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Title: New ordered Structure of Amorphous Carbon Clusters Induced by Fullerene-Cubane Reactions

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Traditional solids can be categorized by their structures into crystalline, quasi-crystalline and amorphous, based on the degree of static translational order. Taking carbon as an example, its known allotropes, such as diamond, graphene/graphite, carbon nanotubes, fullerenes, as well as glassy carbon, etc, are organized in either ordered (crystalline) or disordered (amorphous) forms, defined by the periodicity of the arrangement of building blocks (BBs) in the materials. These carbon materials all have well distinguished structures and remarkable mechanical and electronic properties, thus have great potential in many advanced applications.^[1-7]

Unlike these well-known carbon materials, recent studies on fullerene solvates have observed a new class of crystalline carbon materials composed of amorphous carbon clusters (ACC), which expand our understanding of structure categorization of solids from order to disorder. In such structures, the (BBs) are amorphous clusters created from fullerene molecules collapsed by high pressure, which can be stabilized by the intercalated solvent molecules and thus still retain their long range ordered arrangement in the material. The solvent components in this case modulate the cluster-cluster boundary interactions between the BBs, which define the structure and properties of the high pressure phases. It has been found that these solvent molecules, such as m-xylene, 1,2,4-trimethylbenzene (TMD) and m-dichlorobenzene (m-Cl), which have aromatic carbon rings, are able to stabilize the highly deformed or collapsed fullerene clusters and thus the ordered structure. In contrast, ferrocene with pentagonal carbon rings undergoes amorphization together with the fullerene BBs and thus transform into a disordered structure at high pressure. Interestingly, such

aromatic solvent tuned structures can create indentations on diamond anvils that leads to great potential for practical applications.^[8-11] This approach could also be generalized to produce amorphous building block based carbon structures with the potential for a huge variety of physical properties when suitable interacting molecules have been selected to form co-crystals with fullerenes. In this case, it is very important to know the effects of interacting molecules on tailoring the boundary interactions between the amorphous BBs, which, however, requires more studies to design new ACC based structures and understand the corresponding formation mechanism. Moreover, in traditional crystalline solids structural transitions have been shown to be an efficient strategy to create new structures with different properties. However, whether structural transformations can take place or not and how the structure transforms in such a “crystalline structure” constructed from ACC building blocks have not been studied. Such knowledge should contribute to the development of new strategies for the creation of new carbon structures with desirable properties.

Unlike these solvent molecules with 5- or 6-membered carbon rings studied previously, cubane (C_8H_8) can be taken as a cubic molecule constructed by six 4-membered carbon rings. It consists of eight carbon atoms arranged at the corners of a cube with one hydrogen atom attached to each carbon atom.^[12] The cubic shape requires the carbon atoms to adopt an unusually sharp 90° bonding angle, making the bonds highly strained as compared to the 109.45° angle in tetrahedral carbon. The density of C_8H_8 is 1.29g/cm^3 , much higher than for normal hydrocarbons. The high strain energy and density of cubane make it a potential very-high-energy-density

material, which has been widely studied.^[13] Early in 2005, Pekker *et al.* synthesized the C₈H₈/C₆₀ co-crystal, which consists of distinct rotor (C₆₀) and stator (C₈H₈) molecules and exhibits amazing topochemical properties, being quite different from previously reported fullerene based compounds.^[14, 15] Compared with other intercalated solvents studied, cubane is more unstable and reactive at relative low pressure, such that pure cubane often detonates spontaneously above 3 GPa.^[16] It was reported that C₆₀-cubane copolymers can be formed by annealing above 470 K or by high pressure/high temperature treatment with three different structures, depending on the initial structures of C₆₀-cubane crystal precursors at different pressures and treatment temperatures.^[14, 15, 17] However, considering the unique carbon 4-ring and high energy of the cubane molecule, it is interesting to study its effect on carbon cluster-cluster interactions under pressure and design new phases with promising structures and properties from such fullerene compounds.

In this work, we have studied the transformations of C₈H₈/C₆₀ under pressure up to 45 GPa and found a new ACC-based ordered structure. In contrast to previously studied solvent molecules, the C₈H₈ exhibits unusual roles in the structure formation and transformations under pressure. It starts to polymerize with neighboring C₆₀ molecules above 10 GPa and stabilizes the boundary interactions of the highly compressed or collapsed C₆₀ clusters to retain their long range ordered arrangement up to 45 GPa. When kept at high pressure, a gradual random bonding between C₈H₈ and the surrounding carbon clusters due to “energy release” of highly compressed cubane leads to the loss of boundary stability of the highly compressed or collapsed

C_{60} in the material, and finally results in a transition from short range disorder to long range disorder in the material. Such a bonding reconstruction at the cluster-cluster boundaries most likely results in a 3D network structure in the material, which is found to be able to create ring crack indentations on the diamond anvils.

The as-prepared C_8H_8/C_{60} co-crystals have been characterized by Raman and IR spectroscopy and by XRD measurements at ambient conditions. Raman and IR spectra of the sample are shown in **Figure 1a, b**. For comparison, the simulated vibrational spectra of cubane are also shown at the bottom of the figures. As shown in the figures, the vibrational spectra of the sample show clear spectroscopic features from both C_8H_8 molecules (marked with an asterisk and hereafter named C1-C6)^[18] and C_{60} molecules (two A_g modes and eight H_g modes for Raman, four F_{1u} modes for IR)^[19], suggesting only weak van der Waals interactions between C_{60} and C_8H_8 molecules in the compound. The XRD pattern (**Figure 1c**) of the sample can be well indexed by a face-centered cubic structure (fcc) with lattice constant $a=14.74 \text{ \AA}$. These results are consistent with those reported in previous literature.^[14, 17, 20]

As demonstrated in our previous works, above some critical pressures highly compressed C_{60} molecules in solvates may collapse or highly deform and act as hard building blocks, forming new carbon phases.^[8-10] In these cases intercalated solvent molecules, if stable, play important roles for the boundary interactions of the hard BBs formed. To examine the effect of cubane molecules on the interactions between highly compressed C_{60} BBs, we here pressurized C_8H_8/C_{60} up to 45 G Pa.

Figure 2a shows the XRD patterns of the sample from ambient pressure to 45 GPa. From the figure, we find that the sample undergoes a structural transition in the pressure range from 0.4 to 1.1 GPa, as indicated by the appearance of a new peak at 7.2 degrees and the disappearance of the (111) and (200) planes from the starting fcc phase. This transition is due to the orientational ordering transition of the C₆₀ molecules in the compound.^[21, 22] The new phase most likely can be indexed by an orthorhombic structure with lattice parameters a=0.996 nm, b=1.065 nm, c=1.198 nm, and the corresponding diffraction peaks have been indicated in the figure. As pressure increases, the diffraction peaks become weak and broad, but the orthorhombic phase is retained even up to 45 GPa. In contrast, the structure of pure C₆₀ undergoes irreversible amorphization already above 23 GPa.^[23, 24] This indicates that cubane plays an important role for the structural stability of the material upon compression. We further plot the pressure dependence of the d-spacings of the sample in **Figure 2b**. We can see that the lattice is continually compressed with increasing pressure and the sample becomes very incompressible above ~13 GPa, which should be related to the enhanced interaction between C₆₀ and C₈H₈ above this pressure.

In **Figure 3a**, the XRD pattern of the sample decompressed directly from 45 GPa shows that the released sample still preserves the high pressure orthorhombic structure with broadened diffraction peaks. In agreement with the XRD results, the HRTEM image of the released sample (**Figure 3b**.) shows a large amount of ordered phase with d=0.5 nm, which can be assigned to the (112) plane of the orthorhombic structure (part A in figure), with a small amount of amorphous material (part B in

figure). According to the *in situ* spectroscopic results (**Figure S1, Figure S2, Figure 4** see below), we know that the C_{60} molecules in this sample have already lost their molecular features and transformed into highly deformed or even amorphous carbon clusters above 36 GPa, while part of the molecular vibrations of the intercalated cubane can still be traced at least up to 36 GPa. The fact that these amorphous carbon clusters still form an orthorhombic structure suggests that the presence of the compressed and reacted C_8H_8 can tune the boundary interactions of the carbon clusters to retain their ordered arrangement under high pressure. This is similar to the case of compressing solvated C_{60} (C_{60} -aromatic solvent), in which collapsed or highly deformed C_{60} molecules act as hard building blocks while the long range periodic structure is preserved with their boundary tuned by the intercalated solvent molecules.^[8-10] We thus believe that a new ACC-based ordered carbon phase is formed by compressing C_8H_8/C_{60} co-crystal.

To understand the transformations in the C_8H_8/C_{60} co-crystal under pressure and to study the effect of C_8H_8 on the sample transitions, we quenched samples from several pressures. Raman and IR spectra measured on the released samples are shown in **Figure 4**. The IR spectrum of a sample released from 10.8 GPa is almost identical to that of a pristine sample, suggesting that the molecules in these samples have recovered after the decompression. For samples released from higher pressures (14.9, 19, 27 and 36 GPa), the intensities of the C_{60} and C_8H_8 IR peaks decrease dramatically, with several new peaks appearing at 700 to 800 cm^{-1} and at 2948 cm^{-1} . Furthermore, in the Raman spectra of these released samples, the low-frequency H_g modes become

broad and clearly split, there is a large drop in intensity of the $A_g(1)$ “breathing” mode, and the intensity of the $H_g(3)$ mode increases while the intensity of the $H_g(4)$ mode decreases. More importantly, the $A_g(2)$ mode broadens and shifts significantly downwards to 1460cm^{-1} in the sample released from 14.9 GPa, which in pure C_{60} polymers indicates an average of four intermolecular C-C bonds on each C_{60} molecule (i.e. cycloaddition bonding to two other molecules).^[25] For samples released from higher pressures, the $A_g(2)$ mode further shifts downwards to 1455cm^{-1} , which in pure C_{60} polymers may imply cycloaddition bonding to three neighboring molecules per C_{60} molecule.^[26] (six intermolecular C-C bonds). However, the absence of characteristic peaks for intermolecular bonding between C_{60} molecules at around 960cm^{-1} in these Raman spectra excludes direct polymerization between C_{60} molecules. This is in sharp contrast to the case of compressing m-xylene/ C_{60} solvates, in which some of the C_{60} molecules can overcome the confinement effect of the m-xylene molecules and thus take part in polymerization under pressure.^[10] Furthermore, polymerization between C_8H_8 molecules can also be excluded, because the cubane molecules in the compound are well separated by C_{60} .^[14, 20] In the IR spectrum of the sample directly released from 45 GPa, several IR peaks from either C_{60} carbon clusters or the cubane component still can be observed, for example, the peaks at 1195 and 1427cm^{-1} are from the five- or six-membered carbon rings on the C_{60} cage and the weak peak at 2948cm^{-1} is related to the C-H stretching mode of cubane. The broad bands preserved at the high frequency range in the Raman spectrum of the directly released sample should be evolved from the pentagon shear ($H_g(7)$), the

pentagonal pinch ($A_g(2)$), and the hexagon shear ($H_g(8)$) modes.^[27-29] This spectrum is similar to that of 3D polymerized C_{60} [30-31], but upon heating up to the temperature for depolymerization of 3D C_{60} , the materials irreversibly transform into amorphous carbon (see Figure S2). These results suggest that the C_{60} has irreversibly transformed into highly deformed or amorphous carbon clusters at 45 GPa, while the cubane molecules were highly strained or partially polymerized with neighboring carbon clusters.

Both IR and Raman spectra of the samples released from pressures higher than 10.8 GPa exhibit spectroscopic features for the presence of C_{60} -cubane copolymers.^[17, 20] This indicates that bonding or polymerization between C_{60} and C_8H_8 takes place above 10.8 GPa. The IR peaks of C_8H_8 become much weaker upon decompression from higher pressures and become almost undetectable in the spectrum of the samples released from 27 GPa, while the new peaks associated with the formation of C_{60} -cubane copolymers become stronger, for example, the broad peaks at 700-900 cm^{-1} and 2948 cm^{-1} . This implies that the fraction of C_{60} -cubane copolymers increases at higher pressures and the presence of such indirect interfullerene bonds is in good agreement with the observed shifts of the $A_g(2)$ Raman mode and should be a stabilizing factor helping to keep the fullerene lattice stable to very high pressures. As expected, the spectroscopic features from the C_{60} cages can still be observed in the spectra of the sample released from 36 GPa, in contrast to the irreversible amorphization of C_{60} molecules observed in spectra from pure C_{60} and in m-xylene/ C_{60} solvates at around 34 GPa.^[8, 23] Our results confirm that the intercalated

C_8H_8 and its low-pressure reactions with C_{60} indeed protects the C_{60} cages from early collapse upon compression. Note that direct intermolecular bonding between C_{60} molecules under pressure has been suggested to cause the pressure-induced amorphization of C_{60} .^[32]

To clarify the importance of the stability of the BB boundaries for the high pressure orthorhombic phase composed of highly deformed or collapsed C_{60} , we kept the C_8H_8/C_{60} sample at 45 GPa for 13 hours. Because of the reactivity of the highly energetic cubane, further bonds might form with the neighboring fullerene BBs during this time and once C_8H_8 loses its molecular features, the BBs boundary should become unstable. Thus, we might see a new transition in the material. Remarkably, after 13 hours at 45 GPa both the C_{60} and C_8H_8 molecules in the sample have completely collapsed and amorphized, as indicated by significant changes in the corresponding vibrational spectra of the released sample (**Figure 5a, b**). The Raman spectrum of the released sample shows only two asymmetrical broad bands at 600 – 800 cm^{-1} and 1100 – 1800 cm^{-1} (with the most intensive position at 1552 cm^{-1}), assigned to vibrational modes of the C-C/C=C bonds in fullerenes or fullerene fragments, containing hexagonal and pentagonal carbon rings.^[8, 9, 23] A similar broad and asymmetric peak at 1552 cm^{-1} has also been observed in diamond-like carbon film and in 3D C_{60} polymers containing large amounts of sp^3 carbons.^[33, 34] Such Raman bands are characteristic for mixed sp^2 and sp^3 bonded disordered carbon.^[9, 35, 36] Also, all the IR peaks of the sample released after 13 hours storage at 45 GPa have merged with the background. These spectroscopic features are quite different from those of

the sample directly released from 45 GPa without storage at high pressure, implying that the highly compressed cubane indeed reacts and/or bonds further with carbon clusters when kept for a long time at 45 GPa. These reactions lead to breakdown of the cubane and to bonding reconstruction at the inter-cluster boundaries in the compound. XRD patterns of the sample after 13 hours storage at 45 GPa followed by decompression to ambient conditions show that the diffraction peaks of the sample become rather broad and diffused (**Figure 5c**). The HRTEM observations on such released sample also suggest that it mainly contains disordered phases (**Figure 5d**), suggesting amorphization of the sample. The observed microstructure is different from those of 3D C_{60} polymers and ultrahard fullerite derivatives reported in previous literatures [31,37]. Strikingly, the disordered phase created clear ring cracks on the diamond anvils after decompression (**Figure S2**), implying that it might be a highly incompressible or superhard phase.^[3, 38] All these results show that the structure, spectroscopic features and even mechanical properties of the sample after 13 hours storage at 45 GPa are different from those of the directly released sample or the sample at 45 GPa before storage.

As discussed above, cubane molecules separate the C_{60} BBs in C_8H_8/C_{60} and partly polymerize with C_{60} upon compression. This behavior stabilizes the boundaries between highly deformed or collapsed C_{60} BBs both by the direct separation or confinement effect of the C_8H_8 in the octahedral voids of the C_{60} lattice and by the stabilizing effect of the hydrocarbon chain links formed between C_{60} molecules by the reaction products of C_8H_8 ($C_{60}-C_xH_y-C_{60}$). The C_{60} BBs are thus protected from

diffusing and bonding with each other, thus contributing to the structural stability even up to 45 GPa. This, on the other hand, prevents the formation of 3D networks via direct cross-linking between fullerene building blocks at high pressure. However, as dwell time increases at 45 GPa, the high energy and reactive properties of cubane cause gradual bonding between the highly compressed or collapsed C_{60} BBs and the cubane component, which can be taken as an energy release process of the highly compressed cubane. This leads to the loss of boundary stability of the C_{60} BBs and irreversible amorphization of compressed C_8H_8/C_{60} via a complete random 3D cross-linking of cubane reaction products with surrounding amorphous carbon cluster BBs in the material. The ACC-based ordered carbon structure formed in our sample thus undergoes a transition from a short range disordered (i.e. the carbon building blocks are amorphous while their arrangement is long range ordered) to a long range disordered structure (i.e., amorphization). The formation of such 3D networks gives a reasonable explanation for the ring cracks left on the diamond anvils after compression. Strikingly, our results are quite different from our previous studies of compressing m-xylene/ C_{60} and m-xylene/ C_{70} , in which aromatic solvents act as linker and spacer but are stable in the transformed OACC (ordered amorphous carbon cluster) structures. In this case, the diffusion of carbon clusters was hindered and thus the formed OACC structure was stabilized even up to 60 GPa. This can be understood by the fact that bonding between C_{60} s occur in m-xylene/ C_{60} even at relatively low pressure and cross-linking of the system into 3D networks takes place at higher pressure. Diffusion of carbon clusters was thus hindered and the 3D network formed

in such OACC structures was stable, incompressible and hard enough to create ring crack indentations on diamond anvils at high pressure.^[8-10] These results suggest that the solvent components in fullerenes solvates strongly affect the bonding interaction among fullerene building block boundaries, which define the phase transformations and properties of the OACC structures formed under pressure.

In summary, a new ordered carbon structure composed of ACC has been created by compressing C_8H_8/C_{60} co-crystals. It is found that the highly energetic cubane molecules exhibit unusual roles in the structure formation and transformations under pressure, quite different from those of previously studied aromatic solvents. One significant role of C_8H_8 is to stabilize the boundary interactions of the highly compressed or collapsed C_{60} clusters to preserve their long range ordered arrangement up to 45 GPa. As holding time increases at high pressure, the gradual random bonding between C_8H_8 and carbon clusters under pressure due to energy release of highly compressed cubane leads to a loss of the ability of C_8H_8 to stabilize the carbon cluster arrangement, and thus a transition from short range disorder to long range disorder (amorphization) in the material. The spontaneous bonding reconstruction most likely results in a 3D network in the material, which can create ring crack indentations on diamond anvils. This presents new insight into the formation mechanism and the pressure-induced amorphization in OACC structure. These results also indicate that new strategies are possible to tailor the boundary interactions in materials with carbon clusters as building blocks in order to obtain new materials.

Experimental Section

The C₈H₈/C₆₀ co-crystals were synthesized as described in refs. [14, 17]. In brief, pure C₆₀ powder and excess cubane are dissolved into toluene. After slow evaporation of the solution, brown C₈H₈/C₆₀ co-crystals were found at the bottom of the bottle. The structures of the as-grown samples were characterized with X-ray diffraction (XRD, RigakuD/max-RA, CuK α 1 radiation with $\lambda = 1.5406 \text{ \AA}$ (Rigaku, Tokyo, Japan) and *in situ* high pressure XRD experiments were performed at the Beijing Synchrontron Facility at ambient temperature ($\lambda=0.61992 \text{ \AA}$). Raman measurements were carried out using a Raman spectrometer (Renishaw inVia (Renishaw, London, UK)) excited by 785 nm (for *in situ* high pressure Raman measurements) and 514 nm (for Raman measurements on released samples) lasers. IR measurements were carried out using a Bruker Vertex80 V FTIR spectrometer. All *first-principles* calculations for cubane molecules, including geometry optimizations and vibrational spectra, were carried out by the DMOL³ method within the gradient-corrected approximation (GGA).

High pressure experiments were performed in a Mao-Bell type diamond anvil cell (DAC) at room temperature. Samples were loaded into a 100 μm diameter hole drilled in the T301 stainless steel gasket. Two type-Ia diamonds with 0.3 mm culets were installed in the DAC for *in situ* Raman measurements while two type-IIa diamonds with 0.2 mm culets were used as anvils for *in situ* IR measurements. No pressure

transmitting medium (PTM) was used for the Raman measurements while KBr was used as PTM for IR measurements. Small ruby balls were incorporated with the sample for pressure calibration by measurements of the shift of the fluorescence line. The highest pressure for *in situ* Raman, IR and XRD measurements is up to~ 45GPa.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1

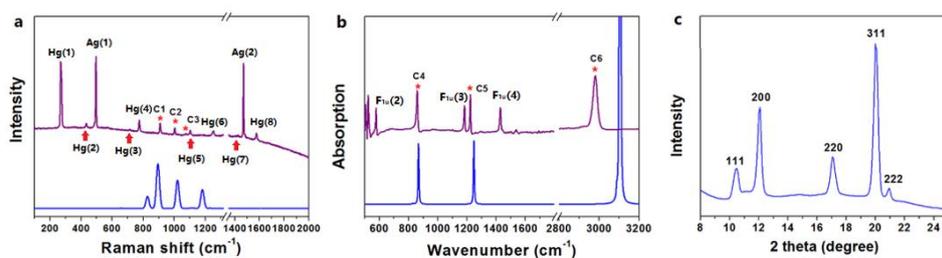


Figure 1. Experimental Raman (a) and IR (b) spectra of C₈H₈/C₆₀ at ambient conditions (purple) together with Raman and IR spectra of C₈H₈ calculated by DMOL³ method within the gradient-corrected approximation (blue). C1-C6 are assigned to the vibrational modes of C₈H₈ molecules. (c) XRD pattern of C₈H₈/C₆₀ at ambient conditions.

Figure 2

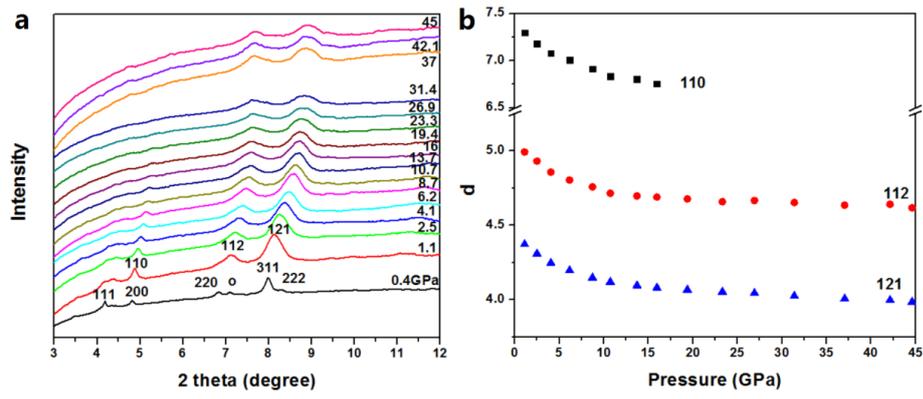
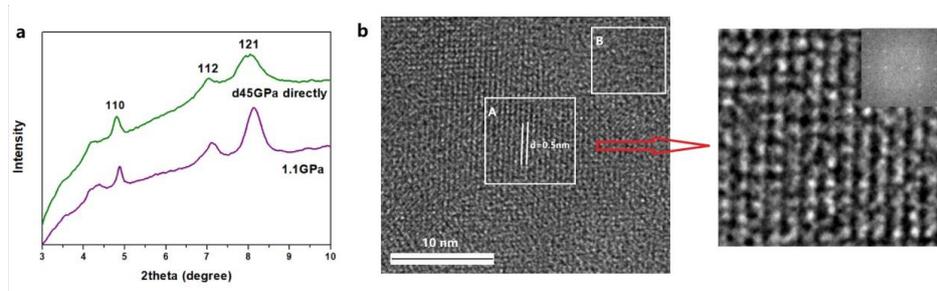


Figure 2. The high pressure XRD patterns (a) and the pressure dependence of the d spacings (b) of C₈H₈/C₆₀ co-crystals.

Figure 3



Comment [MD1]: 图是否需要重做?

Figure 3. (a) The XRD patterns of the sample recovered directly from 45GPa (green, top) and the sample kept at 1.1GPa (purple, bottom). (b) HRTEM image of the sample recovered directly from 45GPa. Insert shows the corresponding FFT image.

Figure 4

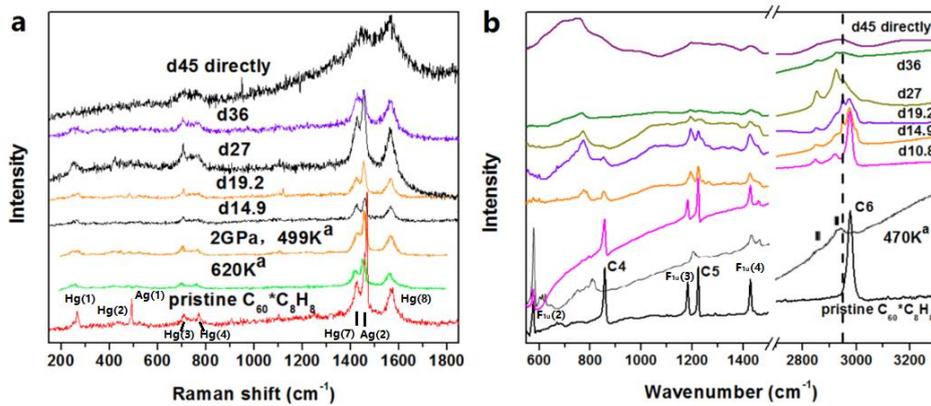


Figure 4. Raman (a) and IR (b) spectra of samples decompressed from different pressures. Superscript ^a denotes data from ref [17, 20] which show the Raman and IR spectra of C₆₀-cubane copolymers synthesized under different conditions

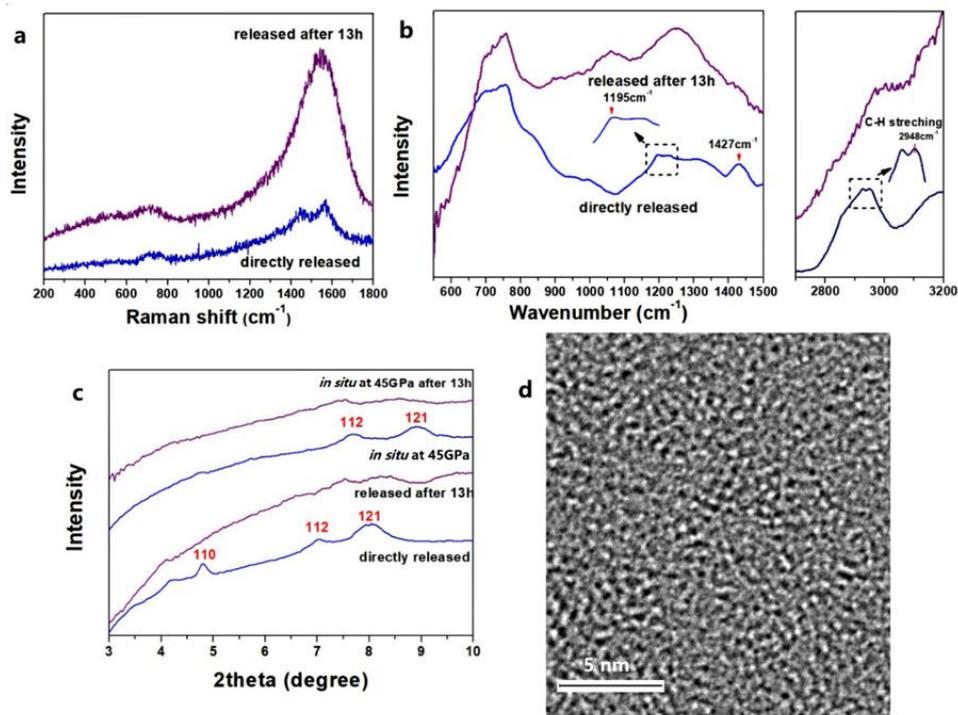


Figure 5. The Raman (a) and IR (b) spectra of the sample released from 45GPa after being kept at 45GPa for 13h in comparison to those of samples directly released from 45GPa. (c) XRD patterns of the same sample after storage for 13 hours at 45GPa and after subsequent decompression to ambient conditions in comparison to those directly released sample and the sample at 45GPa before storage. (d) The corresponding HRTEM image of the sample released from 45GPa after being kept at 45GPa for 13h.

The table of content entry

Cubane, a high energetic molecule, has been found to stabilize the boundary between collapsed C_{60} cluster building blocks and favor the formation of a new ordered amorphous carbon cluster (OACC) structure. As duration time increases under pressure, cubane gradually bonds with C_{60} clusters while losing its ability to stabilize the carbon cluster boundaries, leading to an amorphization of the OACC material, which-can create ring cracks on diamond anvils.

Keyword: rotor-stator compound, cubane, ordered amorphous carbon cluster, high pressures, fullerene

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Title: New ordered Structure of Amorphous Carbon Cluster Induced by Fullerene-Cubane Reactions

TOC figure

