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High-pressure Raman investigations of phase transformations in pentaerythritol (C(CH₂OH)₄)

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Abstract

Our high-pressure Raman scattering experiments on pentaerythritol (C(CH₂OH)₄) show that this compound undergoes at least three phase transformations up to 25 GPa. Splitting of various modes at ~6.3, ~8.2 and 10 GPa suggests that these phase transformations result in lowering of crystalline symmetry. A very small discontinuous change in slope of most of the Raman-active modes is observed at 0.3 GPa. However, no other signature of a phase transition was observed at this pressure. The observed correlation of the pressures for the onset of the two phase transformations with the limiting values of the distances between various non-bonded atoms in the parent phase suggests that the molecular rearrangements across the phase transformations are not very drastic. In addition, our earlier Fourier transform infrared and present Raman investigations indicate that high-pressure compression leads to increase in strength of the hydrogen bond present in this compound.

1. Introduction

Pentaerythritol [2, 2-bis(hydroxymethyl)-1, 3-propanediol], C(CH₂OH)₄, can be viewed as being formed by replacing each H in methane by (CH₂OH) units. At ambient conditions, this compound crystallizes in a high-symmetry tetragonal structure (space group $I\bar{4}$) [1]. In this structure, shown in figure 1, the molecules are arranged in layers parallel to the crystallographic *a*–*b* plane with an inter-layer separation of 4.363 Å. While the cooperative hydrogen bonding constitutes the predominant intra-layer interaction between the molecules, the coupling between different layers is weak and is of van der Waals type. Due to its simple structure, pentaerythritol (PET) is a model compound for studies of the properties of hydrogen bonds and the phase transformations in cyclic and acyclic alcohols under different thermodynamic conditions. In particular, the compression under high pressures can cause significant variations in the relative strengths of the van der Waals and hydrogen bond interactions in PET, affecting the structure considerably. Moreover, such studies may also be useful to understanding the high-pressure behaviour of the related initiating explosives such as pentaerythritol tetra-nitrate (PETN), the explosive sensitivity of which seems to be

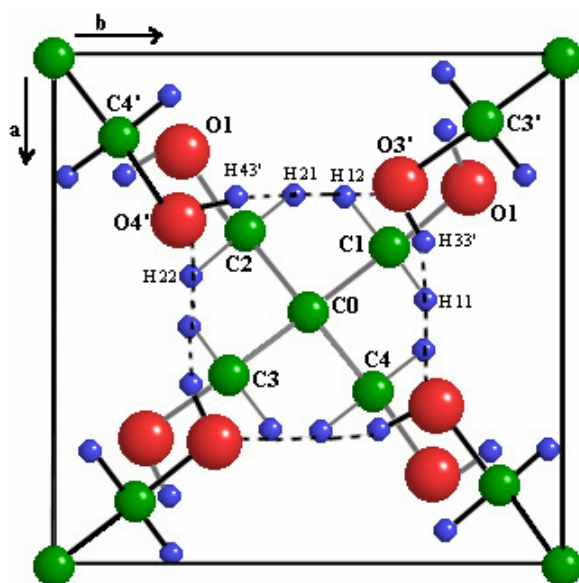


Figure 1. The crystal structure of PET at ambient conditions (space group $I\bar{4}$).
(This figure is in colour only in the electronic version)

closely related to the structural features [2]. For these reasons, several investigations have been carried out on PET [3–9].

At high temperatures (452.7 K), PET is found to transform from its body-centred-tetragonal phase to a plastic face-centred-cubic phase in which the molecules are orientationally disordered [3]. An x-ray powder diffraction study up to 0.88 GPa by Frolov *et al* [4] suggested that this material undergoes a first-order phase transformation to an iso-structural phase at ~ 0.41 – 0.55 GPa. This phase was claimed to be metastable for ~ 30 days after the release of pressure. However, a subsequent x-ray diffraction investigation ruled out an iso-structural nature for the transformation due to the emergence of new diffraction lines across the transformation [5]. The existence of a high-pressure transformation was also supported by the pressure dependence of the electrical conduction [6] and its IR spectra [7]. Recently, the high-pressure behaviour of PET has been re-investigated up to 1.15 GPa with the help of high-pressure single-crystal x-ray diffraction [8]. These results ruled out the existence of any phase transformation claimed to have been observed earlier. In addition, this single-crystal x-ray diffraction study also showed that, as expected, the inter-layer compressibility is several times larger than the intra-layer compressibility and at ~ 0.28 GPa the distance between the centres of the nearest molecules of the neighbouring layers becomes shorter than the distance between the centres of intra-layer hydrogen bonded molecules. Increasing compression at higher pressures is likely to bring about a further reduction in the inter-atomic distances of the non-bonded atoms. Beyond some limiting value of these distances, a further compression will bring about more repulsive contributions to the cohesive energy and thus may result in a phase transformation or a substantial change in the molecular structure [9, 10]. To understand the behaviour of PET at higher pressures we have now investigated this material up to ~ 25 GPa with the help of Raman scattering.

2. Experimental details

High-pressure Raman experiments were carried out using a diamond anvil cell (DAC) employing colourless diamonds, with culet sizes of ~ 0.45 mm. PET powder and a couple of tiny chips of ruby were loaded in a stainless steel gasket with a hole of diameter ~ 0.2 mm, drilled after pre-indenting the gasket to ~ 0.09 mm. The pressure inside the DAC was measured using the ruby fluorescence method [12]. As PET is soluble in most of the pressure-transmitting liquids, the experiments were performed either without any pressure transmitter or with other pressure transmitters such as silicon oil and CsI powder. However, recorded variations in the ruby R-lines showed that the pressure distribution in the DAC is similar in all the experiments irrespective of the pressure transmitter. This is understandable in view of the layered structure of PET, which makes it a very soft material. Thus all the quantitative results reported in this paper are from experiments where PET powder was loaded without any pressure transmitter. In addition to these measurements, some experiments were also performed on single crystals of PET to verify the earlier reported observation of a crystal shattering phase transformation at ~ 1.5 GPa [8]. For these experiments, single crystals were grown from a saturated solution of PET (Fluka; $>97\%$) by slow evaporation. As PET is soluble in 4:1 methanol–ethanol mixture, a saturated solution of PET in methanol–ethanol was used as a pressure transmitter in these experiments. Single-crystal experiments were also repeated with silicon oil and CsI as pressure transmitters. All these powder as well as single-crystal experiments showed similar spectral changes below 5 GPa. However, above 5 GPa the PET crystal in the saturated solution of PET started showing drastically different results. As this difference in spectra is observed only with one pressure transmitter, we feel that it could be due to some interaction between the single crystal and the changes in the complex pressure transmitter.

Raman spectra were excited using an Ar-ion laser (488 nm) or a solid-state pumped diode laser (532 nm). An appropriate super-notch filter was used to block the Rayleigh scattered laser light. Raman spectra at various pressures were recorded using 45° geometry with a half-metre monochromator coupled to a liquid-nitrogen-cooled CCD. Data were collected using an entrance slit of 0.03 mm. Because of the usage of the super-notch filters, Raman modes below 100 cm^{-1} could not be recorded. Also in the DACs the Raman modes falling under the first-order diamond peak at 1331 cm^{-1} cannot be studied. However, several modes lying between $100\text{--}1300\text{ cm}^{-1}$ and $2700\text{--}3400\text{ cm}^{-1}$ were followed as a function of pressure. In the increasing-pressure cycle, Raman spectra were recorded at finer pressure steps up to ~ 14 GPa and then the pressure was raised to ~ 25 GPa in a couple of steps. However, as the Raman spectra beyond ~ 14 GPa show a monotonic broadening of all the observed peaks, the data beyond ~ 14 GPa are excluded from presentation here. Spectra were recorded on the release cycle also. In addition, we have also investigated PET in a restricted spectral region of $2700\text{--}3800\text{ cm}^{-1}$ using the FTIR technique up to ~ 25 GPa [11]. However, in view of the poor resolution obtained in these IR investigations, the results of the present Raman studies are far more conclusive.

3. Results

Group theoretical analysis of normal modes for PET at ambient conditions shows that it has 47 fundamental modes [13]—namely, 16 A + 15 B + 16 E. All the optic modes are Raman active whereas only B and E modes are IR active. Earlier assignments of modes of vibrations of PET, based on experimental Raman [14] as well as IR [15] investigations, are mutually inconsistent. Therefore, we follow the assignments based on the comparison between the experiments and lattice dynamical calculations [13]. Internal and external Raman-active modes observed by us

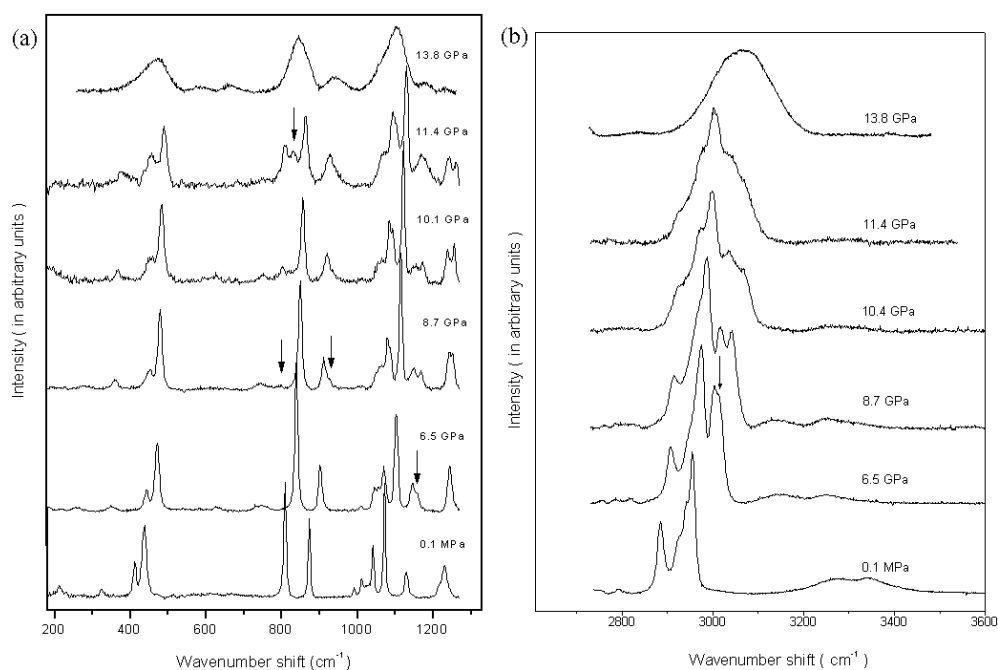


Figure 2. (a) Raman spectra of PET, between 200 and 1300 cm^{-1} , at various pressures. The arrows at 8.2 GPa show the emergence of new peaks across the transition. (b) The pressure variation of Raman modes of PET, between 2800 and 3400 cm^{-1} .

are in very good agreement with the earlier reported values [14]. The O–H deformation mode at 674 cm^{-1} is found to be very weak and broad at ambient pressure but gains intensity at higher pressures. Similar behaviour for this mode was also observed earlier at low temperatures [15]. Figure 2(a) shows the Raman spectra of PET between 200 and 1300 cm^{-1} at a few representative pressures. Figure 2(b) displays the observed pressure-induced variations in the Raman spectra of the C–H and O–H stretch modes, lying in the range $2800\text{--}3800 \text{ cm}^{-1}$.

In the tetragonal phase, all the modes show an increase in frequency with pressure except the O–H stretching modes, which show a decrease with pressure. Figures 3(a)–(e) show the observed pressure-induced shifts of Raman-active modes in the region between 100 and 3600 cm^{-1} up to 12 GPa. At $\sim 0.3 \text{ GPa}$, all the C–O, C–C and C–H modes display a small discontinuous change in the slope ($d\nu/dP$). Figure 4 shows that in the same pressure range, the recorded Raman spectra show a sudden gain in the intensity of the O–H deformation mode at 1432 cm^{-1} with respect to the C–H scissor mode at 1480 cm^{-1} . The O–H deformation mode keeps increasing in intensity beyond this pressure. In this context, we note that at about this pressure, inter-layer and intra-layer inter-molecular distances become comparable [8]. Therefore, beyond this compression, the inter-layer inter-atomic interactions may also be relevant in bringing about pressure-induced changes in the phonon modes. The observed small discontinuity in the slope of most of the modes at $\sim 0.3 \text{ GPa}$ may be an indication of this change in the interactions. Alternatively, it is also possible that this change in slope is a signature of a subtle and iso-structural phase transition. However, this issue cannot be unambiguously settled with the help of just Raman data.

Figures 3(a)–(e) also show that on further increase of pressure, some modes show a sudden change in slope around 6.3 GPa. In addition, several modes show a discontinuous change at

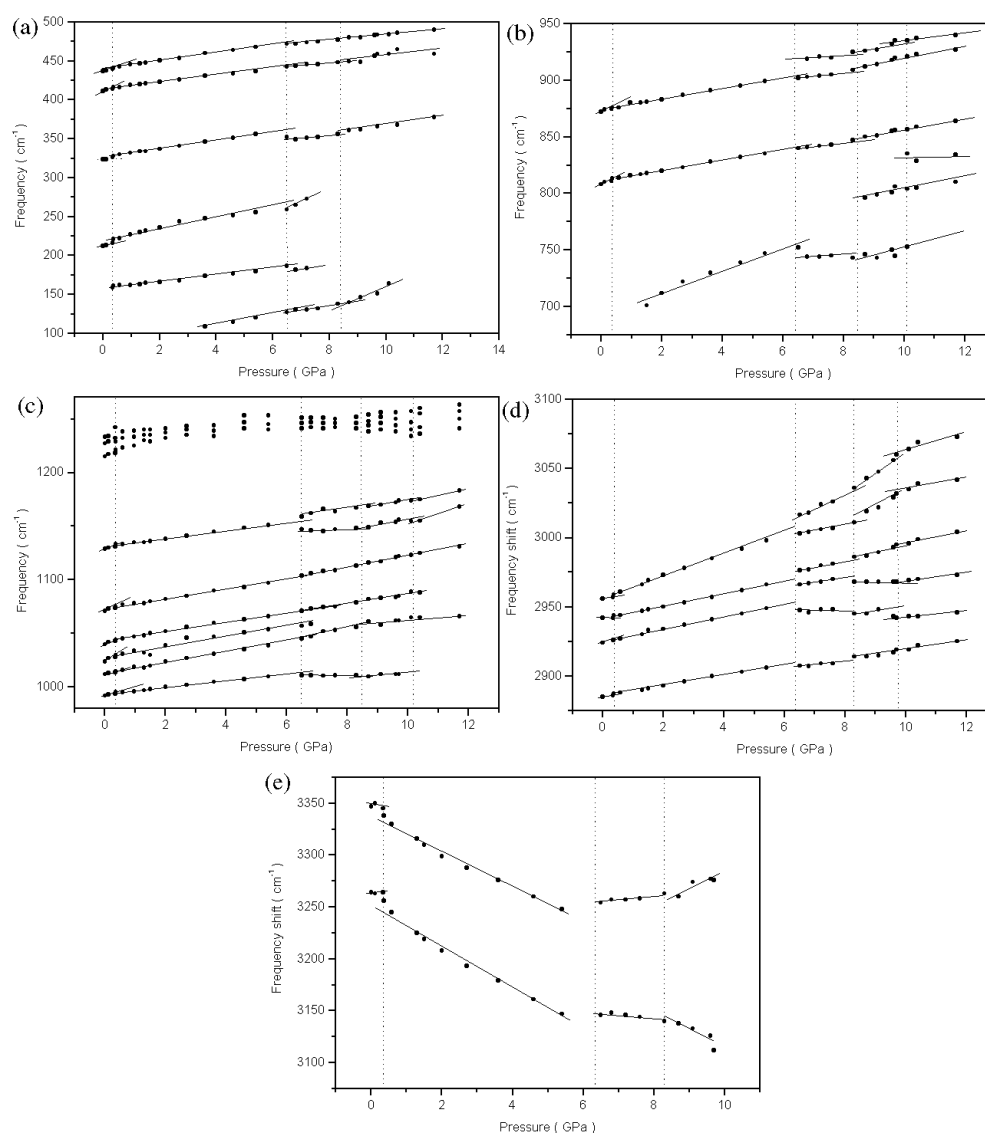


Figure 3. (a) The frequency shift of the Raman modes between 100 and 500 cm^{-1} as a function of pressure. (b) The frequency shift of the Raman modes between 650 and 950 cm^{-1} as a function of pressure. (c) Pressure-induced shifts in the Raman modes between 950 and 1275 cm^{-1} . (d) The frequency shift of the C–H stretching modes as a function of pressure showing the splitting of modes at ~ 6.3 GPa. (e) The pressure-induced shift of O–H frequencies of PET.

~ 6.3 GPa before stiffening again on increase of pressure (figure 3(a)). This is also accompanied by several other changes in the Raman spectra. C–H asymmetric stretch ‘E’ and ‘A’ modes, observed at 2942 and 2956 cm^{-1} respectively at ambient conditions, split at this pressure (figure 3(d)). The C–C stretch ‘E’ mode at 1129 cm^{-1} also splits into two peaks across this pressure (figure 3(c)). A very weak shoulder starts developing at 919 cm^{-1} and becomes more clearly resolved with respect to the C–H rocking mode at around 8 GPa. In addition, a large value of $d\nu/dp$ for the O–H stretch modes at 3265 cm^{-1} ($\sim -25 \text{ cm}^{-1} \text{ GPa}^{-1}$) and 3341 cm^{-1}

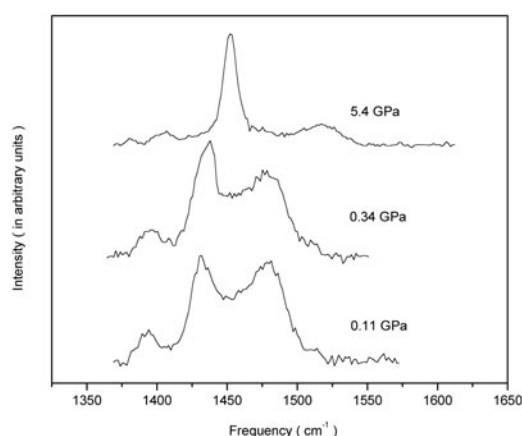


Figure 4. Raman spectra of PET in the $\sim 1400\text{ cm}^{-1}$ region displaying an increase in the intensity of the O–H deformation mode across 0.3 GPa.

($\sim -22\text{ cm}^{-1}\text{ GPa}^{-1}$) is replaced by a negligible variation beyond this pressure (figure 3(e)). OH torsion as well as OH deformation modes also become almost constant beyond this pressure. The change in magnitude of the slope for the O–H modes at $\sim 6.3\text{ GPa}$ is also consistent with our recent FTIR experimental results [11]. While the observed discontinuity of various Raman-active modes indicates a structural phase transformation at $\sim 6.3\text{ GPa}$, the emergence of new Raman-active modes suggests that the daughter phase is one with lower crystallographic symmetry. We shall term this symmetry-lowering transformation a I \rightarrow II structural phase transformation.

As the pressure is raised further, the C–H twist mode at 1229 cm^{-1} shows a splitting at 8.2 GPa (figure 3(d)). In addition, a new peak appears at around 796 cm^{-1} which develops into a sharp peak at $\sim 10\text{ GPa}$. At 10 GPa , another peak develops between this new peak and the C–C stretch peak at 812 cm^{-1} (figure 3(b)). These changes are accompanied by a discontinuous change in slope for various modes. This discontinuity is more pronounced in the C–H stretch modes. We call these phase transitions to two successively lower-symmetry phases, namely III and IV.

On further increase of pressure, the sharp features of the spectra were replaced by broad peaks at $\sim 14\text{ GPa}$ (figures 2(a) and (b)). Under the present circumstances it is difficult to ascertain whether this broadening is due to non-hydrostatic/non-uniform stresses or is inherent to the structure. Pressure was slowly raised further to $\sim 25\text{ GPa}$, to see whether some other structure emerges due to pressure overdrive. However, up to $\sim 25\text{ GPa}$, the spectral variations continue to be monotonic, showing progressive broadening of Raman peaks, implying that no new crystalline phase emerges at higher pressures. On releasing the pressure, all the transitions were found to be reversible. The new modes which appeared at $\sim 8.2\text{ GPa}$ under compression could be seen up to 6.1 GPa . Also, the shoulder of the 873 cm^{-1} mode persisted up to 4.1 GPa . This observed hysteresis along with the observed discontinuities in modes across the pressures of transformations further confirm that all the phase transitions are first order in nature. Moreover, our experiments show that PET returns to its ambient structure on complete release of pressure, thereby ruling out metastable retention of the high-pressure phase claimed earlier [4]. We would also like to point out that our investigations show that, if the crystal does not bridge the diamonds, these phase transformations do not shatter the crystal. Therefore, the shattering of crystals observed earlier and ascribed to the existence of phase transformation [8]

Table 1. Expected pressures of structural instabilities as determined from the steric limits of non-bonded atoms [9, 10, 16], as deduced from the extrapolated structural data of [8].

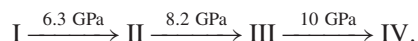
Non-bonded atoms	Normal limit [16] (nm)	Required pressure for normal limit (GPa)	Extreme limit [16] (nm)	Required pressure for extreme limit (GPa)
H33'–H43'	0.2	3.9	0.19	5.2
C1–C3'	0.3	8.8	0.29	9.3
O1–O3'	0.27	9.1	0.26	9.6

is not supported by our experiments. It should also be mentioned that in one preliminary experiment where the crystal bridged the diamonds and got shattered at very low pressures (~ 1 GPa), the shifts of the Raman modes were dramatically different from those for other runs.

We also mentioned earlier that a very different spectrum was observed beyond 5 GPa in the experiments where a saturated solution of PET in a methanol–ethanol mixture was used as the pressure transmitter. To check whether this difference in the spectra is because of the growth of some tiny crystalline nuclei under pressure, an experiment was performed with only the saturated solution of PET in (1:4) ethanol + methanol. No spectral changes were observed in this experiment up to the highest pressure of ~ 8 GPa, beyond which this run was terminated. Therefore, the observed changes in the spectra in the presence of a single crystal imply that these may arise from some interaction between the crystal and the complex pressure transmitter.

4. Discussion

Although from the Raman data one cannot determine the crystal structure of the high-pressure phase, the observed spectral variations may provide some possible clues. For example, the decrease in the frequency of the O–H stretching modes up to ~ 6 GPa suggests that the compression in phase I strengthens the hydrogen bonding. Beyond 6.3 GPa the slope becomes almost constant, implying that there is no further significant change in the hydrogen bonding in phase II. The observed splitting of the C–C and C–H stretch modes at 6.3 GPa and the emergence of new peaks at 8.2 and 10 GPa under compression suggest that under high pressure, crystal transforms to phases of still lower symmetries. These observations should stimulate x-ray diffraction work at high pressures to determine the crystallographic structure of high-pressure phases. The results can be summarized as



It is interesting to note that the observed transformation pressures have a close correlation with the limiting values of distances between non-bonded atoms. A survey of a large number of materials indicates that the extreme limiting value of the H–H distance is ~ 0.19 nm while for O–O and C–C the distances are 0.26 and 0.29 nm respectively [17]. While the structural modifications typically get initiated when the limiting distances cross the normal limit, the structure generally becomes unstable under compression when these limiting distances reach the extreme limits [10, 16]. What is interesting for PET is that for this compound this correlation exists with the distances extrapolated from the pressure variation of the structural parameters of the initial tetragonal structure. Table 1 elucidates this. Here, we should note that, generally, one expects the first (first-order) phase transformation to change the structure significantly, so

subsequent transformation pressures are dictated by the compression of the new high-pressure structures. A reasonable correlation, represented in table 1, with the limits deduced from the ambient structure, implies that the structural changes that brought about the observed phase transformations are not very dramatic. In particular, this table suggests that the I \rightarrow II transition could be due to the limiting value for the intra-layer non-bonded H–H atoms (H33'–H43'). This implies that the structural changes across this transformation may be ones that reduce the repulsive interaction between H33' and H43'. On further compression, as the inter-layer distance reduces, the C–C and O–O distances between the atoms of two successive layers might be approaching the steric limits at \sim 8.1 and 10 GPa respectively, resulting in second and third transitions. However, for a more precise validation of this correlation, an x-ray diffraction investigation at high pressures is required.

On release of pressure, all the transitions were found to be reversible in this compound even from 25 GPa. Similar observations have been reported for various other molecular crystals such as adamantane [17] and resorcinol [18]. This reversibility from moderately high pressures of \sim 25 GPa in molecular solids suggests that there is no fundamental change in the nature of the chemical bonding up to this pressure. The compression squeezes the material to bring about the changes in the inter-atomic distances, changing the effective coordinations of various atoms. However, the studies of several molecular solids mentioned above suggest that though the strengths of interactions become comparable (i.e. intra-layer versus inter-layer), the compression alone fails to bring about a fundamental change in the chemical bonding, which in turn may lead to the formation of new compounds.

5. Conclusions

Our Raman spectroscopy results show that PET undergoes at least three phase transitions. The emergence of new peaks accompanied by splitting of a few modes at 6.3, 8.2 and 10 GPa implies that these successive phase transitions may be resulting in lower-symmetry structures. The observed changes in the slopes of Raman modes at 0.3 GPa do not, in principle, rule out the possibility of a subtle iso-structural phase transition in this pressure range. All the phase transformations are found to be reversible. The correlation of the pressures of the transformations with the extrapolated limiting values of non-bonded atoms suggests that the structural changes across the transformations are not very drastic.

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