symmetry in the $P\overline{4}2_1c$ space group and $S4$ molecular configuration (see Fig. 1) [3–5]. All DFT calculations within periodic boundary condition were carried out using Cambridge Sequential Total Energy Package (CASTEP) [29]. The exchange–correlation interaction was treated within the generalized gradient

approximation (GGA) parameterized by the Perdew-Burke-Ernzerhof (PBE) functional [30]. The norm-conserving pseudopotentials were used to describe the ion-electron interactions [31]. To account for the intermolecular non-covalent interactions in energetic molecular crystals and a long-range dispersion correction in the DFT + D2 formulations of Grimme [32] was employed, which has been proven as a suitable approach in our recent benchmark calculations [33]. As a reasonable compromise between computational cost and accuracy, a $2 \times 2 \times 3$ Monkhorst–Pack k grid for sampling the Brillouin zones [34] and a kinetic energy cutoff of 1000 eV for planewave basis were adopted. The unit cell parameters and atomic coordinates were fully relaxed by the Broyden, Fletcher, Goldfrab, and Shannon (BFGS) algorithm [35]. Convergence criteria of maximum total energies of 5×10^{-6} eV/atom, maximum force of 0.01 eV/Å, maximum stress of 0.02 GPa and maximum displacement of 5×10^{-4} Å were adopted throughout all calculations. Uniaxial strains were gradually applied along the directions of two lattice vectors a and c, i.e. [1 0 0] and [0 0 1] orientations. Uniaxial compression is gradually applied up to 70% of the equilibrium cell volume in steps of 2% along one of the lattice directions. At each step, only the atomic coordinates were allowed to relax while the unit cell was held fixed. For comparison, we also considered PETN crystal under hydrostatic pressure.

Based on the optimized crystal structures under compression, Raman spectra was computed with the density functional perturbation theory (DFPT) [36] based on the linear response formalism. The experimental factors of temperature (10 K) and incident light wavelength (514.5 nm) were taken into account for simulating Raman intensity. The spectrum peak was broadened by Lorentzian function with 20 cm^{-1} width.

3. Results and discussion

First, our DFT calculations reproduced the experimental molecular packing and molecular geometry of PETN crystal at zero pressure. As expected, the computed lattice parameters of $a = b = 9.402$ Å and $c = 6.574$ Å compare well with experimental measurements of $a = b = 9.378$ Å and $c = 6.708$ Å, indicating that the current PBE + D2 scheme gives reasonable descript of the intermolecular non-covalent interaction.

The uniaxial compression associated with the anisotropic shock sensitivity of an energetic material crystal, is particularly important for the plastic deformations and mechanochemical reactions, and the stress tensors are employed to describe the anisotropic response under shock wave loading. Thus, as diagonal elements of the stress tensor, our calculated principal stresses for two uniaxial compressions as a function of compression ratio V/V_0, together with the hydrostatic compression for comparison, are displayed in Fig. 2. Overall speaking, the three principal stresses σ_{xx}, σ_{yy}, σ_{zz} along [1 0 0] and [0 0 1] orientations exhibit apparent increase with decreasing compression ratio V/V_0; however, different variation trends and amplitudes clearly indicate significant anisotropic behavior of PETN crystal. Specifically, the difference in principal stresses σ_{xx}, σ_{yy}, σ_{zz} along the [1 0 0] orientation is 6.38 GPa at $V/V_0 = 0.70$, while σ_{xx}, σ_{yy}, σ_{zz} along the [0 0 1] orientation show a greater difference by 10.96 GPa, indicating more obvious anisotropic compressibility. Concomitantly, principal stresses σ_{xx} and σ_{yy} along the [0 0 1] orientation and hydrostatic compression exhibit nearly identical increase with decreasing pressure possibly originated from the high symmetry of PETN crystal and molecule, whereas σ_{zz} along the [0 0 1] orientation is obviously higher than that of the hydrostatic compression. Under compression up to about $V/V_0 = 0.70$, σ_{zz} reaches up to 28.53 GPa. Thus, we suggest that the [0 0 1] direction is more sensitive compared to the [1 0 0] direction. This distinct anisotropic behavior of the principal stresses is consistent with previous experimental and computational results in which shocks along [0 0 1] orientation was highly sensitive while [1 0 0] orientation was highly insensitive [8–11,17]. In Fig. 2, it is also noteworthy that σ_{zz} shows a subtle