Synthesis of Superhard and Ultrahard Materials by 3D-polymerization of C_{60}, C_{70} Fullerenes Under High Pressure (15 GPa) and Temperatures up to 1820 K

Vladimir D. Blank[a], Sergei G. Buga[a], Gennadi A. Dubitsky[a], Nadejda R. Serebryanaya[a,b], Vyatcheslav M. Prokhorov[a], Boris N. Mavrin[b], Victor N. Denisov[b], Leonid A. Chernozatonskii[c], Sofia Berezina[d], and Vadim M. Levin[e]

[a] Technological Institute for Superhard and Novel Carbon Materials, Centralnaya St. 7 a, Troitsk, 142190 Russia
[b] Institute of Spectroscopy of the Russian Academy of Sciences, 142190 Troitsk, Moscow region, Russia
[c] Institute of Biochemical Physics of RAS, 117977, Moscow, Russia
[d] Department of Physics, University of Zilina, 010 26 Zilina, Slovakia
[e] Center for Acoustic Microscopy, Russian Academy of Sciences, Kosygin St. 4, Moscow, 117334 Russia

Reprint requests to Prof. Dr. S. G. Buga. E-mail: buga@ntcstm.troitsk.ru

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Solid fullerenes C_{60} and C_{70} have been treated at high pressure of 15 GPa and high temperatures of 520 – 1820 K for a time of exposure of 60 s and a quenching rate of 300 K s^{-1} using a toroid-type apparatus. X-ray diffraction and Raman spectra confirm the realization of 3D-polymerized phases in these solids at 15 GPa. The pressure/temperature maps of synthesis of metastable carbon phases on the basis of C_{60} and C_{70} have thus been extended to 15 GPa. The longitudinal and shear sound wave velocities were measured by acoustic microscopy techniques. A maximum sound wave velocity of $(21 \pm 1) \times 10^5$ m s^{-1} was observed in the sample synthesized from C_{60} at T = 1170 K. The elastic constants were calculated using experimental data. The acoustic microscopy images of experimental samples have been investigated.

Key words: Fullerenes, High Pressure, X-ray Diffraction, Raman Spectra, Elastic Properties, Superhard Materials

Introduction

The discovery of fullerenes and the development of methods for their manufacturing initiated extensive studies of their properties and the synthesis of a broad diversity of new materials on their basis [1]. One of the very important properties of the fullerene molecules is their ability to polymerize and create dimers, oligomers, chain, layer and bulk polymers (1D-, 2D- and 3D- polymers) [2]. The 3D-polymeric fullerenes are the hardest and have great prospects for practical applications. Besides outstanding mechanical strength, comparable with diamond, they possess intrinsic semiconductor properties unlike diamond (a wide band gap semiconductor) and graphite (a semimetal) [3]. The disordered carbon structures of highest density on the basis of 3D-polymeric C_{60} have an extremely high hardness and strength, exceeding those of diamond [4]. Two methods of synthesis of 3D-polymeric fullerenes have been explored:

- r. t. synthesis at very high pressures of 18 – 37 GPa and activation by severe plastic deformations [5];
- static high-pressure / high-temperature (HPHT) synthesis with quenching by rapid cooling under a pressure of 9 – 13.5 GPa [6].

The first method was realized using a shear diamond anvil cell [7], which allows *in situ* Raman spectroscopy and X-ray diffraction studies, but the specimen sizes are relatively small: 0.2 – 0.3 mm diameter and 20 μm thickness. The second method employs a toroid-type high-pressure apparatus [6] loaded with a press up to 1000 t force. This apparatus allows the synthesis of bulk specimens up to 50 – 80 ng in weight and up to 4×4 mm in size. An alternative static high-pressure technique for producing bulk samples uses a multi-anvil apparatus [8, 9]. It permits the synthesis under

pressures of up to 22 GPa, but generally samples have smaller sizes and quenching proceeds at lower rates. Thus, metastable polymeric structures may depolymerize or transform into other structures upon slow cooling.

In this work we investigated the synthesis of superhard and ultrahard carbon structures from C_{60} and C_{70} fullerenes by high-pressure / high-temperature treatment in a modified toroid-type apparatus under a pressure of 15 GPa and at temperatures of 670 – 1820 K. The structures of quenched specimens have been investigated by powder X-ray diffraction and Raman spectroscopy. Scanning acoustic microscopy imaging (mapping) has been employed to investigate the inhomogeneity of the structures and for local measurements of longitudinal and shear sound wave velocities. The elastic module numbers have been evaluated using sound velocity data and the density of the samples taking into account their inhomogeneity.

Samples and Methods of Investigation

Samples were synthesized from the commercially available C_{60} (99.98%) and C_{70} (99.2%) powders. Prior to the experiments, the high-pressure apparatus was pressure-calibrated according to the electrical resistance jumps at phase transitions in reference solids like Ba (12 GPa), Pb (13 GPa), ZnSe (13.7 GPa), and ZnS (15 GPa). Temperatures were measured directly by Pt/Pt-Rh thermocouples. The isothermal exposition time at given temperatures was 60 s. The quenching to r. t. was made at a rate of ~ 300 Ks^{-1}. The dimensions of the specimens were up to 3 mm in diameter and 3 mm in height. For ultrasonic studies the upper and bottom faces of cylindrical specimens were polished after the synthesis. The density of the specimens was measured by the flotation method in mixtures of diiodomethane and acetone liquids of different concentrations.

The X-ray diffraction patterns were obtained using an X-ray diffractometer KARD-6 with a flat proportional chamber on the fast delay lines [10]. CuK_α radiation and a graphite monochromator were applied. During the exposition specimens were rotated to provide a better intensity averaging over the individual crystallites. The diffractograms were obtained from different parts of the samples. The Raman spectra were obtained by excitation with an 514.5 nm Ar-laser line.

The wide-field pulse scanning acoustic microscope (WFPAM) was applied in a reflection mode at the driving frequency f = 50 MHz to measure local values of ultrasonic velocities and elastic moduli (microacoustic technique) and to visualize the bulk microstructure of a specimen (scanning acoustic microscopy). The method allows studies of small specimens and inclusions with submillimeter resolution. The mean diameter of the acoustic spot on the specimen face was less than 100 μm. More details of acoustic microscopy studies can be found elsewhere [11]. The typical acous-

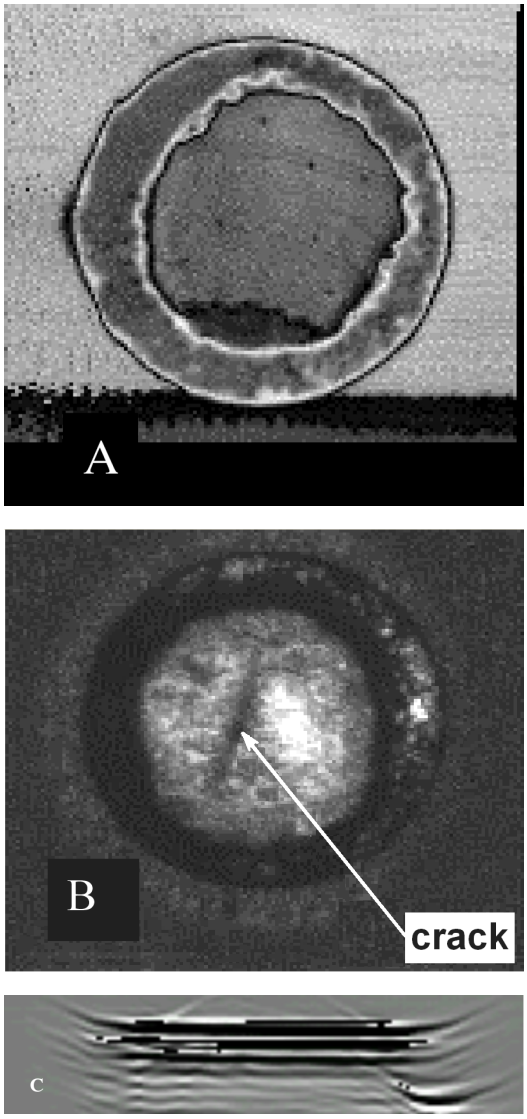

Fig. 1. Scanned acoustical microscopy images of an experimental sample (in the center). A: front face reflection of the acoustic beam; B: bottom face reflection of the acoustic beam; C: echogram of the reflected acoustic pulse; the vertical direction is the time scale.

tic microscopy images of a sample and its echogram are shown in Fig. 1. The echoes from the front face of the sample give the upper straight black line in the echogram (Fig. 1C). The reflection of longitudinal and shear waves from the bottom of a sample are depicted by lower lines. The time scale distance between these lines depends on the thickness of the sample and the sound velocities. We measured longitudinal and shear sound velocities using the record of the echo-signal oscillograms. The time interval τ_L between the signals reflected at the front (A-signal) and back (B-signal) faces of the sample determines the magnitude of the longitudinal sound velocity V_L : $V_L = 2d/\tau_L$, where d is the specimen thickness (time-of-flight method). The transverse wave velocity magnitude was derived from measurements of the time intervals τ_L for the longitudinal wave and τ_{LT} for mixed mode of propagation: $V_t = d/(\tau_{LT} - \tau_L/2)$. Local and averaging elastic moduli were calculated on the basis of the measured velocities and densities of the samples. The acoustic microscopy images show the microstructure of fullerene specimens. Such images revealed significant changes of the echo's arrival time along the scanning line for both the longitudinal and shear waves. These time variations relate to spatial inhomogeneity of the elastic properties of the samples. B-scans also reveal defects inside the specimens. The disrupt in bottom reflections in Fig. 1B indicates a crack or an internal boundary. While the front surface image reflects only the grinding traces, the image formed by the bottom echo shows the heterogeneity of the interior.

Results and Discussion

X-ray diffraction studies

The diffraction patterns of C_{60} and C_{70} quenched after 15 GPa and high-temperature treatment are shown in Figs. 2 and 3, respectively. The diffraction patterns indicate the same structures as were formed after treatment at the lower pressure level of 13 GPa, but roughly 100 – 150 K higher temperatures [12 – 14]. The hardest crystalline 3D-polymeric phases with the unit cell parameters a = 8.67, b = 8.81, c = 12,6 Å, space group *Immm*, were formed at 13 GPa and 820 K, and at 15 GPa and 670 K. A similar crystalline structure was obtained at r. t. in a diamond anvil cell from pristine C_{60} at 22.4 GPa [15] and independently from a 2D-polymer at 20 GPa [16]. The molecular shape is strongly deformed in such a structure (Fig. 4a). Fig. 4b shows the (010) projection of the structure. Amorphous phases appear after treatment at $T > 820$ K, and the samples are totally amorphous after treatment at $T > 1470$ K. As can be seen in Fig. 2, the XRD patterns of the face and side parts of cylindrical samples quenched after treatment at $T \geq 1120$ K are different: the side part diffraction has one diffuse peak at

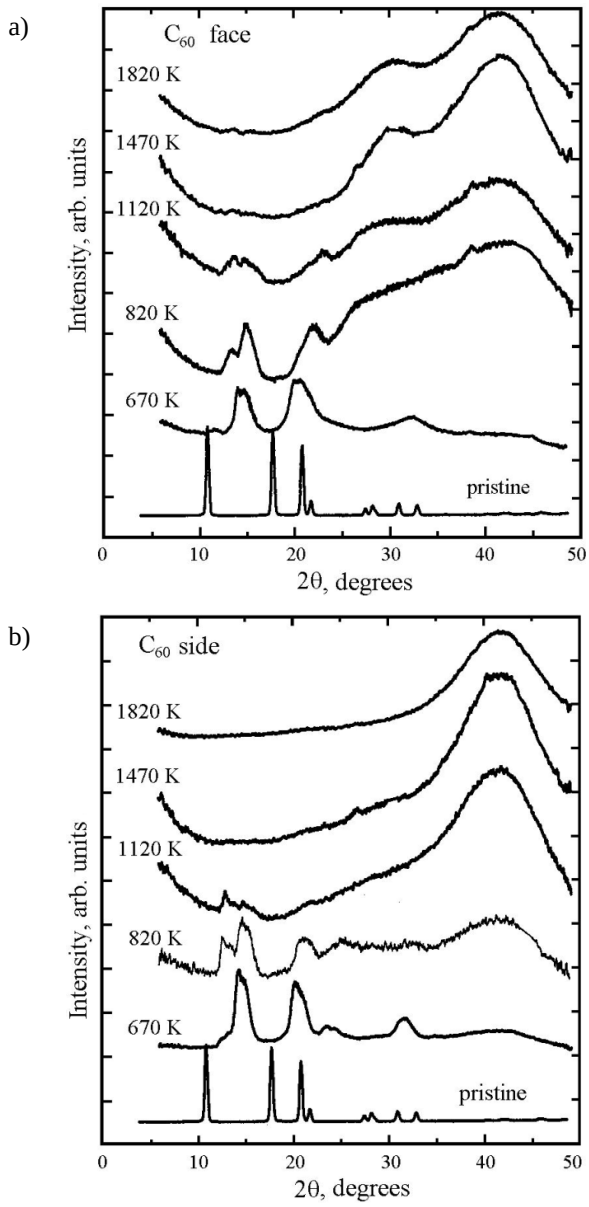

Fig. 2. X-ray diffractograms (CuK_α radiation) of samples obtained from solid C_{60} after treatment at 15 GPa and $670 \leq T \leq 1820$ K. (a) scattering at the face part of the samples; (b) scattering at the side part of the samples; pristine: the initial C_{60} powder.

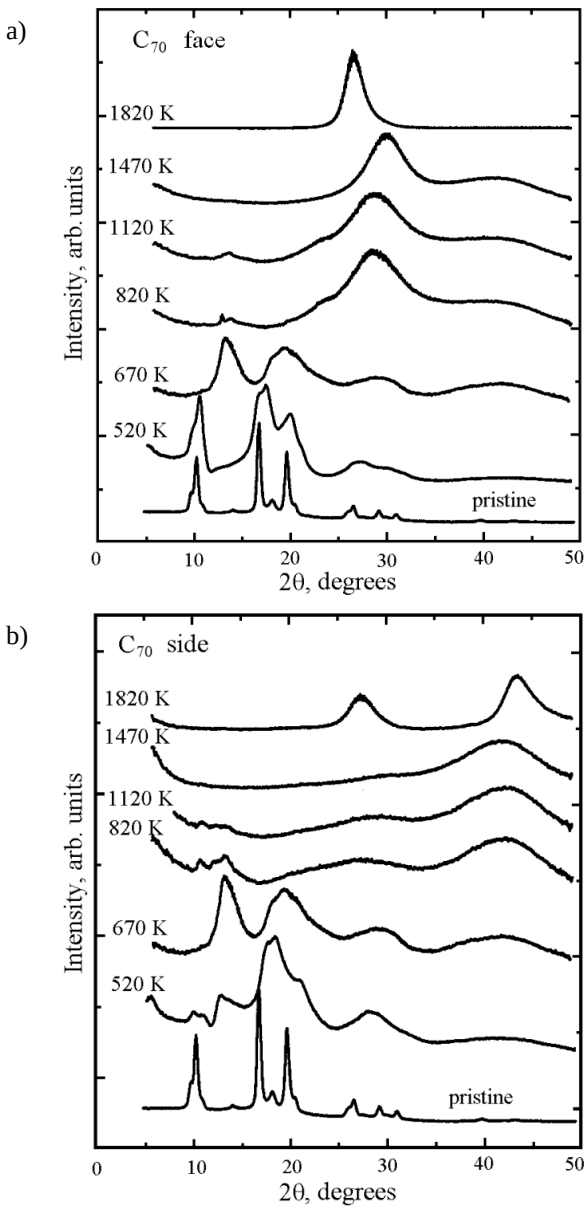

Fig. 3. X-ray diffractograms (CuK_α radiation) of samples obtained from solid C_{70} after treatment at 15 GPa and $670 \leq T \leq 1820$ K. (a) scattering at the face part of samples; (b) scattering at the side part of samples; pristine: the initial C_{70} powder.

$2\theta \approx 42^\circ$ ($d \sim 2.15$ Å), while the face part shows two broad lines at $2\theta \approx 42^\circ$ ($d \sim 2.15$ Å) and at $2\theta \approx 30-31^\circ$ ($d \sim 2.93$ Å). The amorphous samples with one broad diffraction peak at $2\theta \approx 42^\circ$ are harder than diamond, *i. e.* ultrahard [6]. As we wrote in [14], the diffraction pattern with two broad lines probably corresponds to the layered structure with a set of interlayered distances between the corrugated graphene sheets cross-linked by sp^3 bonds. These layers can remain after the collapse of the fullerene cages.

The diffraction patterns of C_{70} samples obtained after HPHT treatment at 15 GPa (Fig. 3) confirm the decrease of the synthesis temperature of polymerized phases. Disordered layered structures analogous to those in samples obtained by treatment at 12.5 GPa were found in a face part of the samples. However, the diffractograms from a side part of the samples obtained at $T \geq 820$ K (Fig. 3b) have a broad peak at $2\theta \approx 42^\circ$. Such an amorphous structure was obtained from C_{70} fullerene for the first time. This structure of the sample obtained at 1470 K is similar to that obtained from C_{60}. The clear-cut distinction between amorphous phases obtained from C_{60} and C_{70} appears in samples at 1820 K. The diffraction pattern of the sample produced from C_{70} indicates a disordered graphite-like layered structure (Fig. 3) with a mean interplane distance of 3.32 Å while the structure of the material produced from C_{60} is mainly 3D-polymeric with a mean interplane distance of 2.18 Å (Fig. 2).

The crystalline phases obtained from C_{70} and quenched at 15 GPa have the same diffractograms as the ones obtained at 12.5 GPa [17]. The comparison of Fig. 3b with Fig. 5 (diffractograms obtained after treatment at 12.5 GPa) shows that 3D-polymerized crystalline phases are realized at a lower temperature at a pressure of 15 GPa than at 13 GPa. The structure of the 3D-polymerized C_{70} phases obtained after treatment at 12–15 GPa and 670–820 K (Fig. 3b: 670 K; Fig. 5: 820 K) has not been solved yet. As we discussed earlier [17], because its diffractogram conforms to that of the superhard phase of C_{60} [14], the structure of 3D-polymeric C_{70} fullerenes should resemble the packing of C_{60}.

Raman studies

The Raman spectrum of C_{60} quenched after treatment at 15 GPa and 670 K is similar to that of the 3D-polymerized phase produced from C_{60} at 13 GPa and $T > 600$ K. Instead of 10 narrow lines of the pristine C_{60} spectrum, it shows one intense broad band at 1568 cm^{-1} (Fig. 6a). This spectrum looks similar to that of C(sp^3)-rich diamond-like films [18], which are amorphous. However, according to the X-ray data (Fig. 2) the sample quenched at 670 K is crystalline with retention of the C_{60} cage. Thus the observed spec-

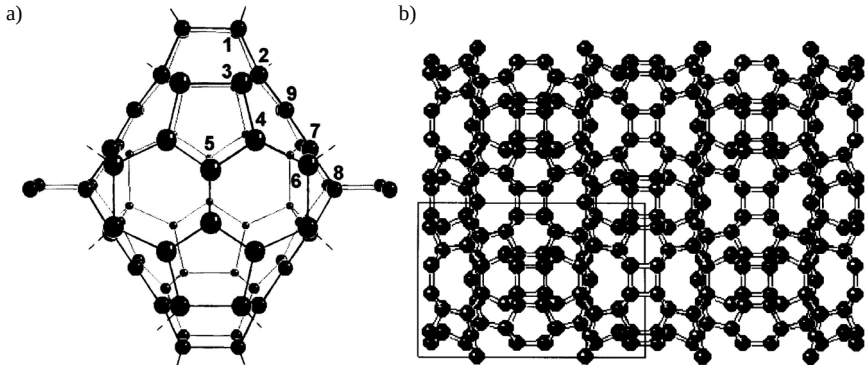

Fig. 4. Models of a C_{60} cage in a 3D-polymeric structure (a), and one of the projections of the crystalline structure (b). The unit cell is shown in a box.

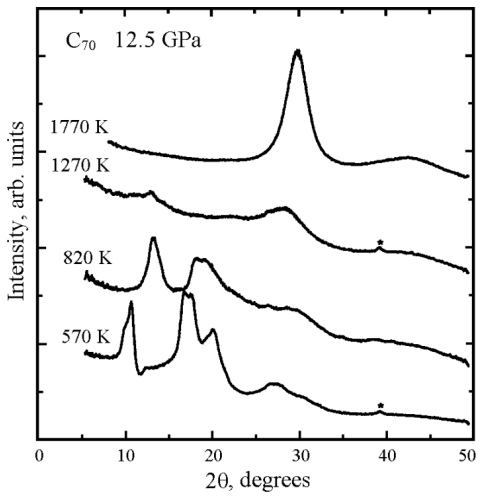

Fig. 5. X-ray diffractograms (CuK_α radiation) of samples obtained from solid C_{70} after treatment at 12.5 GPa and $570 \leq T \leq 1770$ K. * reflection of the sample holder.

trum corresponds to a crystalline 3D-polymeric C_{60} structure. The observed spectrum is close to the calculated spectrum of the crystalline 3D-polymeric C_{60} phase [13]. Since the spectrum does not change upon treatment at up to 1820 K, one may suppose that the cage short-range order is retained in the amorphous samples quenched after treatment at these high temperatures.

Earlier it was found [19] that a pressure up to 31 GPa is insufficient to destroy the C_{70} molecules and that after decompression the sample recovers to the pristine state. The Raman spectra after HPHT treatment at 15 GPa are strongly distinct from those of samples quenched at 12.5 GPa and lower pressures. At pressures < 12.5 GPa the spectra were like those of molecular C_{70} up to 700 – 800 K, only the bands became broader. After HPHT treatment at 15 GPa and

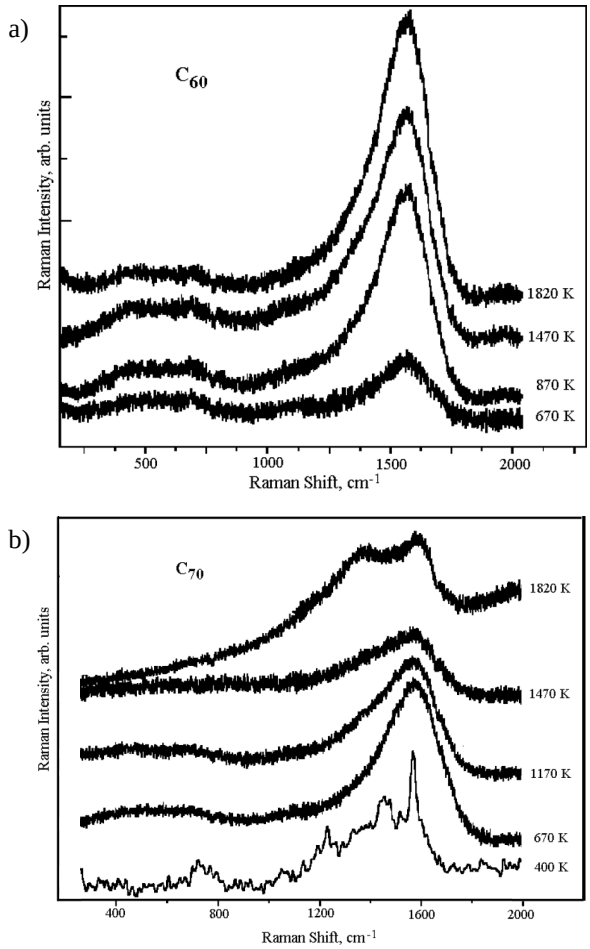

Fig. 6. Raman spectra of samples obtained from solid C_{60} after treatment at 15 GPa and $670 \leq T \leq 1820$ K (a), and from solid C_{70} after treatment at 15 GPa and $400 \leq T \leq 1820$ K (b).

670 K the spectrum had only one band at 1572 cm^{-1} (Fig. 6b), whereas the high-frequency mode in pris-

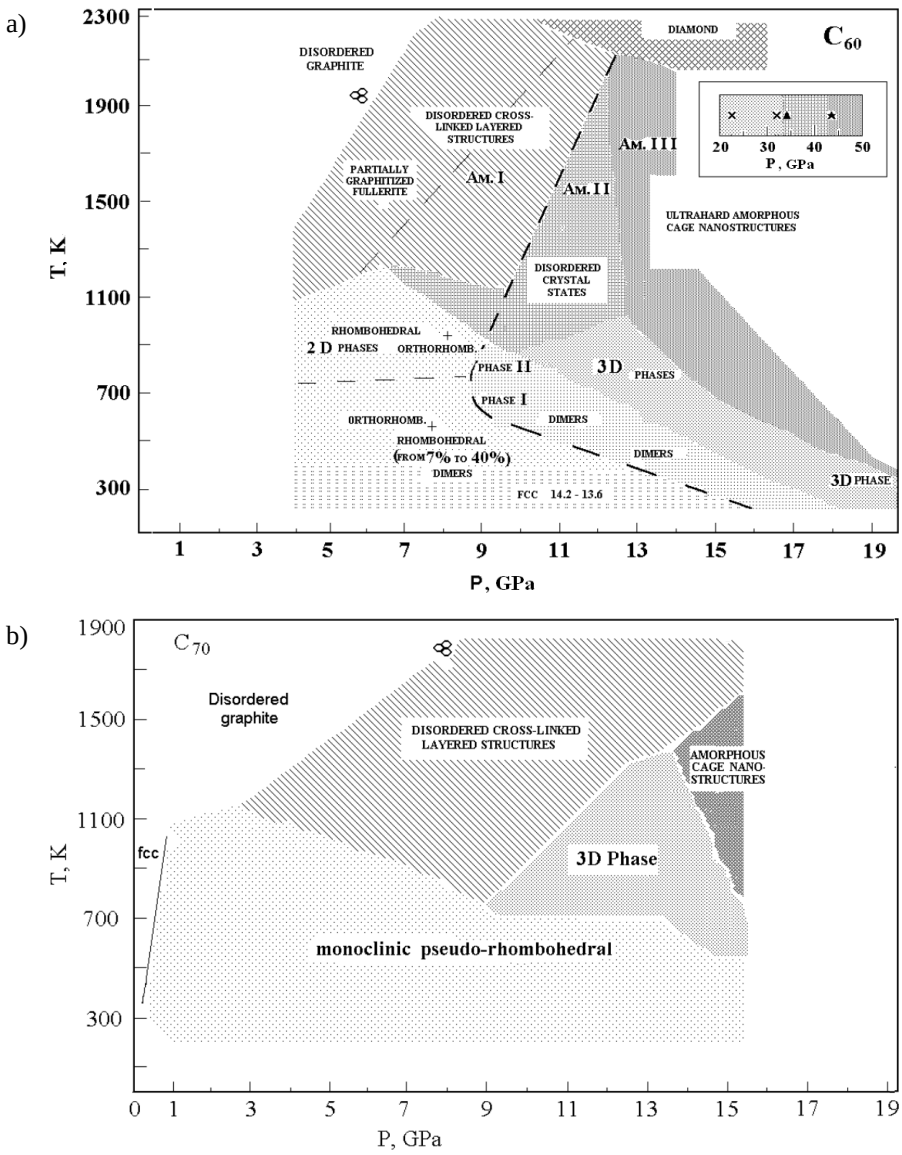

Fig. 7. (Pressure/temperature) map of new carbon structures from solid C_{60} (a) and C_{70} (b).

tine molecular C_{70} appears at 1564 cm^{-1}. It is possible to suppose, in analogy to the C_{60} spectra, that the appearance of the single band in the C_{70} spectrum is due to 3D-polymerization of C_{70} molecules. This assumption is in agreement with X-ray data, according to which the C_{70} cage is retained after HPHT treatment at 15 GPa and 670 K (Fig. 3). When the temperature of the HPHT treatment is increased a shoulder on the low-frequency wing of the 1572 cm^{-1} band appears that turns into an additional maximum at 1370 cm^{-1} in the spectrum of the sample synthesized at 1820 K. The 1572 cm^{-1} band shifts to 1582 cm^{-1}. The spectrum of the quenched sample previously treated at 15 GPa and 1820 K is similar to that of microcrystalline graphite [20]. One can assume that a gradual graphitization of the sample occurs as the temperature increases beyond above 700 K with the result that the sample transforms into nanocrystalline graphite at 1820 K.

(Pressure / temperature) maps

The XRD and Raman scattering studies of samples obtained from C_{60} and C_{70} fullerenes at 15 GPa and

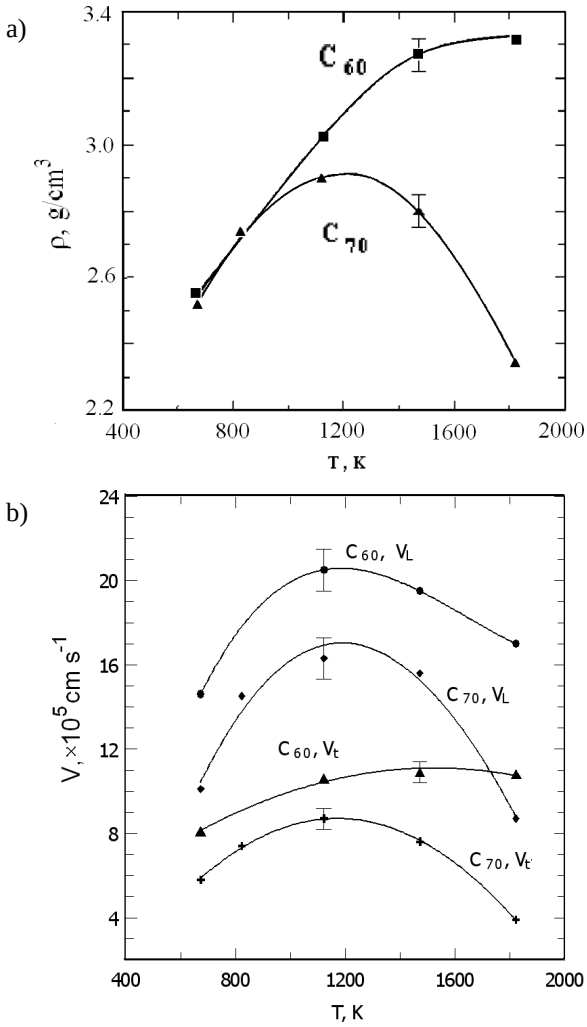

Fig. 8. The temperature dependence of the mean densities (a), and mean velocities of sound (b) for carbon structures obtained from C_{60} and C_{70} fullerenes after synthesis at 15 GPa.

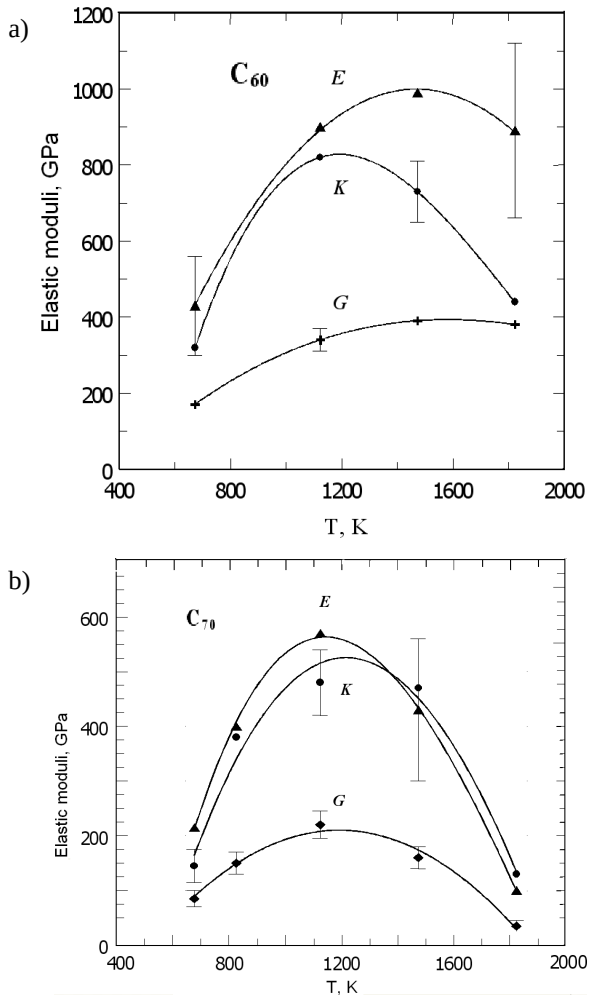

Fig. 9. The temperature dependence of elastic moduli of carbon structures obtained from C_{60} (a) and C_{70} (b) fullerenes after synthesis at 15 GPa.

670 – 1820 K allow us to refine and expand the earlier plotted pressure/temperature-diagrams [4, 17] and to see distinct differences between the behavior of the two fullerenes (Fig. 7). The main difference in the diagrams of superhard and ultrahard carbon structures from C_{60} and C_{70} fullerenes is related to the structure and properties of amorphous cage nanostructures, obtained under a pressure above 13 GPa. Solid C_{60} fullerene transforms into a cage nanostructure based on the 3D-polymerized crystalline structure shown in Fig. 4, while C_{70} transforms into a disordered cross-linked laminated structure with lower density and hardness. The densities of the samples obtained from C_{60} and C_{70} fullerenes after treatment at 15 GPa and different temperatures are shown in Fig. 8a.

Elastic properties

The data for sound velocities V_L and V_t obtained from echograms with an accuracy of $\sim 3\%$ are plotted in Fig. 8b. From these data the values of elastic modules, such as the bulk modulus K, the shear modulus G and the Young modulus E were calculated using the data for the mean densities of the samples. The local values of longitudinal and transverse wave velocities and of the mean density increase significantly at $T > 1100$ K in the C_{60} specimens. In C_{70} specimens' elastic parameters have their maximum values at this

temperature. The data for the elastic moduli *versus* temperature of synthesis at a pressure of 15 GPa are presented in Fig. 9. Generally data in this study represent mean values of elastic parameters. However, we observed large sound velocity variations along the scan direction line. Similarly, the radial variation of sound velocity was not symmetric and varied with the angular variation of the scanning line.

Conclusion

A set of fullerene samples was manufactured by high-pressure / high-temperature treatment of solid C_{60} and C_{70} at 15 GPa and 300 – 1820 K. The X-ray diffraction and Raman spectra were studied. At $T \geq$ 670 K, 3D-polymerized structures were realized with both fullerenes. The crystalline state of the samples was retained up to 1120 K. At higher temperatures the long-range order disappeared and the structures became disordered. The samples synthesized from C_{60} at temperatures of 1120 – 1820 K possess unique mechanical properties including the highest value of the longitudinal sound velocity ($V_L = 21 \cdot 10^5$ m s^{-1}) and values of the bulk module ($K \approx 600 - 900$ GPa) substantially higher than the bulk elastic module of diamond ($K \approx 440 - 490$ GPa). At 1820 K graphitization of C_{70} occurred, while C_{60} transforms into a cage nanostructure with a density close to that of diamond. The (pressure/temperature) map of synthesis of new carbon structures from C_{60} and C_{70} fullerenes in toroid-type high-pressure apparatus was extended to 15 GPa.

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