In situ Raman study of C_{60} polymerization during isothermal pressurizing at 800 K

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A V Talyzin and L S Dubrovinsky

Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

Abstract

The first *in situ* Raman study of C_{60} isothermal compression at 800 K and up to 32 GPa was performed using rhombohedral and tetragonal phases as starting materials. The rhombohedral phase shows a phase transition to 3D polymer above 10 GPa, similar to that in experiments where isobaric heating was used at pressures of 9–13 GPa. It is shown that the T–P diagram of C_{60} polymeric phases (temperature increase followed by pressurizing) is significantly different from the known P–T diagram (pressurizing followed by heating). Tetragonal polymer exhibited significantly stronger stability and can be followed at least up to ∼15 GPa. Heating up to 800 K of tetragonal polymer at pressures of 6–8 GPa confirms that, due to geometrical frustrations, the tetragonal phase remains stable even at pressure and temperature conditions at which rhombohedral polymer is usually formed.

1. Introduction

Under high pressure and high temperature conditions (HPHT) C_{60} is known to undergo polymerization. Below 9 GPa and 900 K several kinds of one- and two-dimensional polymeric phases [1–5] have been obtained: orthorhombic (O), tetragonal (T) and rhombohedral (rh). One- and two-dimensional polymeric phases are well characterized by different techniques including Raman spectroscopy and XRD study [1–9]. So far, very few *in situ* studies of polymerization under HPHT conditions are available [10–15]. Most of the studies were performed *ex situ* after cooling the sample and release of pressure.

Three-dimensionally polymerized superhard fullerites have been reported to exist at pressures above 12–13 GPa and temperatures above 800 K [15–25]. Several structural models have been proposed for these 'superhard' phases, including different hypothetical kinds of bonding between C_{60} molecules, but none of them is well proven [22–24]. The problem with characterization of these 'superhard' phases is that they exhibit very few XRD lines. Raman spectra of these phases are also typically almost featureless. Similar Raman spectra have been also obtained for C_{60} samples pressurized at room temperature above 25 GPa [26–28]. A significant problem in studies of the 'superhard' phases is poor reproducibility. The

samples obtained by different groups at the same pressure–temperature conditions showed different properties. One of the most interesting points in the $P–T$ diagram of C_{60} is at about 13 GPa and 800–830 K. Samples obtained at these conditions have been reported as harder then diamond by Blank *et al* [16–19] but softer then diamond by Brazkin *et al* [20, 21]. Recently it became clear that not only pressure and temperature, but also some other experimental parameters such as heating time, stress and $P–T$ history can be directly connected to physical properties of synthesized samples. For example, studies in a diamond anvil cell (DAC) have shown that pressure variations during the heating can be very strong and therefore a special design of DAC is required to maintain pressure unchanged [13–15]. This observation is rather important because in most of the studies which were conducted *ex situ* the $P–T$ history of samples remains unknown. It is especially true for experiments by Blank *et al* [16–19], because they used very short heating time (1 min) without control over pressure variation during the heating. It is clear also that the experimental method applied by Blank *et al* results in a strong shear deformation of their samples. The deformations have been so strong that the samples studied by Marcus *et al* exhibited ellipse-like x-ray diffraction patterns instead of normal Debye–Scherrer rings [25]. Other studies conducted on the same pressure–temperature region without strong stress showed no elliptical x-ray diffraction patterns [13–15]. It has also been shown that strong stress favours polymerization [29].

The $P–T$ history of the treatment is known to influence the outcome of HPHT experiments very strongly. Two-dimensional polymerization gives different results depending on the path in the $P–T$ space. Increase of temperature followed by pressure ($T–P$ path) favours formation of tetragonal phase, while pressure increase followed by heating ($P–T$ path) applied for the same final $P–T$ conditions (about 2.2 GPa and 870 K) results in synthesis of a mixture of tetragonal and rhombohedral polymers [4, 5, 8, 14]. It was proposed that the $T–P$ path gives an advantage to polymerization in the (001) direction of the original fcc structure of C_{60}, while the $P–T$ path favours polymerization in the (111) direction. So far all studies of the 3D polymerization have been performed only using pressurizing followed by heating ($P–T$ path). Due to the experimental difficulties the $T–P$ path has never been tested for the pressure region above 6 GPa.

Recently a new approach to synthesis of three-dimensional C_{60} polymers was proposed by Meletov *et al* [30–32]. A DAC was loaded with already polymerized C_{60} samples (tetragonal and rhombohedral). Only tetragonal phase has been reported to transform into new, probably 3D polymeric phase [31, 32]. Although this result was not confirmed by other studies [33, 34], it is important to check different possibilities for producing 3D polymeric phases at conditions different from those used in previous studies.

The purpose of this work was to study other possible routes for synthesis of 3D polymers of C_{60}. It is noted that all studies of the 3D polymerization have been performed only using pressurizing followed by heating ($P–T$ path). Due to the experimental difficulties the $T–P$ path has never been tested by Raman spectroscopy for the high pressure region (above 6 GPa). In the present study the $P–T$ region at about 13 GPa and 800 K was approached from lower pressure at isothermal conditions starting either from (mostly) rhombohedral phase, or from (mostly) tetragonal phase. The phase transformations were followed by modifications of Raman spectra recorded *in situ* during $P–T$ treatment. We also studied a possibility of direct transformation from tetragonal to rhombohedral polymeric phase at HPHT conditions.

2. Experimental details

A powder sample of C_{60} (99.9%, purchased from MER corporation) together with a small piece of ruby was loaded into the TAU-type diamond anvil cell (DAC) with 250 μm flat culets without

pressure-transmitting media. The special design of the DAC included a ceramic heater with resistively heated wire inside [35]. The temperature was controlled by a K-type thermocouple inserted inside the cell at the diamond/gasket interface. It was shown in our previous works that heating often results in a strong decrease of pressure due to the mechanical relaxation of the cell. Pressure was measured using the ruby fluorescence scale corrected for temperature effects [36]. Due to the special design of the cell, pressure could be corrected during experiments even at high temperature. Variations of pressure during isobaric heating did not exceed 1–2 GPa. Raman spectra were recorded *in situ* during P–T treatment using a LabRam spectrometer equipped with a 632 nm He–Ne laser and with resolution of 2 cm^{-1}. Using an 632 nm excitation laser appeared to be an advantage compared to using 785 and 514 nm lasers as in our previous studies [13, 14]. Our previous experience showed that a 514 nm laser provided rather poor quality C_{60} spectra at HPHT conditions but good quality for ruby spectra. Raman spectra of ruby at high temperature conditions could not be recorded using a 785 nm laser at high temperature (less precise external pressure calibration had to be used), but C_{60} spectra could be recorded with relatively high quality. The 632 nm laser allows one to record acceptable quality spectra of both C_{60} and ruby. At ambient pressure the quality of spectra recorded from polymeric phases using 632 nm is rather poor due to the strong luminescence effects, but above 2–3 GPa luminescence is suppressed and high quality spectra can be recorded. It is noted that at high temperature the quality of spectra decreases significantly due to the heat radiation. The pressure gradient at the highest pressure (27 GPa) was about ± 1 GPa within 100 μm of the central part of the sample. Raman spectra were always recorded in the central part of the sample in approximately the same spot close to the ruby chip.

Two experiments were aimed at observation of 3D polymerization by isothermal compression at 800 K using 2D polymeric phases as precursors. In the first experiment rhombohedral phase was synthesized *in situ* prior to compression at 8 GPa and 800 K. In a second run, a sample of tetragonal phase (synthesized in a piston–cylinder apparatus by heating C_{60} at 2.5 GPa and 800 K for 60 min) was used.

During the heating, the temperature was allowed to stabilize every 100 K for 10–20 min and Raman spectra were recorded using acquisition times of 5–30 min. Some measurements with shorter exposure were also carried out at intermediate temperatures. Experimental points taken at 800 K and in the pressure range 2–32 GPa are shown in figure 1.

3. Results

3.1. Isobaric heating followed by isothermal pressurizing for non-polymeric C_{60}

3.1.1. Synthesis of rhombohedral phase by isobaric heating. In the first experiment the purpose was to synthesize mostly rhombohedral polymer by isobaric heating of C_{60} at around 6–7 GPa and after that to increase pressure at 800 K up to 13–15 GPa in order to observe 3D polymerization.

Raman spectra recorded during the heating of the C_{60} under high pressure conditions are shown in figure 2. It is known from previous studies [14, 37] that pressurizing of the C_{60} at room temperature and non-hydrostatic conditions already results in slight polymerization above 5 GPa. The spectrum recorded at 290 K and 7 GPa exhibited clear signs of polymerization, such as a new peak at 1646 cm^{-1}, two weak peaks at 1007 and 978 cm^{-1} and some weak peaks in the 500–600 cm^{-1} spectral range. The Ag(2) peak was found at 1489 cm^{-1} which is significantly higher as compared to the peak position at ambient pressure. It is important to note that Raman peaks of C_{60} show a different dependence of position versus pressure. All peaks above 1300 cm^{-1} typically exhibit a clear upshift during pressurizing, while peaks found below
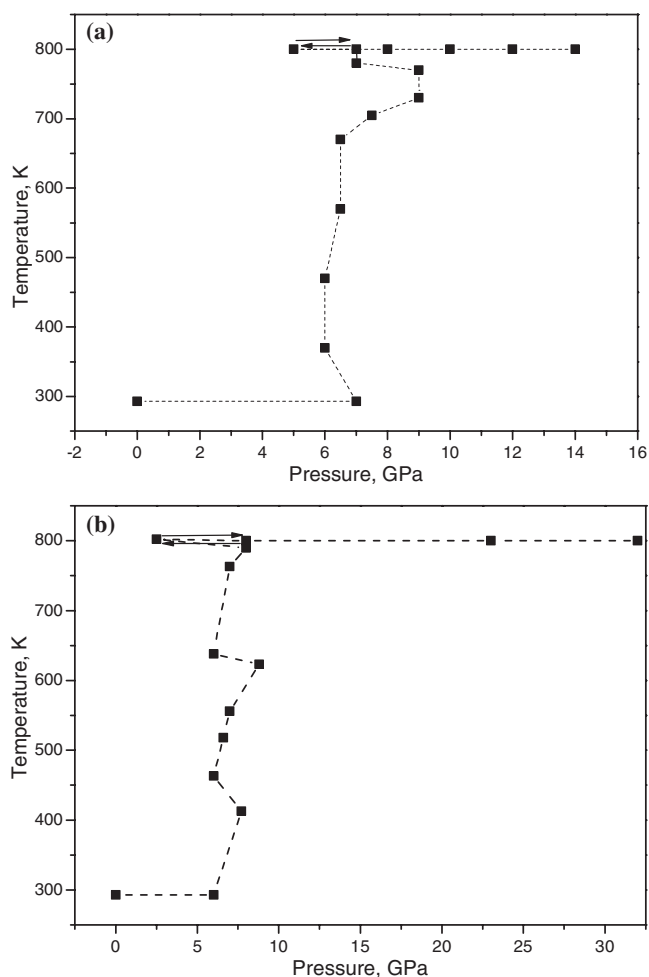
Figure 1. The $P–T$ path for experiments N1 (starting material—monomeric C_{60}) and N2 (starting material—tetragonal C_{60}) polymer.

1100 cm^{-1} remain at almost the same position. An especially interesting spectral region for phase identification is around the Ag(2) mode. At ambient conditions the Ag(2) peak position is known for different polymeric phases and identification of these phases during pressurizing can be performed using their relative positions (see [14] for more details). Detailed analysis of 'signature peaks' of rhombohedral and tetragonal polymeric phases for spectra recorded *in situ* will be also discussed in detail below; see section 3.2.1 and figure 5. Most probably, the spectrum recorded at room temperature represents a mixture of dimers and chain polymers of C_{60}. During the heating the first remarkable modifications can be found in the Raman spectrum recorded at 470 K. As was reported in our previous studies, above 450 K chain polymers start to link with the formation of polymers with tetra-coordination [14]. The 470 K spectrum exhibits strong broadening of the Ag(2) peak, strong increase of intensity for the 1646 cm^{-1} peak, as well as some other evidence of the increased degree of polymerization. The first signs of rhombohedral polymer can be recognized in the spectrum recorded at 670 K and become clearer at 705 K. At that point the pressure started to increase due to the mechanical deformation
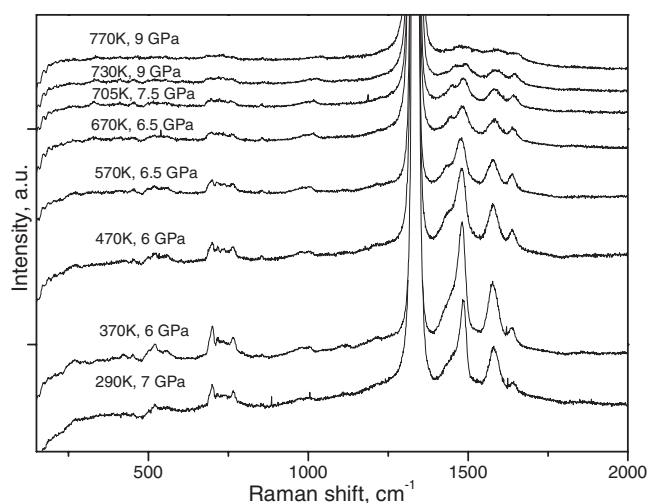
Figure 2. Raman spectra recorded *in situ* during isobaric heating of C$_{60}$ at 6–8 GPa.

in the DAC and at 730 K it reached 9 GPa. The phase transformation into rhombohedral phase at these conditions appeared to be rather slow. At 770–800 K pressure was corrected down to 5 GPa (see figure 1). The spectrum recorded at 800 K and 5 GPa (see figure 3) is typical for rhombohedral phase and can be easily recognized from the strong downshift of the Ag(2) mode as well as the appearance of new sharp peaks at 415 and 725 cm^{-1}. These peaks were identified as typical for rhombohedral polymer in our previous studies [14]. This spectrum is shown also in figure 6 and discussed in more detail below (section 3.2.1). Since the peak position of the Ag(2) mode depends strongly on pressure, it is difficult to see directly the downshift due to the polymerization. This downshift can be recognized only by careful analysis of relative peak positions for Ag(2) peaks from different polymeric phases (dimer, chains, tetra-coordinated polymer) during their transformations. The peak at 725 cm^{-1} is an especially good vibrational signature for rhombohedral phase since its position practically does not depend on pressure. In our previous study this peak was found at 728 cm^{-1} (785 nm laser) and showed rather remarkable behaviour. Among many small overlapping peaks typically found for polymeric phases in the spectral range 700–800 cm^{-1}, this peak is difficult to recognize at ambient conditions, but at high pressure it increases in intensity very strongly and dominates over all other peaks. The present study confirms these observations and the 725 cm^{-1} peak will be used as the most important vibrational signature of the rhombohedral polymer.

The spectrum recorded at 800 K and 5 GPa (see figure 3) is very similar to spectra which were found in our previous studies for rhombohedral phase (although the relative intensities of some peaks are different, most probably due to the different lasers used). Samples with such spectra have been analysed by means of XRD after quenching to ambient conditions in our previous study [14]. It was proven that they consist mostly of rhombohedral polymer phase. Therefore, we can conclude that the first step of the experiment was successful: at 800 K and 5 GPa the sample consists mostly of rhombohedral polymer.

3.1.2. Isothermal pressurizing of rhombohedral polymer at 800 K up to 12 GPa. The next step in the experiment was to increase pressure while keeping temperature stable at 800 K until transformation of rhombohedral polymer into 3D polymeric phase occurs. Results of this second step are shown in figure 3. The spectrum recorded after increase of pressure to
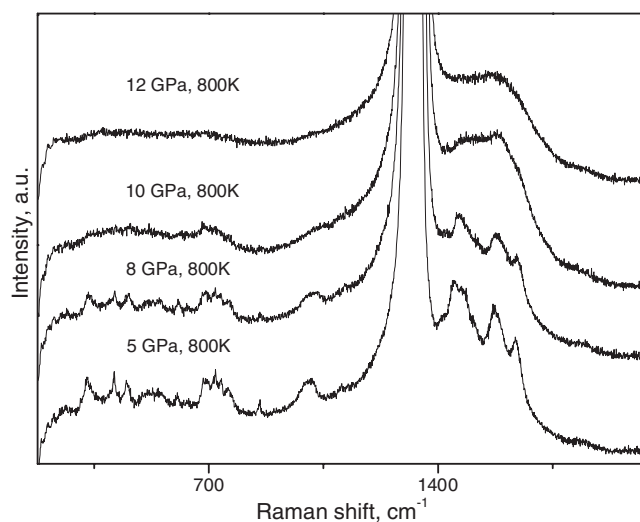
Figure 3. Raman spectra recorded during isothermal pressurizing of rhombohedral polymer from 5 to 12 GPa.

8 GPa shows no significant changes, but the spectrum recorded at 10 GPa exhibited strong modifications. Only remains of the rhombohedral phase can be recognized at 10 GPa and 800 K, while some rather broad features appear. The spectrum recorded at 12 GPa showed only two broad features, the strong one centred at approximately 1565 cm^{-1}. Such spectra are typical for so-called 'superhard phases' of unidentified nature. According to the data from the present experiment the transformation into a similar kind of supposedly hard phase occurs at 800 K in the pressure range 10–12 GPa.

This experiment represents the first isothermal section of the P–T diagram of C$_{60}$ polymeric phases at high temperature. The general conclusion is that 3D polymerization (when a Rh phase is used as the precursor) does not shows so strong a difference depending on the P–T path as was observed for two-dimensional polymeric phases [4, 5, 8, 14]. Isothermal pressurizing from 5 to 12 GPa at 800 K (T–P path) and isobaric heating at around 13 GPa up to 830 K (P–T path) resulted in a very similar outcome. It is emphasized that not only were the P–T paths different in these two cases, but also the phase compositions of samples prior to amorphization (or 3D polymerization) differed. It is believed that heating at 13 GPa (P–T path) results in the formation of chain polymers which start to link chaotically in all directions at around 600–800 K. When T–P is obtained at 800 K and a starting pressure of 5 GPa, the initial phase is well ordered crystalline rhombohedral polymer with planar structure. This kind of structure can polymerize in the third dimension only by linking of polymeric planes. From the Raman data obtained in our experiment it is impossible to see any difference between the spectra recorded from our sample (T–P path) and spectra published in the literature for samples obtained by the P–T path. X-ray diffraction studies will probably provide more information, but taking into account that 3D polymeric phases are almost amorphous (giving very poor diffraction patterns), this kind of study will definitely require the use of synchrotron radiation.

3.2. Isobaric heating of tetragonal polymer followed by pressurizing up to 32 GPa

It could be very interesting to check *in situ* how polymerization occurs at 800 K starting from zero pressure, but technically it is very difficult to do this. Without any pressure applied, the

C$_{60}$ sample will oxidize at 800 K. In order to prevent oxidation, the DAC will have to be placed into a box with inert gas, but in that case pressure corrections will be very difficult to perform. In order to avoid these technical complications we chose other way to make the experiment. According to existing P–T diagrams, C$_{60}$ at 800 K starts to polymerize approximately around 2 GPa. In our previous study it was shown that C$_{60}$ polymeric phases obtained at HPHT conditions can be efficiently depolymerized into monomeric C$_{60}$ at 800 K if the pressure is decreased to 2 GPa [14]. This observation was used in the experiment with isothermal pressurizing from 2 to 30 GPa at 800 K.

3.2.1. Isobaric heating of tetragonal polymer. Both one- and two-dimensional polymeric phases are known to depolymerize at high temperature [14]. Therefore, it was decided to combine two experiments into one. Instead of using non-polymeric C$_{60}$ as the starting material, the tetragonal polymeric phase was loaded into the DAC. Heating of the tetragonal phase up to 800 K at 6 GPa allows us to address the problem formulated below.

It is known that tetragonal polymer is formed in the (001) plane of the initial fcc structure of C$_{60}$, while rhombohedral polymer is formed by polymerization in the (111) direction [4, 5]. The first is favoured by the P–T path, the second by the T–P path. It is interesting to check what will happen to tetragonal phase if it is subjected to the P–T conditions typical for formation of rhombohedral polymer. Rhombohedral phase cannot be obtained directly from tetragonal phase without breaking some polymeric bonds. Such a transition requires at least two steps: the first is the breaking of tetragonal polymer into chains and the second is the formation of new polymeric bonds in the (111) direction. It is not possible to say *a priori* whether such a two-step process could be realized or not.

Instead, some alternative scenarios could be suggested:

(1) Tetragonal phase remains stable even at P–T conditions where rhombohedral polymer is formed from orthorhombic chain polymers.
(2) Polymerization of the tetragonal polymer in the (111) direction of the initial fcc C$_{60}$ structure occurs without breaking bonds, thus resulting in the formation of 3D polymers.

The evolution of Raman spectra during the heating is shown in figure 4. Analysis of these spectra is not easy because they obviously represent mixtures of different phases. First of all, the tetragonal polymer is always obtained in a mixture with chain or dimeric phases. During the heating these phases could show different phase transformations and if the transformations are not finished due to the limited time of experimentation we may see Raman spectra from several different phases.

Spectra of the sample of tetragonal phase recorded at ambient conditions prior to *in situ* experiments showed two strong peaks at 1446 and 1465 cm^{-1}. The peak at 1446 cm^{-1} is assigned to the Ag(2) mode of tetragonal phase. The second weaker peak at 1465 cm^{-1} is most probably from the Ag(2) mode of the chain polymer or C$_{60}$ dimers. It is interesting that this peak is downshifted due to the photopolymerization effect when the laser power is increased, while the 1446 cm^{-1} peak does not show any downshift. It is known that photopolymerization produces maximally branched chains and it is reasonable that tetragonal polymer does not polymerize more strongly under the laser light irradiation, while chain polymer is able to transform into branched chains which results in downshift of the Ag(2) mode. Therefore, it is clear that the starting sample consists of a mixture of mostly tetragonal polymer and some fraction of chain polymers.

The Raman spectrum of the tetragonal phase at 6 GPa (figure 4) exhibited the same peaks as at ambient pressure, but with some change in relative intensity. The most remarkable change is observed for Ag(2) peaks. After pressurizing to 6 GPa the relative intensity of the two
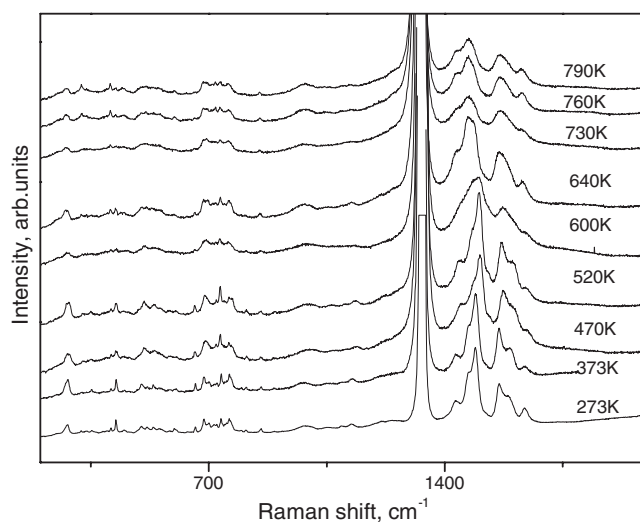
Figure 4. Raman spectra recorded during isobaric heating of tetragonal polymer up to 800 K.
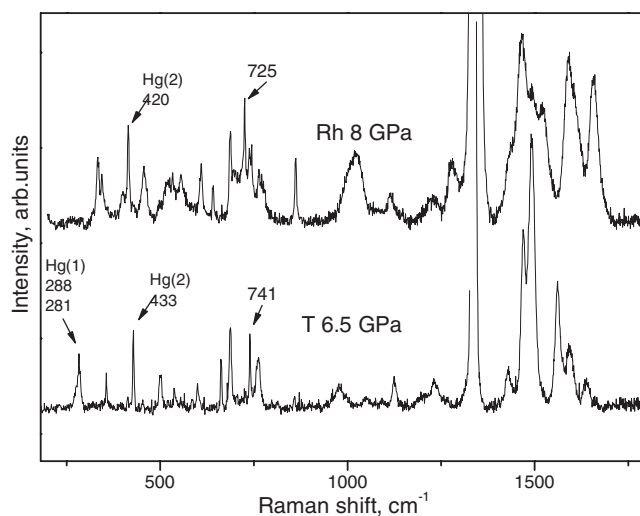

Figure 5. Raman spectra of rhombohedral and tetragonal polymers recorded at ambient temperature at high pressure conditions.

Ag(2) peaks was changed dramatically: the peak from chain polymers (found at 1492 cm^{-1} due to the pressure shift) became much stronger compared to the peak from tetragonal phase (1470 cm^{-1}). This is most probably due to different dependences of the peak intensity on pressure, but not due to real changes of relative amounts of phases. A control experiment with pressurizing of tetragonal phase to 6 GPa shows that changes of relative intensity of the Ag(2) peaks are completely reversible upon pressure release. The identification of polymeric phases during *in situ* studies is complicated also by pressure dependent shifts of Raman modes. However, we demonstrated recently that the relative positions of Ag(2) peaks from different polymeric phases remain more or less unchanged during HPHT treatment. This observation is confirmed in the present study as well. Another possible problem with identification of the
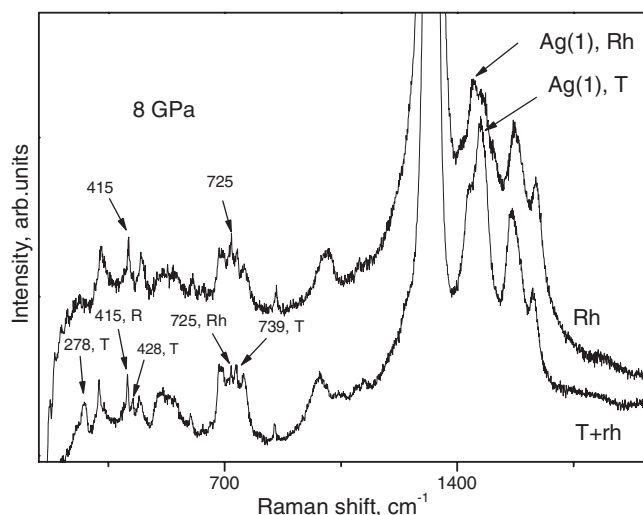
Figure 6. Raman spectra recorded *in situ* at 8 GPa and 800 K for the samples of mostly rhombohedral and tetragonal polymers.

tetragonal phase by means of the position of the Ag(2) mode is that tetra-coordinated polymers could also be obtained by chains linking in the (111) plane of the original fcc structure of C$_{60}$ as an intermediate product in the synthesis of the rhombohedral phase. This possibility was discussed in detail in our previous work [13, 14] and we concluded that the Ag(2) mode of such a tetra-coordinated polymer would behave like the Ag(2) mode of tetragonal phase.

During the heating two main components originating from Ag(2) modes of chain polymers and tetragonal phase become broader (figure 4) and at high temperature look like one broad feature, which poses difficulties for unambiguous interpretation. Therefore, it is important to find some additional clear vibrational signatures for different phases, first of all for tetragonal and rhombohedral ones. Analysis of the Raman spectra given below allows us to select such vibrational signatures. Some of the very clear differences can be found by analysis of the spectra from these two polymeric phases recorded at ambient temperature *in situ* at high pressure conditions (see figure 5).

Our previous observations on rhombohedral phase have shown that a clear signature peak of this phase can be found in the spectra recorded *in situ* at ∼725 cm^{-1} [13, 14]. The tetragonal polymer shows a similar clear characteristic peak at ∼741 cm^{-1} with intensity much stronger compared to the intensities of other peaks in the spectral range 600–800 cm^{-1} [34]. The position of this peak is almost independent of pressure. It is also noted that the 741 cm^{-1} peak can be found only in the spectra recorded *in situ* at high pressure (similar to the case for the 725 cm^{-1} peak of rhombohedral polymer).

Another good signature of tetragonal and orthorhombic phases is the H$_g$(1) peak which is found at ambient conditions at 274 and 282 cm^{-1} respectively. The spectrum shown in figure 5 exhibits both a strong peak from tetragonal phase found at 288 cm^{-1} and a weaker peak recognized as a shoulder at 281 cm^{-1} (the upshift is due to the influence of pressure). Unfortunately, at higher temperature the quality of spectra become worse and these two peaks are difficult to separate. One more clear signature peak can be found at 433 cm^{-1} for tetragonal phase and 420 cm^{-1} for rhombohedral phase and this can be assigned to H$_g$(2) modes. Table 1 shows a number of characteristic peaks for both Rh and T phases and their possible assignment based on literature data [4, 14] and our own observations.

Table 1. Signature peaks for tetragonal and rhombohedral polymers.

Probable assignment	T, 8 GPa, 800 K	T, 6 GPa, RT	Rh, 8 GPa, 800 K	Rh, 8 GPa RT
Hg(1)	278	288		
Hg(2)			415	420
Hg(2)	428	433		
Hg(3), Hg(4)?			725	725
Hg(3), Hg(4)?	739	741		

Using vibrational signatures described above it is possible now to analyse data shown in figure 4 in more detail. The first significant modification of the Raman spectra can be observed at around 600 K. These changes become more clear in the spectrum recorded at 640 K. First of all, the relative intensity of two major components in the Ag(2) peak has changed dramatically. The component assigned to tetragonal polymer found in this spectrum at 1473 cm^{-1} become stronger compared to the second component from chain polymers (1494 cm^{-1}). Increase of intensity for the peak at 414 cm^{-1} is also clearly recognized and could be considered as an indication for the beginning of the transformation into rhombohedral polymer. The presence of rhombohedral phase becomes obvious at 760 K. The spectrum recorded at this temperature shows characteristic peaks of both tetragonal and rhombohedral phases found at 429, 739 and at 414, 725 cm^{-1} respectively. Another remarkable change occurs in the region of the Ag(2) mode. The peak due to the chain polymers almost disappeared and can be recognized only as a weak shoulder, while the Ag(2) mode peak from rhombohedral phase appears as a weak component. Note that pressure increased slowly upon heating from 6 GPa at 640 K to 8 GPa at 800 K.

The final composition of the sample at 800 K can be better understood by comparison with the spectrum of mostly rhombohedral phase recorded at 800 K and 8 GPa in the previous experiment (figure 6). Peaks marked by arrows on figure 6 represent signatures for rhombohedral and tetragonal phases. Comparison of Ag(2) modes (figures 4, 6) is difficult due to the difference in pressure. However, peaks in the spectral region below 800 cm^{-1} showed almost no shift due to pressure changes (see above). It is also interesting that the broad feature found at around 1000 cm^{-1} and typically assigned to vibrations from polymeric bonds connecting neighbouring C_{60} molecules is upshifted in the rhombohedral phase by approximately 15 cm^{-1} compared to the bottom spectrum representing mostly tetragonal phase.

Analysis of the spectra shown in figure 6 allows us to draw several conclusions. First of all, heating of tetragonal phase to 800 K does not lead to transformation of the whole sample into rhombohedral phase. Tetragonal phase is still present at 800 K and constitutes a significant part of the sample. It is difficult to estimate relative amounts of tetragonal and rhombohedral phases, since signature peaks show different relative intensities. Taking into account that the initial sample consisted partly of chain polymer phase, it can be argued that most of the rhombohedral phase was formed due to transformation of chain polymers, while the tetragonal phase remained stable. This suggestion is strongly supported by the strong intensity decrease of the Ag(2) peak from chain polymers at around the same temperature where the first signs of rhombohedral phase can be observed (around 600–700 K).

3.2.2. Isothermal pressurizing at 800 K from 2 to 30 GPa. According to the *P–T* diagrams of C_{60} phases, decrease of pressure from 8 to 1–2 GPa at 800 K must result in breaking of polymeric bonds and formation of non-polymeric C_{60}. The first experimental confirmation of depolymerization at these conditions was observed in our previous study [14] and it is
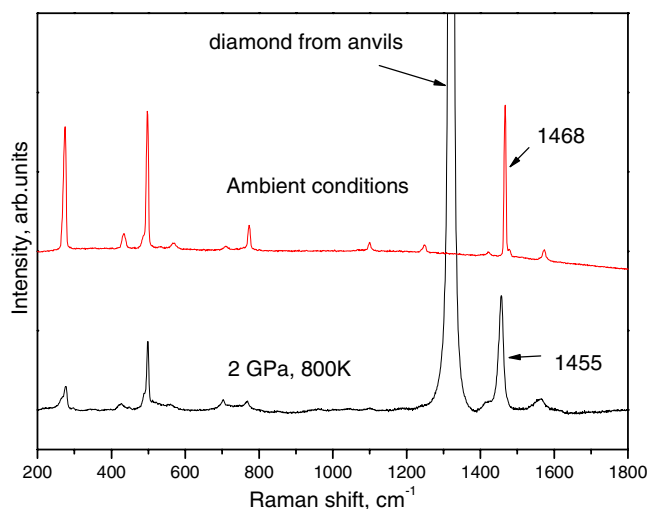
Figure 7. Raman spectra of monomeric C$_{60}$ recorded at HPHT conditions compared to the reference spectrum recorded at ambient conditions.

(This figure is in colour only in the electronic version)

confirmed by new data. The sample at 800 K and 8 GPa consisted of a mixture of tetragonal and rhombohedral polymers (figure 6). Pressure decrease from 8 to 2 GPa at 800 K resulted in dramatic changes of Raman spectra. The Raman spectrum of the sample recorded at 800 K and 2 GPa (figure 7) exhibits several sharp peaks from non-polymeric C$_{60}$ and only traces of remaining polymeric phases represented by some very weak peaks. The spectrum recorded at 2 GPa (figures 7 and 8) is very similar to the C$_{60}$ Raman spectra recorded at ambient conditions but with one pronounced difference. Surprisingly, the Ag(2) peak at 2 GPa and 800 K is found at 1455 cm^{-1} compared to 1468 cm^{-1} for ambient conditions. This downshift cannot be assigned to polymerization effects because there are no other peaks typical for polymeric phases in this spectrum. Moreover, the real downshift is even stronger if we take into account the pressure influence which usually upshifts Raman peaks. Taking into account the pressure induced upshift of the Ag(2) mode of approximately 2 cm^{-1}/1 GPa, the total downshift of the Ag(2) mode at 2 GPa and 800 K compared to ambient conditions is about 18 cm^{-1}. Such a strong shift due to the temperature effect is rather unusual and is difficult to explain at the moment, especially taking into account that polymeric phases (both tetragonal and rhombohedral) exhibit no shift of the Ag(2) mode with increase of temperature up to 800 K. It could be argued that our sample is polymeric even if no additional peaks are observed, but this suggestion can be ruled out. The monomeric nature of the sample at 2 GPa and 800 K was clearly proved in our previous studies when the sample with the same Raman spectra was polymerized step by step into chain polymers, tetragonal phase and rhombohedral phase [14]. Photopolymerization effects can also be ruled out, because we used low laser power and anyway laser induced downshift has never been observed to be so strong (the typical Ag(2) peak position for photopolymers is downshifted by only 10 cm^{-1}). Photopolymers are also known to show many additional peaks which cannot be found in the present spectrum. Therefore, we believe that the starting material for pressurizing at 800 K is monomeric C$_{60}$. The Raman spectra recorded during pressurizing are summarized in figure 8.

Pressure increase results in polymerization of monomeric C$_{60}$ into a mixture of tetragonal and rhombohedral polymers (figure 8). Comparison of the spectra recorded at 800 K and
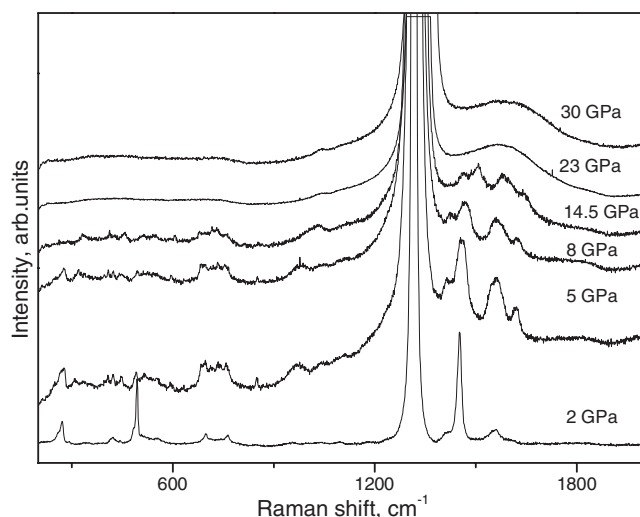
Figure 8. Raman spectra recorded during isothermal pressurizing of C_{60} from 2 to 30 GPa at 800 K (see the text).
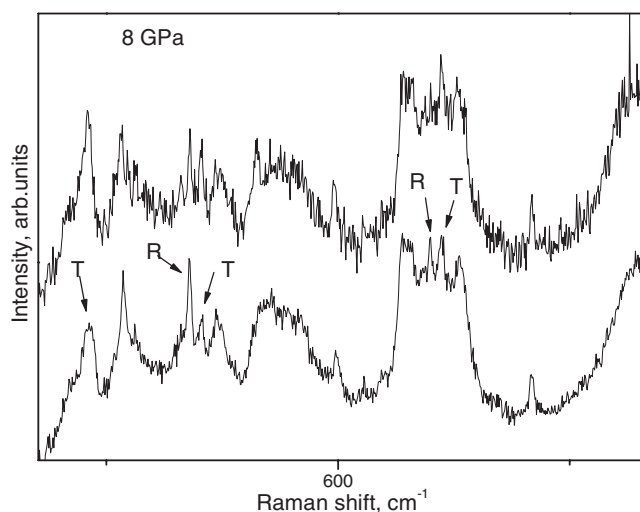

Figure 9. A fragment of Raman spectra recorded at 8 GPa and 800 K prior to depolymerization (bottom) and after depolymerization followed by compression back to 8 GPa (top).

8 GPa before and after depolymerization proves that isothermal pressurizing results in a higher amount of tetragonal phase. This can be recognized by comparison of intensities of signature peaks from both polymeric phases as shown in figure 9. This observation is in good agreement with previous publications [4, 5, 8, 14], which reported that isothermal pressurizing at high temperature favours polymerization in the (100) direction of the original fcc structure with formation of tetragonal polymer.

According to the idea of the experiment, the tetragonal phase (synthesized *in situ* at 8 GPa as shown above) was used as a precursor for three-dimensional polymerization. This must be compared to the experiment described in section 3.1 where mostly rhombohedral sample

was pressurized at the same P–T conditions. Comparison of figures 3 and 8 shows that, in fact, the difference is very strong. The tetragonal polymeric sample remains stable at least up to 14.5 GPa, while the rhombohedral polymer become amorphous with only a few broad features in the Raman spectra already present at 10 GPa. The difference seems to be very strong in this medium pressure range, but at 23 GPa tetragonal polymer also transformed into amorphous-like phase with Raman spectra typical for 'superhard' phases, although some weak indications of remaining tetragonal phase were still recognizable. Complete 'amorphization' was observed in Raman spectra only at 30 GPa. No new sharp peaks due to the formation of three-dimensional polymers were observed in experiments with tetragonal and rhombohedral polymers.

Meletov *et al* [31, 32] suggested that tetragonal polymer could be easily transformed into a new three-dimensional polymeric phase by pressurizing at room temperature. Such a transformation would be even more favourable at high temperature. Our experiments do not confirm the data obtained by Meletov *et al* [31, 32]. In contrast, tetragonal phase shows remarkably higher stability under pressure compared to rhombohedral polymer and chain polymers.

4. Discussion

It is known that tetragonal phase is formed by polymerization in the (001) plane of the initial fcc structure of C$_{60}$, while rhombohedral phase forms due to polymerization in the (111) plane. The direction of polymerization can be controlled by choosing the right pressure–temperature path. The P–T path (pressure increase followed by heating) leads to formation of mostly rhombohedral polymer at pressures below 8–9 GPa, while the T–P path (heating followed by pressurizing) results in mostly tetragonal phase [4, 5, 8, 14]. This difference is explained by increased rotational freedom of C$_{60}$ at high temperature ($\sim$800 K).

Due to geometrical frustrations, rhombohedral phase cannot be obtained directly from tetragonal phase without breaking some polymeric bonds. The reverse transition from rhombohedral phase to tetragonal phase is also difficult for the same reason. The absence of such a transformation was observed experimentally by Davydov *et al* [5]. Therefore, it is of interest to consider what will happen with tetragonal polymer when it is pressurized and heated by the same P–T path which led to the formation of rhombohedral polymer if pristine C$_{60}$ is used as a starting material. Our experiments show that at pressures of 6–15 GPa and high temperature ($\sim$800 K), tetragonal phase remains stable even in the pressure–temperature region where rhombohedral phase is typically synthesized.

These data also support the suggestion which was made in our previous publication: formation of rhombohedral phase during isobaric heating at 6–7 GPa occurs by continuous increase of the number of polymeric bonds in the (111) plane: the formation of chains, followed by transforming to branched chains, later to tetra-coordinated polymer (different from tetragonal phase) and finally to hexa-coordinated polymer (rhombohedral phase) [13].

Due to the remarkable stability of tetragonal phase at about 5–8 GPa and 800 K, it is possible also to use it as a precursor for 3D polymerization, which occurs around 800 K and 12–13 GPa according to literature data. It is noted that in all previous studies the region of 3D polymerization was approached using only pressurizing followed by heating (P–T path). In the present study 3D polymerization was studied for the first time using a T–P path and two different precursor phases: tetragonal and rhombohedral polymers. Due to the increased mobility of C$_{60}$ molecules at high temperature (800 K) the process of polymerization goes more easily. On the other hand, C$_{60}$ molecules in the two-dimensional polymeric phases are
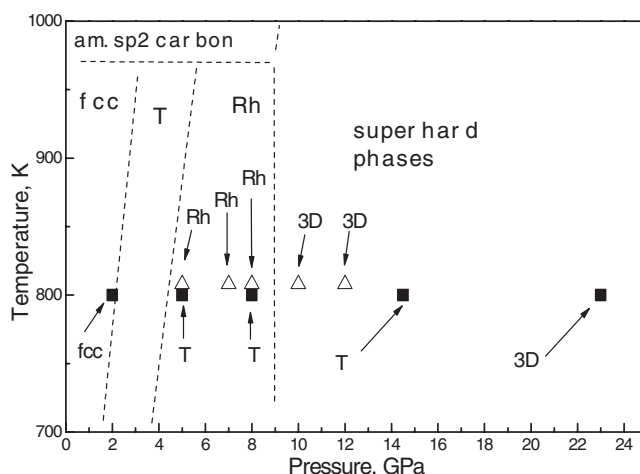
Figure 10. Phases observed during *in situ* high pressure and temperature experiments with tetragonal (black squares) and rhombohedral (open triangles) phases as starting materials.

already connected by rigid bonds and cannot rotate. Therefore, polymerization can proceed only by linking two-dimensionally polymerized planes.

Our experiments proved that tetragonal and rhombohedral polymers exhibit significantly different transformations during isothermal pressurizing at 800 K. Rhombohedral phase undergoes 3D polymerization (or amorphization) above 10 GPa in very good agreement with existing P–T diagrams of C_{60} polymeric phases (see figure 10). A very different result was observed for tetragonal phase which remained stable at least up to $\sim$15 GPa; some traces of this phase can be observed even at 23 GPa. Tetragonal phase was obtained in our experiment *in situ* by compression of monomeric C_{60} starting from 2 GPa. Therefore, this represents almost the complete section of 'kinetic phase diagram' or—it is better to say—the 'T–P diagram' of C_{60} polymeric phases.

All P–T diagrams presented in the literature [4, 5, 19] were constructed using a P–T path (isobaric heating) and the present work shows that a P–T diagram constructed using a T–P path (isothermal pressurizing) is remarkably different. This once more emphasizes that true phase diagrams of C_{60} polymers do not exist (because C_{60} is a metastable form of carbon); only 'experimental maps' or 'kinetic P–T diagrams' can be constructed. It is clear that many more isothermal pressurizing experiments at different temperatures are required to construct 'T–P path kinetic phase diagrams'. Nevertheless, at least one strong difference is clear from the present study. In contrast to indications of currently available P–T diagrams, in the 'T–P path phase diagram' the most stable phase at 800 K and 6–15 GPa pressure is not rhombohedral, but tetragonal polymeric phase.

5. Conclusions

In the present study the P–T region at about 13 GPa and 800 K was approached from lower pressure at isothermal conditions. The phase transformations were followed by modifications of Raman spectra recorded *in situ* during P–T treatment. Experiments were performed in such a way that prior to 3D polymerization one sample consisted mostly of rhombohedral phase and another one mostly of tetragonal polymeric phase. These two phases showed strong differences under isothermal compression at 800 K. Rhombohedral polymer exhibited amorphization of

the sample around 10 GPa with formation of a phase with Raman spectra typical of so-called 'superhard phases'. These Raman spectra exhibit only two broad features and no sharp peaks. Amorphization of tetragonal polymer was observed at much higher pressure (above 15 GPa) and some features in the Raman spectra persisted up to 23 GPa.

Isobaric heating of the tetragonal polymer at 6–7 GPa up to 800 K also confirms a remarkable stability of this polymer. No direct transformation of tetragonal polymer into a rhombohedral one was observed, while chain polymers (which were present as part of the sample) polymerize into rhombohedral phase very easily. Depolymerization of tetragonal phase at 800 K was observed when pressure was decreased from 8 to 2.5 GPa. When pressure was increased again to 8 GPa, polymerization appeared again with an increased amount of tetragonal phase.

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