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## Bulk nanostructured carbon phases prepared from C<sub>60</sub>: approaching the ‘ideal’ hardness

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### Abstract

New nanomaterials have been prepared by high-temperature treatment of fullerite C<sub>60</sub> at moderate (0.1–1.5 GPa) pressures attainable for large-volume pressure apparatus. The structure, EELS spectra, Raman spectra, hardness and elastic moduli of these carbon substances have been studied. The materials have a high (90%) elastic recovery, fairly high hardness  $H \sim 10\text{--}15$  GPa and record values of the hardness-to-Young-modulus ratio  $H/E \sim 0.22$ . The observed hardness is close to the ‘ideal’ limit, which is associated with the nanostructure of the materials. This structure represents a combination of interlinked curved fragments of C<sub>60</sub> molecules and nanographite nuclei.

Macroscopic mechanical properties of a material, such as hardness, strength, fracture toughness and others, are determined not only by the inter-atomic interaction and atomic/molecular structure of a substance, but also by the structure of the material at the nano- and meso-scales (see [1, 2] and references therein). As a consequence, the hardness and strength for most substances are dozens of times lower than the possible ‘ideal’ values (the upper limits defined by atomic forces) for ordinary materials and several times lower than those for superhard materials [1, 2]. The ‘ideal’ hardness  $H_{id}$  can be defined as the ratio of load to imprint area in the elastic limit; the hardness-to-Young-modulus ratio for the ‘ideal’ hardness is  $H_{id}/E \sim 0.25\text{--}0.3$  [1–3]. Mechanical characteristics may be improved and brought closer to their ‘ideal’ values in two alternative cases [1, 2]: first, in the case of a defect-free single crystal and, second, in the case of a nanopolycrystal with the grain size of 2–20 nm, where the nucleation and movement of dislocations, as well as other types of defects, are hampered. For example, synthetic impurity-free diamond single crystals [4] and diamond nanopolycrystals [5]

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have the Knoop hardness  $H_k \approx 140$  GPa, which is 1.5 times greater than the values for the majority of diamonds, both ordinary natural and synthetic.

Graphite is a rather soft carbon material ( $H \sim 0.2\text{--}1$  GPa); however, there are bulk hard graphite-type carbon modifications, such as glassy carbon ( $H \approx 2$  GPa,  $H/E \approx 0.07$ ). There are also sputtered or evaporated nanographite or amorphous carbon films featuring the hardness of  $H \sim 5\text{--}30$  GPa and in some record cases up to 40 GPa [6]. For these hard nanographite films, the  $H/E$  ratio is as high as for diamond,  $H/E \approx 0.1$  [6]. Apart from high hardness, hard nanographite films show record high values of the elastic recovery  $\sim 80\text{--}85\%$  [6]. Recently, the method of preparation of bulk hard nanographite phases by high-pressure–high-temperature treatment has been elaborated. These phases are formed from  $C_{60}$  fullerites at  $T > 1000$  K in a wide range of pressures, 2.5–12 GPa [3, 7–11]. The mechanism of the formation of new hard nanographite modifications and peculiarities of their structure are discussed in [11]. The hardness of nanographite phases is 10–40 GPa [7–11]; however, an *in situ* nanoindentation study [8] has revealed that the reliable hardness values in most cases, in fact, are  $\sim 10$  GPa, while the values of the hardness  $\sim 30$  GPa seem to be truly achieved only for the samples with an appreciable portion of diamond-like  $sp^3$  states prepared from  $C_{60}$  at  $P > 8\text{--}9$  GPa.

The possibility of the production of hard carbon materials from  $C_{60}$  fullerites at  $P < 2$  GPa has not been looked into thus far, although it is known that the heating of  $C_{60}$  at ambient pressure leads to the formation of amorphous carbon at  $T > 1200$  K. It should be noted that the breakup of the molecular structure and the formation of hard nanographite phases at  $P > 2$  GPa take place through intermediate polymerized  $C_{60}$ -based modifications, since at  $P < 2$  GPa the destruction of molecules on heating should occur directly in the initial molecular phase  $C_{60}$  [3]. The purpose of the present work is to examine the structure and properties of carbon phases formed from  $C_{60}$  fullerites in an unstudied pressure–temperature area, at moderate pressures from 0.15 to 1.5 GPa and high temperatures from 1000 to 1600 K, and to compare the structure and properties of obtained modifications with the data for hard nanographites prepared at higher pressures from 3 to 12 GPa. The basic result of this study is a synthesis of new carbon nanostructured materials. Although the mechanical properties of these phases deteriorate with synthesis pressure decrease, they still feature quite high values of hardness. Moreover, the new phases demonstrate a record elastic recovery and record values of the hardness-to-Young-modulus ratio among all materials known to date.

The main set of 23 samples of 16 mm in diameter and 7 mm in height was produced in a piston–cylinder high-pressure device at synthesis pressures  $P_s$  from 0.5 to 1.5 GPa and temperatures  $T_s$  from 1100 to 1600 K. Several samples (3 mm in diameter and 2 mm in height) were synthesized at pressures  $P_s \approx 3\text{--}12$  GPa in a toroid-type high-pressure device. Besides, three samples (6 mm in diameter and 5 mm in height) were obtained at  $P_s \approx 0.15\text{--}0.2$  GPa in a gas cell with the use of nitrogen gas pressure. The duration of the temperature treatment under pressure was  $\sim 5\text{--}10$  min. The samples obtained at the same  $P, T$ -conditions possessed the identical structure and properties.

The recovered samples were analysed by powder x-ray diffraction. A Seifert MZ III powder x-ray diffractometer, employing Cu  $K\alpha$  radiation in the Bragg–Brentano geometry, was used. The structure of the samples was also examined by using a JEM 2010HR (JEOL) transmission electron microscope operating at 200 kV. The microstructure of the samples was characterized by bright-field (BF) and high-resolution transmission electron microscopy (HRTEM), as well as by selected area electron diffraction (SAED).

The hardness of the samples was measured independently by means of three different techniques. The Vickers hardness  $H$  was found by using a PMT-3M instrument at 5 N loading. To obtain the correct data on the sizes of an imprint, a thin layer of paint was applied on a polished surface of the sample. Hardness measurements of the sample have also been

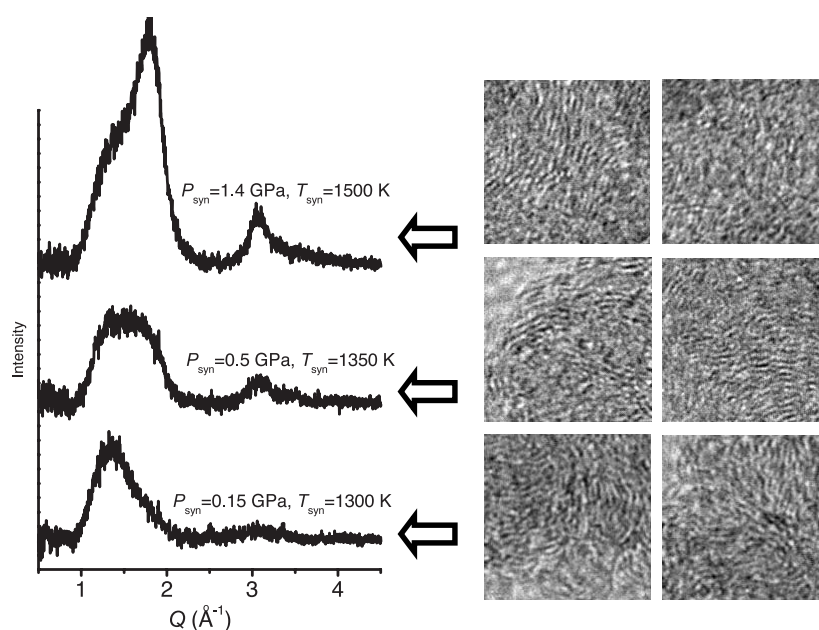
**Table 1.** Synthesis conditions, density, and elastic moduli from ultrasonic measurements, Young modulus from the nanoindentation curves, hardness measured by different techniques,  $H/E$  ratio (where the hardness and Young modulus are averaged from different techniques), and elastic recovery for different nanocarbon phases. Details of the notations are presented in the text. The last row shows absolute uncertainties.

$N$	$P_s$ (GPa)	$T_s$ (K)	$\rho$ (g cm <sup>-3</sup> )	$B$ (GPa)	$G$ (GPa)	$E$ (GPa)	$E^*$ (GPa)	$H$ (GPa)	$H_1$ (GPa)	$H^*$ (GPa)	$H/E$	$R$ (%)
1	0.15	1300	1.6				28	4		3.5	0.13	78
2	0.5	1350	1.75	26	18	44	45	6.5	7	7.5	0.16	83
3	1.1	1300	1.82	35	22	55	57	8.5	7.5	10.2	0.18	88
4	1.2	1400	1.78	35	22	55	59	11.5	12.5	12.8	0.22	92
5	1.4	1500	1.87	42	17	46		6	5.5		0.14	
6	3.5	1400	2.05				77	10.5		11	0.13	79
7	7.0	1150	2.2				115	18		16	0.14	82
$\pm\Delta$	0.05–0.2	30–60	0.05	2	2	3	2	1	1	0.5	0.02	2

performed with a microhardness tester (Duramin-20, Struers) under 1–10 N load ( $H_1$  notation). *In situ* measurements of the hardness ( $H^*$  notation) were carried out using a Nano Indenter–II (MTS Systems, Oak Ridge, TN, USA). It was also used for measuring the Young modulus ( $E^*$ ). The elastic moduli (the bulk ( $B$ ), shear ( $G$ ), and Young ( $E$ ) moduli) were independently found through ultrasonic measurements of the transverse and longitudinal velocities in a 5–10 MHz frequency range.

The density of the samples  $\rho$  was measured by the bottle method. The electron energy loss spectra (EELS) of the B-K and C-K edges were detected with a GIF2000 (Gatan) parallel electron energy-loss spectrometer. The Raman scattering measurements were performed at 300 K using a Dilor XY system with a 514.5 nm Ar<sup>+</sup> ion laser as an excitation light. In addition, the temperature dependences of the electrical resistance of the synthesized carbon modifications were measured.

The samples of carbon phases synthesized at pressures ranging from 0.15 to 1.5 GPa have quite low density, varying between 1.6 and 1.9 g cm<sup>-3</sup>, while for the synthesis pressures from 3 to 12 GPa the density lies in the range from 2 to 2.8 g cm<sup>-3</sup> (table 1). The selected typical structural data for the nanocarbon phases are presented in figure 1. One of the main results of the present study is the observation that the structure of the samples obtained at moderate pressures is noticeably different from that of nanographite phases prepared at high pressures  $P_s > 3$  GPa. The main maximum of the structure factor of carbon phases obtained at low pressures corresponds to the wavevector values  $Q \approx 1.3 \text{ \AA}^{-1}$ , which is far from the main graphite peak ( $\approx 1.87 \text{ \AA}^{-1}$ ) and fairly close to the (220) line of molecular C<sub>60</sub> ( $\approx 1.25 \text{ \AA}^{-1}$ ), determined by the distances between the centres of the C<sub>60</sub> molecules,  $d = 4\pi/Q_{(220)} \approx 10 \text{ \AA}$ . At the treatment temperature exceeding 1300 K, an additional maximum, along with the first one, appears at  $Q \approx 1.8 \text{ \AA}^{-1}$ , which can be clearly associated with expanded graphite. The intensity of the maximum at  $Q \approx 1.8 \text{ \AA}^{-1}$  increases with the rise of the treatment temperature, while the peak intensity at  $Q \approx 1.3 \text{ \AA}^{-1}$  decreases. If the treatment pressure exceeds 3 GPa, the main peak of the structural factor corresponds to nanocrystalline graphite ( $Q \approx 1.85\text{--}1.9 \text{ \AA}^{-1}$ ), and the weak halo at  $Q \approx 1.3 \text{ \AA}^{-1}$  is only observed in a narrow range of the synthesis temperatures from 1100 to 1200 K. The TEM pictures of the samples (see figure 1) confirm the x-ray diffraction evidence that the structure of the nanocarbon modifications prepared at moderate pressures and temperatures  $T \approx 1300$  K incorporates interlinked curved molecular fragments, while at  $T \approx 1500$  K the material is mainly composed of graphite nanograins,

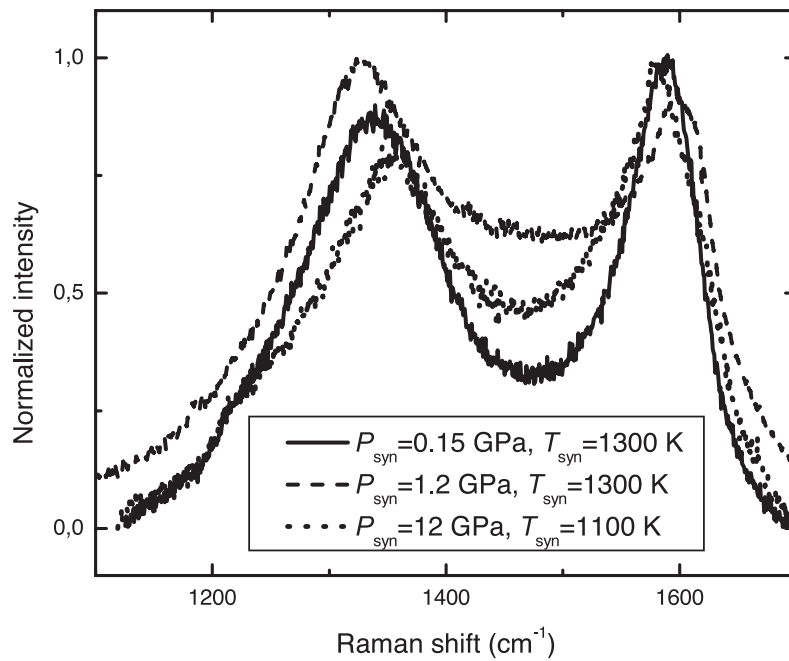


**Figure 1.** X-ray diffraction patterns from samples synthesized at different  $P$ – $T$  conditions together with the corresponding TEM images. The size of images corresponds to 10 nm.

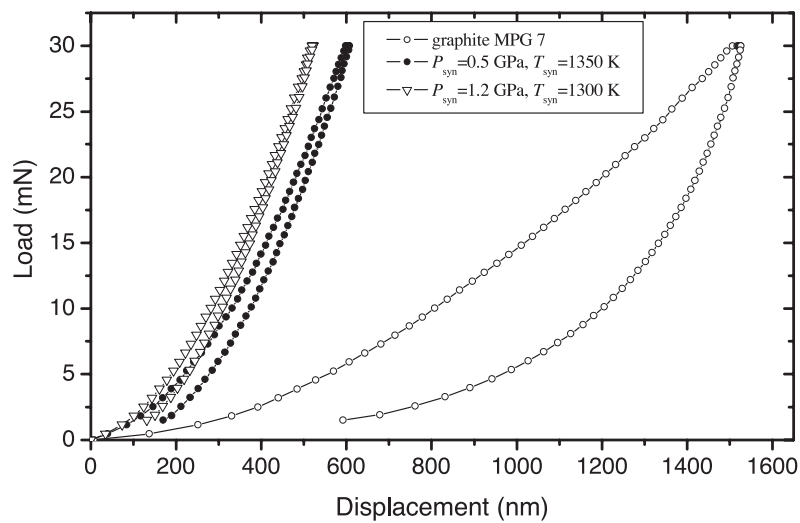
although the atomic planes also show some curvature. The EELS spectra for the new carbon modifications are slightly different from those for graphite and pristine fullerite [12], but still confirm an  $sp^2$  nature of the material.

The Raman spectra (figure 2) are similar to those for disordered graphites and amorphous  $sp^2$ -based carbon modifications. Aside from the weak maxima near  $450$  and  $800 \text{ cm}^{-1}$ , all the spectra show two main maxima with the peak positions at  $1330$ – $1350$  and  $1580$ – $1605 \text{ cm}^{-1}$ . The given maxima are usually interpreted as the D and G bands of disordered graphite [7–9]. Note that the D band, as a rule, is located at  $1350$ – $1360 \text{ cm}^{-1}$ , and the G band at  $1580$ – $1590 \text{ cm}^{-1}$ , that is, the positions of the D and G bands in our experiments are slightly shifted. The lower the synthesis pressure, the higher the frequencies of the corresponding peaks in spite of the lower density of the samples. All features of the Raman spectra correspond to disordered graphitic materials [13].

The results on the hardness and elastic moduli for several typical samples are presented in table 1. The samples obtained at moderate pressures  $P_s$  have sufficiently high hardness values  $H \sim 5$ – $15 \text{ GPa}$  and record high  $H/E$  ratio values  $\approx 0.18$ – $0.22$ , as well as record high values of the elastic recovery,  $\approx 85$ – $92\%$  (figure 3). It should be mentioned that for the nanographite modifications prepared at high pressure ( $3$ – $12 \text{ GPa}$ ) the  $H/E$  ratio is around  $0.11$ – $0.14$  (table 1). The data on the hardness and elastic moduli, obtained through various techniques, are in good agreement (table 1). It should be mentioned that the properties did not change throughout a 1 year treatment at normal conditions. Let us note that the nanocarbon samples having the hardness values  $H > 8 \text{ GPa}$  can easily scratch a tungsten carbide hard alloy with the hardness  $H \approx 15 \text{ GPa}$ , the capability attributable to the high elastic recovery of the new phases. The values of the elastic moduli for the hard carbon phases produced at moderate pressures exceed those for graphite despite the lower density, although being below those for carbon modifications obtained at high pressures  $P_s > 3 \text{ GPa}$ . Thus, the synthesis of



**Figure 2.** Typical Raman spectra for nanocarbon modifications prepared at low, moderate and high pressures.



**Figure 3.** Nanoindentation curves for new nanocarbon modifications compared with that for ordinary high-quality dense graphite.

nanocarbon modifications at moderate pressures in a narrow temperature region around 1400 K permits a possibility to prepare a carbon material with hardness and elastic recovery close to their ‘ideal’ levels.

The compression strength of the obtained samples is not very high  $\sim 0.2\text{--}0.3$  GPa but is still higher than the strength of an ordinary bulk glassy carbon ( $\sim 0.1$  GPa). The samples

demonstrate rather brittle behaviour when being compressed elastically before the destruction onset. A relatively low value of the strength-to-Young-modulus ratio ( $\sim 0.005$ ) is similar to that for diamond and originates from the appearance of microcracks.

The conductivity of the new nanocarbon modifications is 10–100 times lower than that for graphite, and it decreases 10–100-fold with temperature lowering from 300 to 4.2 K.

The closeness of the hardness to the ‘ideal’ level and the record elastic recovery values of the samples under study are evidently related to the peculiarities of their structure at the nanometre scale. This structure, being in some respects similar to the structure of schwarzite-1248 and amorphous schwarzite [14, 15], combines the inter-linked curved parts of the  $C_{60}$  molecules and graphite nuclei that grow and absorb the curved parts at heating. The randomness of the structure and the lack of ‘soft’ directions ensure quite high values of the elastic moduli (1.5–2 times higher than those for graphite), in spite of the lower density. The difficulty of an inter-grain sliding in the given structure, heterogeneous at the nanoscales, causes the hardness to rise. The record elastic recovery can be explained in the framework of a ‘squeezed chicken wire’ model [6]. In a  $C_{60}$  molecule, the bonds between carbon atoms, as distinct from graphite, are disparate, as there are both single and double ones. After the breakup of a molecular structure, a considerable portion of the double bonds is obviously retained in nanocarbon phases, which leads to a slight increase in the Raman G-band frequencies. The EELS spectra indirectly testify to the existence of the double bonds in a new nanocarbon structure.

At  $P > 2$  GPa the graphitization of a polymer  $C_{60}$  phase at heating is an easier process than the graphitization of a molecular  $C_{60}$  in the pressure range 0.15–1.5 GPa. This is due to the fact that the density of polymer  $C_{60}$  phases at 2–10 GPa and  $T \sim 1000$  K is close to that for graphite, which facilitates an easy formation and growth of the nucleation centres. Some of the carbon atoms ( $\sim 10$ –20%) in polymer phases are in the  $sp^3$  four-coordinated states; after the destruction of molecules these atoms can serve as stress relaxation centres at the boundaries of the graphite nuclei being formed. At moderate pressures, 0.15–1.5 GPa, a molecular  $C_{60}$  has a considerably lower density than graphite, and, after the destruction of molecules, it transforms into a disordered carbon state consisting of curved molecular fragments. Graphite nucleation begins only after significant overheating as a diffusion driven nanorecrystallization. As a result, a wide pressure–temperature region appears, in which a new nanomaterial, representing a nanomixture of nanographite nuclei and curved molecular fragments, emerges. At a ratio of the nanographite atoms to molecular fragments around 3:1 (sample number 4) one can achieve rather high elastic recovery and hardness. It would be very interesting to study in future the structural details of this nanomixed state and to define more definitely the  $P, T$ -region of the formation of the material with the optimal characteristics.

Minimal pressures of the synthesis of hard nanocarbon phases  $P_s \approx 0.15$  GPa employed in this work are dictated by the necessity to compact a pristine  $C_{60}$  powder. If one has large  $C_{60}$  fullerite single crystals, it seems possible to produce hard carbon nanostructured phases by heating the samples at ambient pressure. Moderate values of pressure,  $\sim 1$  GPa, required to obtain nanostructured carbon with the hardness  $\sim 10$ –15 GPa and elastic recovery  $\sim 90\%$  enable synthesizing samples of an optional shape dozens of centimetres in size, which is promising for industrial applications of these new materials.

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