

High-pressure structural transformations of amorphous fullerene-based molecular and quasi-chain forms of carbon

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We present the study of high-pressure transformations in two amorphous carbon materials, including molecular fullerite C_{2n} (mixture of fullerenes C_{2n} with varied size of fullerene buckyballs, $50 < 2n < 170$) and quasi-chain sp^1 -type form of carbon – cumulene carbyne, using quenching experiments, *in situ* energy-dispersive x-ray diffraction in the cubic-type multi-anvil press at the Spring-8, and *in situ* optical measurements of absorption edge in the DAC. The measurements were carried out at high temperatures (up to 1000 °C) up to 8-9 GPa and at the room temperature up to 40-70 GPa. At pressures up to 9 GPa, the both studied materials demonstrate transformation to strongly disordered graphite-type states upon heating, whereas the pressure slightly influences on the scenarios of these graphitization processes. The both transformations are accompanied by semiconductor-to-semimetal transitions. It have been shown that carbyne is less stable with respect to high-temperature treatment, where graphitization occurs at 500 to 800 °C. The main stage of graphitization of fullerite C_{2n} takes place at 900 to 1000 °C as in the case of C_{60} . The studied amorphous forms of carbon don't demonstrate a collapse of a semiconductor gap upon room-temperature pressurization, and their gaps begin to increase at $P \sim 20$ -30 GPa after slight decrease at lower pressures, whereas the details of particular scenarios are dependent on initial structure of amorphous phase.

Introduction

Carbon materials attract considerable attention of researchers because carbon-carbon bonds are among the shortest and strongest ones and therefore the majority of carbon phases should have an advantageous combination of high mechanical characteristics and low density. The binding energy between carbon atoms is very large and carbon structures are potentially very stable against temperature degradation. Carbon atoms can occupy the two-, three-, or four-fold (sp -, sp^2 -, and sp^3 -hybridized, respectively) sites in solids. Due to this diversity of chemical bonding in solid carbon, carbon allotropes are combined into a great family of materials with the covalent topology varying from zero-dimensional (Van der Waals cluster solids) to three-dimensional (3D) structures. The discovery of new all-carbon allotropes, such as fullerenes [1], carbon nanotubes [2], and carbynes (chain polymers) [3], as well as the synthesis of various sp^2 - sp^3 amorphous phases [4-6] demonstrate a great potential of carbon for material science and solid state physics. The theoretical developments of numerous hypothetical carbon structures, including the 3D arranged all- sp^2 phases [7-9], graphitic sheets with negative curvature (schwarzites) [10,11], acetylenic all-carbon compounds [12,13], and exotic planar structures (graphynes [14] and Haeckelites [15]), promise a discovery of novel unique carbon materials in the near future.

Whereas new crystalline, amorphous, cluster-based and nanocrystalline carbon phases are actively experimentally synthesized and theoretically developed, the high-pressure and/or high-temperature behavior of many carbon materials is still a grey area for researchers. In this respect, the influence of dimensionality and topology of covalent carbon networking on the structural stability and evolution of structure under extreme conditions needs to be recognized in many cases. Here we present the results of the quenching experiments, *in situ* energy-dispersive x-ray diffraction in the cubic-type multi-anvil press at the Spring-8, and *in situ* optical measurements of absorption edge in the DAC, carried out for the study of high-pressure transformations in two amorphous carbon materials, such as molecular fullerite C_{2n} and quasi-chain sp^1 -type form of carbon – cumulene carbyne.

Carbyne is an allotropic form of carbon in which carbon is predominantly in the divalent sp state. Solid carbynes include a wide group of crystalline and amorphous chain structures prepared using various chemical and physical methods [3,16,17]. There are two types of carbon chains – cumulene ($=C=C=C=$) with the symmetric bonding of atoms and polyene ($-C\equiv C-$). The investigation of carbyne under pressure has been sporadic though even the physical properties of carbyne under normal conditions have not been adequately studied systematically.

The last years there were a lot of articles concerned with behavior of fullerenes C_{60} and C_{70} and their solid phases under pressure, but other fullerenes have not been studied as yet. In this respect, the mixture of fullerenes C_{2n} with varied size of fullerene buckyballs (fullerite C_{2N} , $50 < 2n < 170$) is attracting object for high-pressure study. The C_{2N} mixture can be obtained by separation of C_{60} and C_{70} fullerene molecules from the carbon soot obtained by laser or electric arc heating of graphite surface in buffer gas. The study of fullerite C_{2N} is also interesting because this substance is an example of molecular carbon system with a disorder in size of molecules.

Experimental

For quenching experiments we use the “Toroid”-type chambers for creating high pressure up to 8 GPa. The details of such type investigations can be found in [18-20]. Initial samples were placed in the high-pressure assemblies with various container materials (Pt, NaCl, graphite, and Ta). The cumulene-type carbynes were synthesized by low-temperature dehydrohalogenation of polyvinylidene chloride [3,17] at A.N. Nesmeyanov Institute of Elemental-Organic Synthesis, Russian Academy of Sciences. Carbyne was found to contain K, Cl and Si impurities (~1 %), whereas carbyne 2 included about 1 to 5 % of F. The presence of impurities in the initial material was detected by mass spectroscopy (in some cases) and by x-ray emission spectroscopy. The fullerite C_{2n} have been produced at the Russian Scientific Center “Kurchatov Institute”. The density of the samples obtained after pressure-temperature treatment was measured by the bottle method. The structure of the samples was studied by X-ray diffraction ($Cu K_{\alpha}$). The resistance of samples was measured using a cryogenic installation specially designed for the study of small samples by the van der Paw method.

The “in situ” structural study of amorphous carbon materials were performed by the X-ray diffraction method with the use of the MAX-80 installation on the SPRING-8 synchrotron (Japan) (beam BL14B1). The pressure up to 6.5 GPa was generated by a cubic press. Pressed cylindrical tablets of 1÷1.5 mm in diameter and 0.6÷1.2 mm in height were prepared from the carbyne and fullerite C_{2n} powders and placed into a high pressure cell. The outer part of the cell was a cube from amorphous boron, and the sample was placed in a container from graphite or hexagonal boron nitride. The heating was produced by passing alternating current through a graphite heater; the temperature was measured by a chromel-alumel or platinum-platinum rhodium thermocouple. The pressure was determined from the equation of state of the reference (NaCl, BN).

For the optic study under pressure we use the DAC with the diameter of culets of diamond anvils about 300 μ m. The diameter of the gasket hole was about 100 μ m. Tungsten was used as the gasket material. As the pressure medium we used silicon organic

liquid or standard alcohol mixture. The shift of ruby fluorescence was used to determine pressure.

High-temperature transformations

1. Carbyne

X-ray diffraction patterns for the phases prepared from carbyne under pressure 7.7 GPa are shown in Fig. 1. There are no significant changes in the structural data up to 500 °C, and the diffraction patterns display a high degree of disorder in carbyne. When the synthesis temperature is further increased ($T_{\text{syn}} \sim 700$ °C) the structural transformation leads to a phase with a much sharper diffraction pattern, but still disordered. This pattern corresponds to amorphous graphitic-like carbon with the predominantly sp^2 hybridization of atoms. More careful analysis of the structural data (see inset in Fig. 1) shows that the peak near 3 \AA^{-1} appears in the diffraction curves of high-temperature specimens ($T_{\text{syn}} = 500$ °C). It is natural to attribute this peak to an increase in the fraction of atoms in the sp^2 states. No changes in the disordered structure of carbyne were detected up to the synthesis temperature 400 °C (although in the Carbyne 2 we observed the appearance and then dissolving of a small amount of crystalline KCl in the range 200–400 °C).

The absorption edge spectra for cumulene carbynes (Fig. 2) show that they are semiconductors with the band-gap energy about 1–1.5 eV. The spectra display the indirect absorption edge and significant absorption edge tail corresponding to the amorphous state of carbyne. Even slight heating of carbyne under pressure appreciably changes the absorption edge (Fig. 2), whereas x-ray data don't allow one to detect any structural changes. One can suppose that main polymeric quasi-one dimensional structure of carbyne is kept at this temperatures, but, e.g., cross polymerization between carbon chains influence on the optic properties.

Thus, the temperature-induced transformation in carbyne ($P = 7.7$ GPa) can be described as gradual cross-polymerization and subsequent graphitization, i.e., the sp - sp^2 transition. The resistivity vs synthesis temperature dependence for different samples (Fig. 3) directly confirms this conclusion. The semiconductor-to-metal transition occurs near 600 °C. One should note that the resistivity of carbon phases graphitized from carbyne is higher than those for graphite ($\sim 10^{-3}$ Ohm·cm) and carbon phases graphitized from C_{60} ($\sim 10^{-2}$ Ohm·cm). The detailed study of low-temperature electronic transport in the temperature-treated under pressure have been made in [21,22].

The results of the quenched experiments are directly confirmed by *in situ* energy-dispersive x-ray diffraction experiments carried out at the Spring-8 at 2 and 7.8 GPa (Fig. 4).

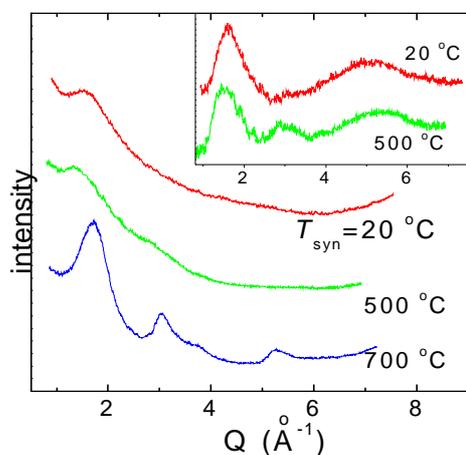


Fig. 1. X-ray ($\text{Cu } K_{\alpha}$) diffraction patterns of carbyne temperature-treated at pressure 7.7 GPa.

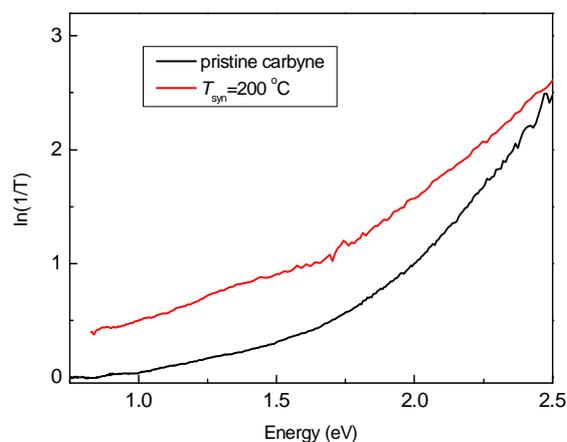


Fig. 2. Inverse-transmission spectra for pristine and temperature-treated at $P = 7.7$ GPa carbynes.

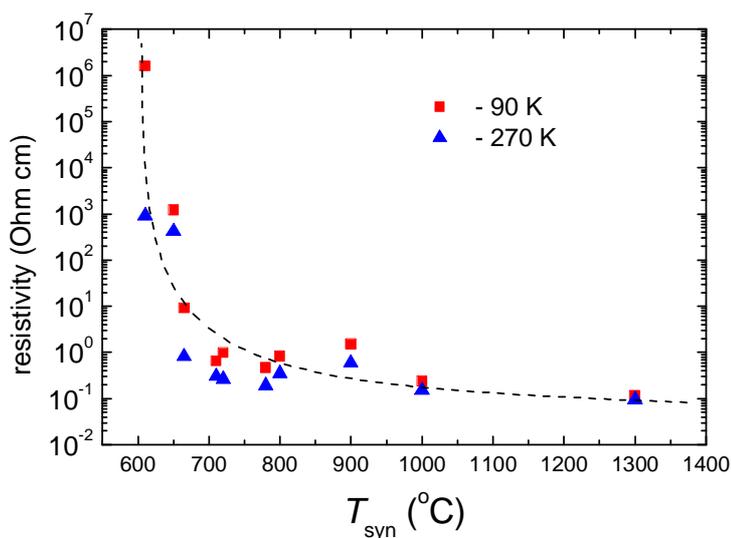


Fig. 3. Resistivity (measured at 90 and 270 K) vs synthesis temperature for carbyne samples after heating at $P=7.7$ GPa. The dashed lines are guides for eyes.

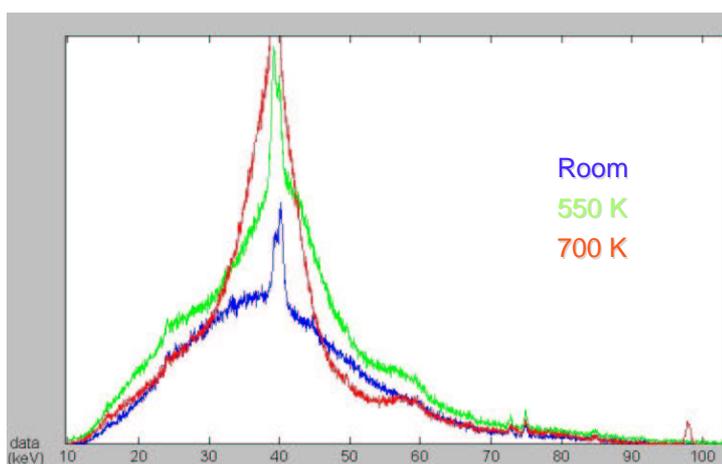


Fig. 4. Examples of the experimental *in situ* energy dispersive x-ray diffraction from carbyne at $P=7.8$ GPa, measure at different temperatures. The crystalline peaks at 40 keV corresponds to diffraction from the material of the heater/container (graphite) surrounding the sample.

2. Fullerite C_{2n}

The mass spectroscopy data for fullerite C_{2n} (Fig. 5) clearly show its molecular nature, since the mass-spectrum shows evident maxima corresponding to C_{2n} with a plateau of maximum intensities at $2n$ from 88 to 106.

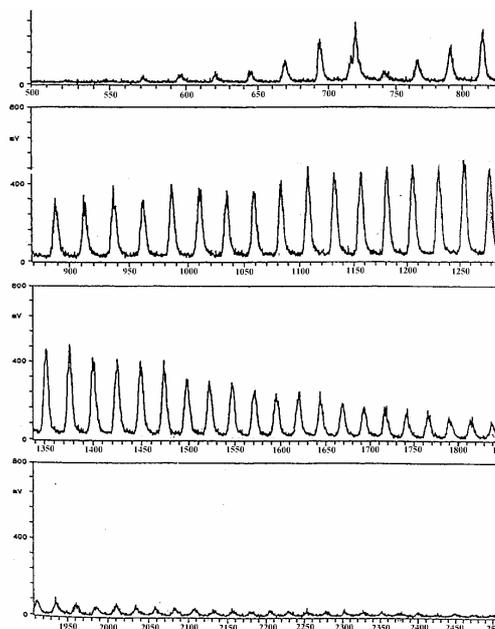


Fig. 5. The mass spectroscopy data for fullerite C_{2n}

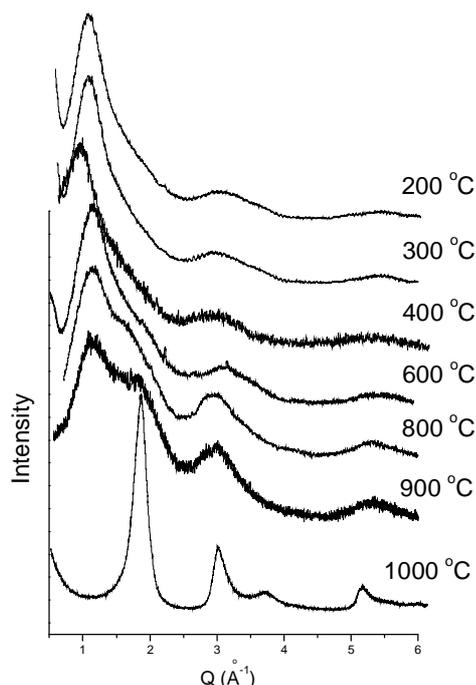


Fig. 6. X-ray ($Cu K_{\alpha}$) diffraction patterns of fullerite C_{2n} temperature-treated at 8 GPa.

The changes of C_{2n} structure after pressure-temperature treatment is presented in Fig. 6. This data show that diffraction curve of pristine C_{2n} (it is very similar to a curve obtained upon heating to 200 °C) is a picture typical for amorphous substance with wide peaks at scattering vectors near 1 and 3 \AA^{-1} . At small heating to 400 °C there are no essential structural changes. At the further heating since temperature 600 °C a new peak appears at 2 \AA^{-1} , which clearly corresponds to the position of the (002) reflection of graphite and consequently can be attributed to a disordered graphite-type phase. In a range of temperatures 900-1000 °C a sharp graphitization occurs, since the curve obtained at $T=1000$ °C is a typical picture for disordered graphite.

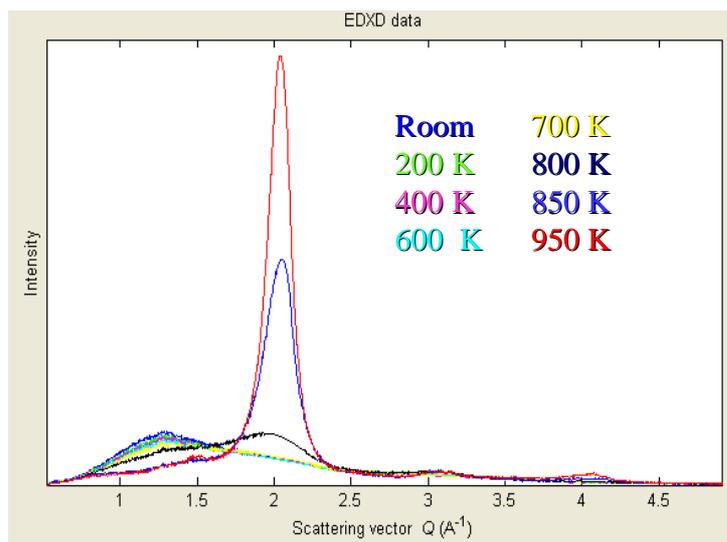


Fig. 7. Examples of the experimental *in situ* energy dispersive x-ray diffraction from C_{2n} at $P=8.8$ GPa, measure at different temperatures.

The detailed analysis of structural data and comparison between transformations in fullerite C_{2n} and fullerite C_{60} in similar conditions allow us to determine following stages of transformation in C_{2n} : i) initially, the partial polymerization of fullerene molecules and increase of the polymerization degree with temperature; ii) the destruction of fullerene molecules and formation of graphite-like clusters. It's clear that the temperature, which is enough for destruction of fullerene molecules, depends on the size of molecule, and, in contrast to C_{60} , such molecule destruction starts in C_{2n} at about 600 °C. But a complete

graphitization of the whole volume of fullerite C_{2n} takes place at temperatures 900 to 1000 °C as in the case of C_{60} . Measurements of conductivity show a significant increase of electron transport in this temperature interval from semiconductor levels ($<10^{-9} \text{ Ohm}^{-1}\text{cm}^{-1}$ to values typical for disordered graphite $\sim 1\text{-}10 \text{ Ohm}^{-1}\text{cm}^{-1}$).

The *in situ* energy-dispersive x-ray diffraction measurements at the Spring-8, carried out in the pressure range from 1.5 to 8 GPa show the same scenario of transformations (Fig. 7). It is important to emphasize that similar scenario has been observed in the quite wide interval of pressures.

Room-temperature compression

Evolution of the inverse-transmission spectra for carbyne and fullerite C_{2n} with pressure at room temperature are shown in Figs. 8 and 9, respectively. The figures show corresponding shifts of energy gaps. There are both common feature and difference in the behavior of carbyne and fullerite C_{2n} on room-temperature compression. The both amorphous carbon substance demonstrate initially a decrease of absorption edge. But in carbyne, a gradual increase of absorption edge start near 20 GPa. The absorption edge of fullerite is observed up to 33 GPa, but the increase occurs abruptly, like during phase transition.

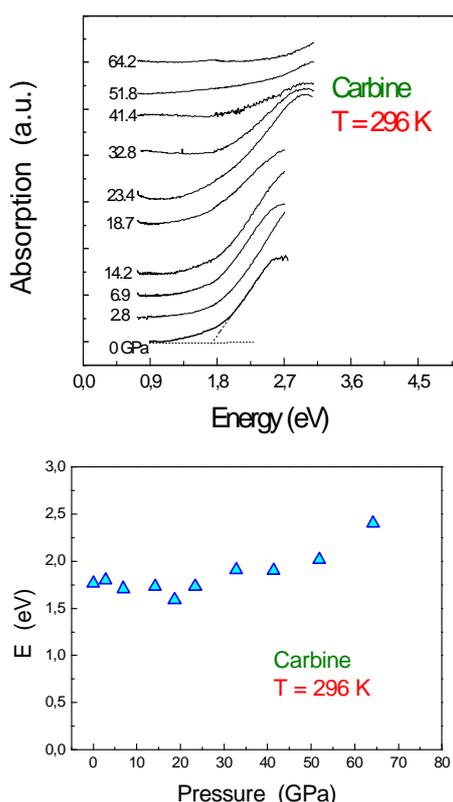


Fig. 8. Change of the inverse-transmission spectra (top) for carbynes (spectra are shifted for clearness) with pressure and corresponding shift of absorption edge (bottom) approximated as for 0 GPa. Measurements were carried out at room temperature.

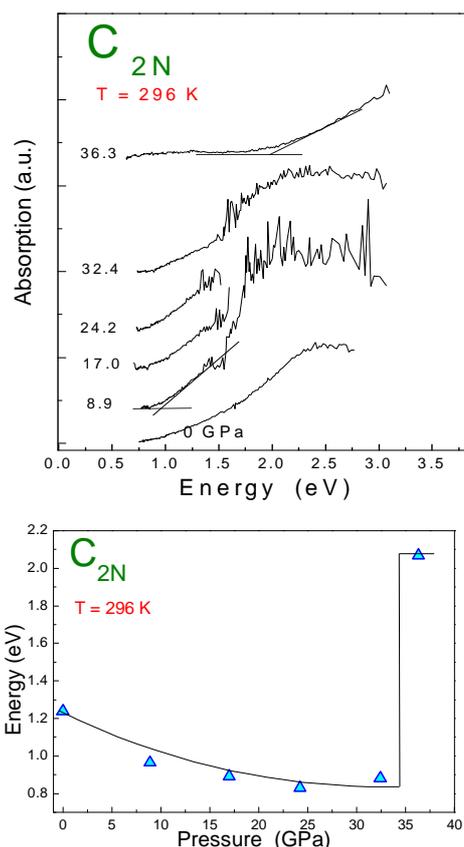


Fig. 9. Change of the inverse-transmission spectra (top) for C_{2n} (spectra are shifted for clearness) with pressure and corresponding shift of absorption edge (bottom) approximated as for 36.3 GPa. Measurements were carried out at room temperature.

The difference in the high-pressure behavior of carbyne and fullerite C_{2n} should be related to the differences in their structure. Indeed, fullerene molecules are closed covalent clusters and are quite stable with respect to external pressure (fullerene C₆₀ is the most stable molecule among others). The high compressibility of fullerenes at low pressures is due to fast change of intermolecular distances between molecules interacting via weak Van der Waals forces. One can suppose that abrupt change of absorption edge in fullerite C_{2n} occurs due to collapse of molecular structure, although the destruction of particular molecules, e.g., large molecules, can occur at lower pressures. In contrast, carbyne has a quasi-chain (one dimensional) topology and, so, quite small coordination number of covalent bonding near $z=2$. Such covalent network is soft with respect to deformation according to the percolation theory [23]. For this reason carbyne demonstrates the gradual change of the absorption edge. The increase of the absorption edge in the both amorphous carbon phases under discussion clearly relates to the appearance of sp^3 atomic sites and clusters, since these transformations occur in the deep region of stability of diamond.

Conclusion

Summarizing, our results show that high pressure is a powerful tool for change the structure of amorphous carbon phases, providing possibility for their transformation both to semimetallic graphite-type disordered structures and semiconductor phases with large fraction of sp^3 atoms. Particularly, we can vary the average nearest-neighbor coordination number and topology of covalent networking in carbon phases. The data obtained stimulate the discussion concerning interplay between the bonding nature and the physical properties of covalent carbon compounds. It shows quite different scenarios of transformation of amorphous phases upon heating and under compression. In turn, the covalent topology of pristine phases is also very important for detailed picture of transformations.

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