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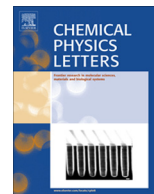


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# Polymorphs of 1,1-diamino-2,2-dinitroethene (FOX-7): Isothermal compression versus isobaric heating



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## ABSTRACT

Raman spectroscopy was used to examine polymorphic changes in 1,1-diamino-2,2-dinitroethene (FOX-7) single crystals under: isothermal compression to 15 GPa and isobaric heating to 500 K. Changes in the Raman spectra were observed at  $\sim 2.0$  and  $\sim 4.5$  GPa, and at  $\sim 390$  K and  $\sim 450$  K. These onsets are in general accord with previously reported onsets from IR measurements under isothermal compression and from X-ray diffraction measurements under isobaric heating, respectively. In contrast to recent suggestions, we show that the high pressure polymorphs have different vibrational structures, and likely different crystal structures, than the high temperature polymorphs.

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## 1. Introduction

High performance and low sensitivity constitute two extremely desirable attributes for a high explosive (HE). Thus, there have been significant and continuing efforts to obtain insensitive high explosive (IHE) crystals that possess these attributes. 1,1-Diamino-2,2-dinitroethene  $C_2(NH_2NO_2)_2$ , also known as DADNE or FOX-7, is a novel HE crystal with considerable potential for applications requiring high performance, insensitive explosive compositions [1–6]. Its low sensitivity to initiation has attracted considerable interest, but there has been little progress in understanding the microscopic factors governing this behavior. An important step toward advancing this understanding is to gain insight into the vibrational and crystallographic structure of FOX-7 at the thermo-mechanical conditions relevant to shock initiation. Toward this objective, the identification of polymorphic phases of FOX-7 at high pressures (HP) and/or high temperatures (HT) is an important need.

FOX-7 crystallizes in a monoclinic structure with a space group of  $P2_1/n$  [2]. As shown in Figure 1, molecules in the crystal are arranged 'head-to-tail' forming wave-shaped layers with extensive intra- and intermolecular hydrogen bonding within the layers. Previous crystal structure studies have demonstrated that the room temperature structure ( $\alpha$ -FOX-7) transforms to two other polymorphs at higher temperatures [7–9]; the transitions were reported to occur above  $\sim 386$  K ( $\alpha$ - $\beta$ ) and  $\sim 446$  K ( $\beta$ - $\gamma$ ). The  $\beta$ - and  $\gamma$ -polymorph structures were determined to be the  $P2_12_1$  and  $P2_1/n$ , respectively. The  $\alpha$ - $\beta$  transformation has a displacive character while the  $\beta$ - $\gamma$  is reconstructive. Both transformations lead to a flattening of the wave-shaped layers and changes in the

displacement of the nitro group with respect to the molecular plane [8,9]; these changes were larger during the  $\beta$ - $\gamma$  transition than the  $\alpha$ - $\beta$  transition.

Recent synchrotron IR experiments [10] implied that the two high temperature phases may correspond to the phases observed at high pressures [10,11]. Because isobaric heating usually affects the crystal structure differently than isothermal compression, we report here a careful comparison of the high temperature and high pressure phases using the same diagnostic method. Raman spectroscopy was utilized because it is a versatile approach for detecting and characterizing polymorphic changes in HE crystals under extreme pressure and temperature conditions [12–16]. Unlike previous IR studies, we used single crystals. Also, the broad range of frequencies in our spectroscopic measurements permitted the first measurements of lattice modes.

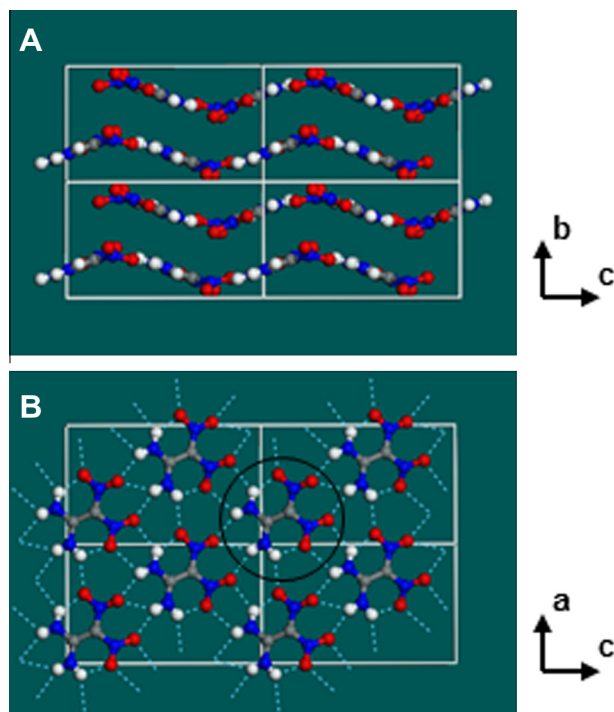
## 2. Experimental procedures

Finely powdered FOX-7 was obtained from Dr. Joel R. Carney of the Naval Surface Warfare Center-Indian Head Division (NSWC-IHD). Single crystals were grown from a solution of the powder in dimethyl sulfoxide (DMSO) at room temperature. Overall, the crystals had rectangular shapes with well-developed (100) or (001) faces. The crystals were used either as grown or cut to dimensions to fit the sample compartment in the high pressure cell.

High pressures were generated using a modified Merrill-Bassett type diamond-anvil-cell (DAC). A rhenium gasket, pre-indented to 0.05 mm with a 0.12 mm hole drilled in the indentation, served as the sample compartment. Cryogenically loaded nitrogen was used as a pressure transmitting medium; the cryogenic loading did not affect the crystal quality. Frequency shifts of the R-lines of the ruby crystals were used to monitor pressure in the sample compart-

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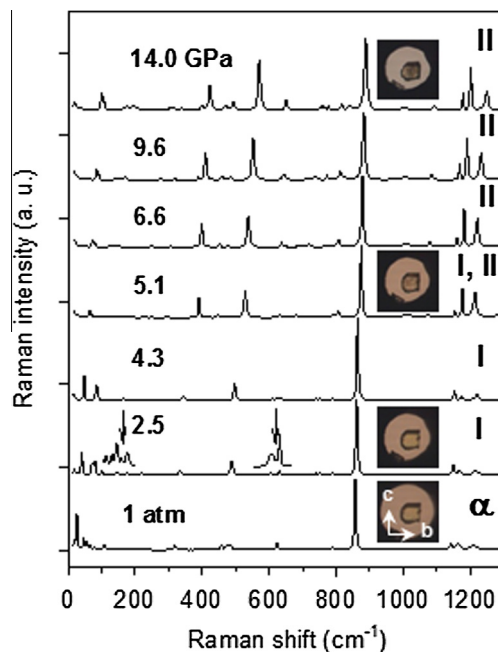
**Figure 1.** Projections of FOX-7 crystal structure at ambient conditions: (A) along the *a* axis, showing the arrangement of wave-shaped layers; (B) along the *b* axis, showing the intra- and inter-molecular hydrogen bonding (blue dashed lines) within one layer. Circle highlights the hydrogen bonds associated with one molecule. Molecules are represented by the ball-and-stick model. Legend: carbon, grey; nitrogen, blue; oxygen, red; hydrogen, white. Crystal unit cells are indicated by white lines.

ment. Precision of our pressure measurements was estimated to be 0.05 GPa. To examine the high temperature polymorphs in nearly identical experimental conditions, the DAC at ambient pressure was heated with a resistive heater wrapped around the cell. The temperature of the sample was monitored using iron-constantan thermocouples. The accuracy of temperature measurements was determined to be  $\pm 2$  K.

The 532 line from a cw diode-pumped solid-state laser was used for Raman excitation. Less than 1 mW of power was used to avoid any damage to the samples. The FOX-7 crystals used in these studies were oriented with the (100) plane normal to the excitation beam. The orientation of crystals was determined on the basis of known cleavage plane and results of polarized Raman measurements. A micro-Raman system (T64000, JY-Horiba) equipped with a microscope was used in this work; it provided a spectral resolution of  $\sim 0.8$   $\text{cm}^{-1}$  and was capable of measuring spectra to frequencies as low as 20  $\text{cm}^{-1}$ . Two different sets of Raman data were obtained: (1) high pressures to 15 GPa at room temperature and (2) high temperatures to 500 K at ambient pressure.

### 3. Results and discussion

Typical Raman spectra, at various pressures and in the frequency range 20–1300  $\text{cm}^{-1}$ , are shown in Figure 2. A close examination of all spectra indicated that changes occurred around  $\sim 2$  GPa and  $\sim 4.5$  GPa. The phases above these pressures are tentatively labeled as I and II, respectively. Minor changes were observed at 2 GPa: two peaks emerged at  $\sim 153$  and 609  $\text{cm}^{-1}$  (indicated by arrows in the figure) and two other peaks merged into one at 486  $\text{cm}^{-1}$ . The peak at 153  $\text{cm}^{-1}$  corresponds to lattice vibrations, while the other two peaks can be tentatively assigned

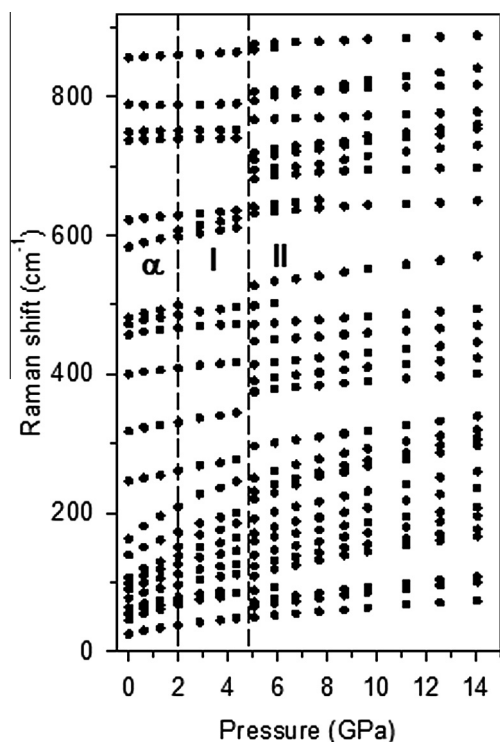


**Figure 2.** Raman spectra and selected sample images of FOX-7 in diamond anvil cell (DAC) at several pressures. Symbols I and II denote the high pressure polymorphs. Intensities of spectra above 5 GPa were multiplied by 2. Parts of the spectrum at 2.5 GPa are enlarged to show new peaks; arrows indicate these peaks. Images show a FOX-7 single crystal with dimensions of  $\sim (30 \times 30 \times 20)$   $\mu\text{m}^3$  in the DAC compartment  $\sim 100$   $\mu\text{m}$  in diameter. Crystallographic axes of the crystal are indicated in the image obtained at ambient pressure.

to NO wagging vibrations [17]. There were no other apparent changes to the spectra as can be seen in Figure 3, and it will be reported in details elsewhere [18]. The present findings are in contrast to the IR studies on polycrystalline samples, where extensive changes, including discontinuities in the pressure shifts of various modes [10,11], were observed at 2 GPa.

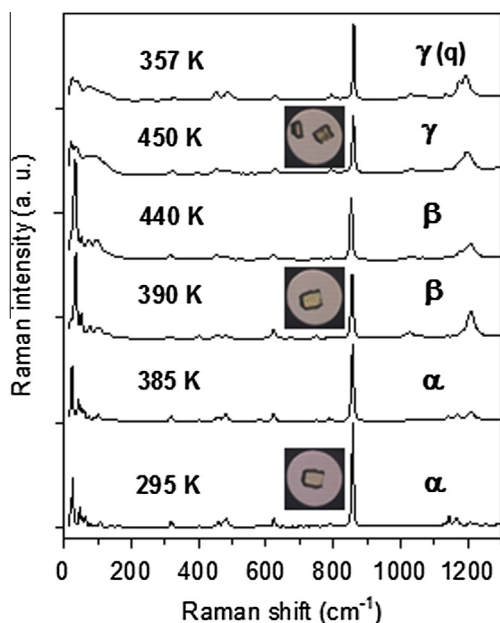
The second onset of changes in the spectra was observed above  $\sim 4.5$  GPa. At this pressure, the following features were observed: (i) intensity decrease for most Raman peaks, (ii) relative changes in the peaks' intensities, (iii) large discontinuities in pressure shifts, and (iv) the four lowest frequency peaks in the lattice modes were 'replaced' by two peaks. All these changes occurred around 4.5 GPa and were completed by  $\sim (6\text{--}7)$  GPa; the changes in pressure shifts of Raman modes are shown in Figure 3. Other details will be presented elsewhere [18]. In addition to the spectral changes, changes in the crystal appearance were also observed. As seen in the image next to the spectrum at 5.1 GPa, the crystal appeared grayish, seemingly due to the lines developed in a direction normal to the crystallographic *b* axis, i.e., between the wave-shaped layers (Figure 1A). With further pressure increase to 15 GPa, the crystal became more grayish and the Raman intensity increased, likely due to the resonance effect. However, there were no additional measurable changes in the spectra other than gradual shifts. Thus, at pressures above 4.5 GPa and up to 15 GPa, the crystal phase was stable. This result is in contrast to the previous proposal of a phase change at 10 GPa [11].

To examine a potential link between the HP and HT phases, we undertook Raman measurements at high temperatures. Typical spectra along with the crystal images are shown at several temperatures in Figure 4. These results confirm the occurrence of spectral changes at temperatures, corresponding to the transitions to the  $\beta$  and  $\gamma$  phases, as determined from X-ray measurements [7–9]. A close examination of the Raman spectra indicates that the both transitions,  $\alpha$ – $\beta$  and  $\beta$ – $\gamma$  introduce changes primarily in the lattice

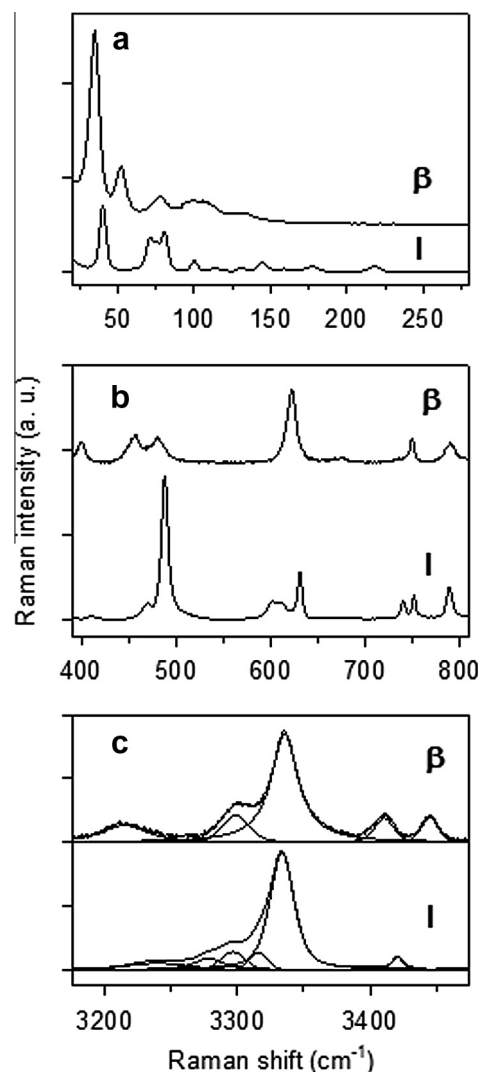


**Figure 3.** Pressure dependence on Raman shifts on vibrational modes in the frequency range 20–900  $\text{cm}^{-1}$ . Dashed lines denote approximate pressure onsets for the phase I and II.

modes. Such changes are expected because these transitions lead to a change in the space group ( $\alpha$ – $\beta$ ), and an increase in the number of molecules in the unit cell ( $\beta$ – $\gamma$ ) [8,9]. However, it is somewhat surprising that the spectral changes were not larger the intramolecular modes, as would be expected on the basis of the reported molecular changes.



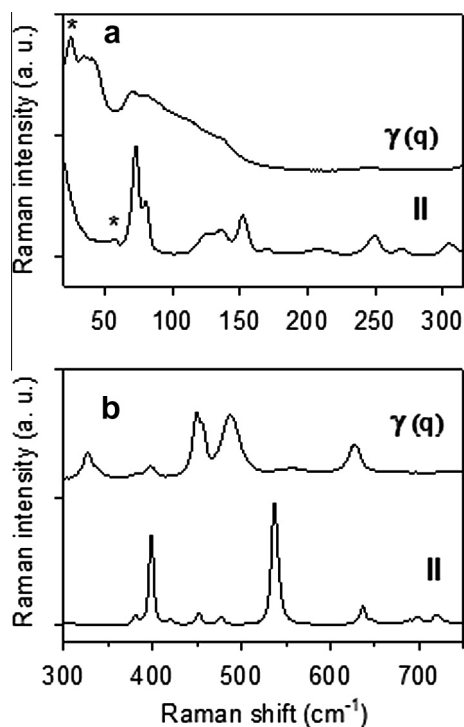
**Figure 4.** Raman spectra of FOX-7 at various high temperatures and ambient pressure.  $\alpha$ ,  $\beta$  and  $\gamma$  denote the room and high temperature polymorphs, while  $\gamma$  (q) the  $\gamma$ -polymorph quenched to 357 K. Note that the  $\beta$  to  $\gamma$  transition leads to splitting and displacement of the crystal.



**Figure 5.** Comparison of FOX-7 Raman spectra for phase-I (HP) and  $\beta$ -phase (HT) in the selected frequency ranges. Phase-I was measured at 2.5 GPa and room temperature (RT) while  $\beta$ -phase was measured at 395 K and ambient pressure. Raman intensities were multiplied by 3 and 12 in panels (b) and (c), respectively. The spectra are fitted in panel (c) to illustrate a difference in the number of peaks in the two spectra.

While detecting the  $\beta$ – $\gamma$  phase transition, we also observed significant changes to the crystal. As seen in the image taken at 450 K (Figure 4), the crystal split and moved/jumped around within the confinement of the cell compartment. This ‘thermosalient’ behavior was quite reproducible in our experiments. This behavior, also known as jumping crystal effect, was observed previously for other crystals [19–21], and recently noted for FOX-7 [9]. This phenomenon is often associated with phase transitions accompanied by a markedly large and anisotropic change in the crystal unit cell. This observation suggests the important role of mechanical strains in association with the  $\beta$ – $\gamma$  phase transition.

Furthermore, our results confirm that the  $\beta$ – $\gamma$  transition is not reversible upon temperature decrease and the  $\gamma$ -phase can be quenched at lower temperatures. The Raman spectrum obtained for the quenched  $\gamma$ -phase at 357 K is shown in Figure 4, and labeled as  $\gamma$  (q). Due to the lower temperature, this spectrum is somewhat better resolved than the spectrum obtained at the  $\beta$ – $\gamma$  transition. Still, the region of lattice modes for this phase is quite complex in contrast to  $\beta$ -phase spectrum, likely due to the overlap of multiple peaks that result from doubling of molecules in the unit cell [9].



**Figure 6.** Comparison of FOX-7 Raman spectra for phase-II (HP) and  $\gamma$ -phase (HT) quenched to lower temperature –  $\gamma$  (q). Phase II was measured at 6.7 GPa and room temperature while  $\gamma$  (q) phase at 357 K and ambient pressure. Raman intensities were multiplied in panel (a) by 2 (phase-II), and in panel (b) by 2 (phase-II) and 5 (phase  $\gamma$  (q)). The features labeled with asterisks represent laser lines.

Figures 5 and 6 compare, side-by-side, the Raman spectra obtained under isothermal compression with the spectra under isobaric heating to assess the suggested link [10] between the HP and HT polymorphs. Since compression and heating typically shift the Raman peaks in opposite directions, a spectral comparison needs to take into account the different location of the corresponding peaks.

In Figure 5, we compare the spectra of phase-I obtained at 2.5 GPa with the spectra of  $\beta$ -phase obtained at 390 K, over three different frequency ranges. In the region of the lattice modes, we note differences in the pattern of the peaks and their numbers: 11 (phase-I) 7 ( $\beta$ -phase). Next, the group of three peaks located around 600–660  $\text{cm}^{-1}$  (NO wagging vibrations), characteristic of phase-I, is not observed in the  $\beta$ -phase. The collection of four peaks between 740 and 800  $\text{cm}^{-1}$ , present in the spectrum of phase-I, looks different and is located at lower frequencies than in the  $\beta$ -phase; the latter is opposite to what is expected from the shifts caused by pressure and temperature. Finally, in the high frequency region – panel (c), dominated by the NH stretching vibrations, the patterns of the peaks and their numbers are different for the two spectra. All these differences clearly indicate that phase-I obtained at pressures above 2 GPa has a different structure than the  $\beta$ -phase obtained at temperatures above 390 K.

Figure 6 compares the phase-II (HP) spectra and the  $\gamma$ -phase (HT) spectra over two sets of frequencies. The spectra of phase-II were obtained at 6.7 GPa, the pressure at which the phase I to II transformation is complete, while the spectra of  $\gamma$ -phase were measured after quenching to 357 K. The spectra of this quenched phase are labeled as  $\gamma$  (q) in the figures. As seen in Figure 6 – panel (a), which largely covers the lattice modes, the  $\gamma$  (q) phase peaks are broad and strongly overlapped with each other within  $\sim 100 \text{ cm}^{-1}$ . In contrast, the phase-II peaks are well separated and markedly shifted to higher frequencies. These two very different

patterns are not easily compared but they do show that the Raman spectra in the lower frequency range are very different. The spectra in the higher frequency range show clearer spectral peaks. As seen in Figure 6 – panel (b), there are several obvious differences between the two spectra. First, the 6 peaks between 370 and 560  $\text{cm}^{-1}$ , present in the spectrum of phase-II, have significant differences from the peaks in the  $\gamma$ -phase spectrum; the latter spectrum has at least 7 peaks between 300 and 530  $\text{cm}^{-1}$ . Furthermore, the group of three peaks located around 700  $\text{cm}^{-1}$  in phase-II is not present in the  $\gamma$ -phase spectrum. These examples indicate clear differences between the spectra of phase-II and the  $\gamma$ -phase, thereby demonstrating their different structures. However, for completeness, we need to mention some similarities in the overall behavior of phase-II and  $\gamma$ : (i) transitions to these phases were irreversible at their phase boundaries, (ii) both phases were recoverable either at lower pressure or temperature, respectively, and (iii) sample appearance changed at the transitions. These similarities suggest that both the I–II transition and the  $\beta$ – $\gamma$  transition have a reconstructive character.

The present results have demonstrated that the high pressure phases (I and II) and the high temperature phases ( $\beta$  and  $\gamma$ ) have different Raman spectra. Pressure induced changes at  $\sim 2$  GPa (phase-I) are minor, implying minimal structural changes. Since the changes at this transition are observed in the NO wagging modes, this suggests a change of the nitro groups' angle with respect to the molecular plane. In contrast, temperature induced changes at 390 K ( $\beta$ -phase) were observed in both the lattice and the intramolecular modes. X-ray diffraction studies [8], demonstrated that these changes result from the monoclinic to orthorhombic structure change, and the  $\text{NO}_2$  groups' displacement with respect to the molecule plane. Differences in the Raman spectra of phase-I and  $\beta$ -phase provide evidence that these phases represent two different FOX-7 polymorphs.

The spectral changes at  $\sim 4.5$  GPa (phase-II), in contrast to changes at 2 GPa, are quite extensive. They indicate both molecular and intermolecular changes. Furthermore, changes in the crystal appearance and a large pressure hysteresis upon unloading suggest a reconstructive character for this transition. While our inference of a reconstructive transition (phase-II) is similar to that observed for the temperature induced  $\beta$ – $\gamma$  transition, the differences in the Raman spectra for the phase-II and the  $\gamma$ -phase suggest that the high pressure phase-II likely has different structure than the  $\gamma$ -phase.

#### 4. Conclusions

Using Raman spectroscopy and imaging measurements, we compared the polymorphic behavior of FOX-7 single crystals under isothermal compression with the polymorphic behavior under isobaric heating. Isothermal compression to 15 GPa showed two instances of changes in the Raman spectra at  $\sim 2$  and  $\sim 4.5$  GPa, indicating phase transitions to phase-I and II, respectively. These pressure onset values are in general accord with recent IR data [10]. However, in contrast to that study, our work demonstrates that the extent and the character of the spectral changes are significantly different at 2 and 4.5 GPa. Isobaric heating to 500 K showed changes in the Raman spectra at  $\sim 390$  K and  $\sim 450$  K associated with the  $\alpha$ – $\beta$  and  $\beta$ – $\gamma$  transitions, respectively, consistent with the X-ray diffraction results [8,9]. Comparison of the Raman data under these two different experimental conditions showed clear differences in the vibrational structure between the high pressure and high temperature phases. Hence, in contrast to inference from the previous high pressure IR measurements [10], our results suggest that the high pressure phases likely have different structures than the high temperature phases. X-ray diffraction measurements



are required to establish the crystal structures of the high pressure phases.

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