High Pressure Synthesis, Structure, Physical and Mechanical Properties of C₆₀ Fullerite Superhard and Ultrahard Phases

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New data on the synthesis conditions, structure and physical properties of the superhard and ultrahard samples created from solid C₆₀ by static high-pressure high-temperature treatment in the range of 9.5-13 GPa ; 600 -2100 K are represented. Measured velocities of the compressional sound waves in the ultrahard fullerites exceed the highest values for diamond. Bulk elastic modulus for the hardest fullerite samples more than twice exceeds that of diamond. Ultrahard fullerite tip is applied for measurements of hardness of diamond and fullerites. Maximum hardness of fullerite is measured to be 310±40 GPa.

[solid C₆₀, ultrahard fullerite, elastic constants, hardness, diamond]

1. Introduction

Since the first predictions of extreme bulk elastic modulus for the C₆₀ fullerite under high pressure [1,2] a set of investigations were performed in the diamond anvil cells to probe the stability limit of the C₆₀ molecule and a new carbon states were obtained with the hardness close to the hardness of diamond and even exceeding it [3-7]. At room temperature only a pressure of about 18 GPa was sufficient to create hard metastable states, thus the dimensions of the obtained samples were very small. In order to increase the volume of the quenched samples the other types of static high pressure apparatus attached with hard-alloy anvils were used and combined high-pressure high-temperature treatment was applied. Under p = 3 GPa and T = 700°C a disordered carbon state was obtained with the hardness of 4000 kg/mm² (about 40 GPa) [8]. Increase of pressure to 9.5 - 12.5 GPa allowed us to obtain first bulk samples of new quenched fullerite states with the hardness exceeding that of cubic BN and (100) face of diamond [9,10]. Under the highest attained pressure level of 13 GPa an ultrahard fullerite states were obtained with the hardness higher than that of the hardest (111) face of diamond [11,12]. Use of the shock-compression apparatus with the pressure of about 55 GPa and temperatures higher than 2000 K allowed to obtain very hard micropowder of amorphous diamond [13] or so-called "new amorphous diamond" [14].

By means of X-ray diffraction, Raman scattering and electron microscopy we have studied the structure of the superhard and ultrahard fullerite samples and found the differences to the known carbon forms and C₆₀ fullerite phases [10,11,15,16]. The structure of these materials is represented by 3 main groups: crystal structures, amorphous structures on the basis of sp²-linked C₆₀ molecules and the cage nanostructures of the random sp³-linked carbon networks. A diagram of p-T regions for the synthesis of these states was presented in [11,12] and some physical properties of the obtained materials were described. In this study we present a refined and extended diagram of synthesis of different quenched states and new data about the hardness, sound waves velocities and elastic constants of ultrahard fullerites.

2. Samples

Pure fcc fullerite (C₆₀: 99.98%, C₇₀:0.01%) was used for the

synthesis. Powder was stored in a sealed tubes. Some samples were prepared for the synthesis on the air and the other group of the samples was prepared in a dry argon atmosphere. The toroid-type high-pressure apparatus is used for the synthesis under pressure of up to 13 GPa and temperature up to 2100 K. 13 GPa pressure was calibrated by the known phase transition in lead. The dimensions of the produced samples were about Ø3.5 × 3 mm³. New crystal structures of distorted body-centred cubic type and transient to graphite and diamond states are revealed in the synthesized samples. Transformations of the solid C₆₀ to graphite and diamond were also observed under high pressure and elevated temperatures. The p-T regions for the synthesis of these states at 1 min. heating are presented in the Figure 1.

Fig. 1. p-T regions for the synthesis of quenched C₆₀-phases and the other carbon forms.

Symbols in the Figure 1 denote some of the p-T coordinates where experiments have been carried and the structure of the quenched samples were studied. The bold dashed curve at 9-16 GPa divides semimetal and semiconductor states at T > 1100 K and "soft" and "hard" states at T < 1100 K. Very hard disordered molecular crystal states are distinguished by the

peculiar x-ray and TEM diffraction patterns. A diffuse (002) ring corresponding to a lattice spacing of 3.14- 3.3 Å is divided into four intense arcs [10,11,16]. The basic elements of this structure seem to be tetrahedrons consisting of four sp^3 -linked molecules.

Disordered cross-linked layered structures are characterised by a diffuse (002) and joint (100) ; (101) rings, but the peak of interlayer distances corresponds to 3.14- 3.3 Å that is less than that of crystalline and disordered graphite. These structures are very hard: 40-70 GPa, thus we assume that these layers are strongly cross-linked.

Temperature dependencies of densities of the samples treated at different values of pressure are presented in Figure 2. Density of the samples was measured by flotation method using a mixtures of diiodomethane and acetone liquids of different concentrations.

Fig. 2. Density of quenched samples as a function of treatment temperature T for four different treatment pressures.

3. Elastic properties

Elastic constants of different superhard and ultrahard fullerites were calculated after measurements of the sound waves velocities by means of acoustic microscopy at the Center of Acoustic Microscopy of RAS, Moscow. The ultra-short pulse wide-field scanning acoustic microscope WFPAM was applied in reflection mode. Operation frequency of the microscope is 25 - 100 MHz, probe pulse duration 50 ns, aperture of the acoustic lenses was 30- 60°. At 30 MHz operating mode and water as an immerse media a diameter of the spot of the acoustic beam on the surface of the sample was about 0.1 mm. After polishing the thickness of the samples with plane-parallel reflecting surfaces was 1.5 - 2 mm. The time delay interval (flight-time) between probe and reflected impulse was in the range 10 -20 μ s depending on the type of wave (longitudinal or shear) and thickness of a particular sample. Knowing the thickness of the sample, type of wave and flight-time, the acoustic wave velocities were calculated. After that, neglecting the nonlinear effects, linear elastic modulus were calculated on the basis of the measured velocities and densities of the samples. The results of measurements and calculations for ultrahard

samples obtained at 13 GPa pressure and different temperatures are represented in the Table 1.

Table 1. Density of the samples ρ , velocities of the longitudinal c_l and transverse c_t acoustic waves, shear modulus G , bulk modulus K , Young's modulus E and Poisson's ratio ν as a function of temperature of the synthesis T of the fullerite samples under pressure of 13 GPa. Asterisks note that the samples were prepared for the synthesis in a dry argon atmosphere. Other samples were prepared on the air.

T / K	$\rho /$ g/cm	$c_l /$ km/s	$c_t /$ km/s	$G /$ GPa	$K /$ GPa	$E /$ GPa	ν
1500	3.15	17.0	8.0	200	640	550	0.36
1670;*	3.1	16.2	7.4	170	590	460	0.37
1770	3.3	20.2	8.5	240	1030	660	0.39
1870;*	3.15	22.3	7.0	155	1360	450	0.45
diam.	3.51	17.5-	11.6-	354-	550	1040	0.08
		19.6	12.8	535			

Values of velocities are averaged over 3-4 different points for each sample. The accuracy of measurements is ± 0.1 km/s. Values for monocrystal diamond are represented for comparison.

4. Hardness

The measurements of hardness of the fullerite samples have been a problem because it is comparable with the hardness of the diamond indenter and even exceeds it [7,9-12]. We have used the criterion of plastic deformation of the tested specimen in the indentation point to show that the hardness of ultrahard fullerites is higher than that of diamond. Even the hardest (111) face of diamond was deformed plastically at room temperature by the sharp edge of an ultrahard fullerite sample (Fig. 3), while indentation of this surface by a diamond indenter caused a brittle cracking (Fig. 4).

Fig. 3. Indentation made by ultrahard fullerite on the (111) face of diamond.

Fig. 4. Indentation made by diamond (motion of indenter from left to right) on the (111) face of diamond.

These pictures were obtained by use of "NanoScan" (NS) measurement system based upon the principle of the atomic force microscope [17,18]. This NS system was specially designed to carry out hardness tests by sclerometric method together with the study of the surfaces of solids. Both a diamond and an ultrahard fullerite tips were used as a microindenter, however the ultrahard fullerite tips were 5-10 times more durable than the diamond tips.

Sclerometric method of tests was preferred because it does not imply a standard shape of the indenter. According to this method the hardness value H is calculated as $H = kF/b^2$, where k is a coefficient of the tip shape, F is the indenter load and b is the scratch width. It is known, that the sclerometric tests provides the same Vickers hardness as the indentation method [19]. Hardness of the different fullerite samples, cubic BN and diamond were measured at constant value of k/b^2 after calibration by the hard solids with known hardness like as sapphire, topaz, etc. More detailed description of these measurements is presented in [17]. The results of measurements are presented in Fig. 5.

Fig. 5. Hardness of fullerite samples treated at pressures of 9.5 and 13 GPa as a function of temperature of synthesis.

Conclusion

This study confirms our earlier estimations [12] of the hardness of ultrahard fullerites 200-300 GPa. Ultrahard fullerite deforms plastically the hardest face (111) of diamond at room temperature. Direct measurements of the hardness of diamond by sclerometric method were carried out. We discovered at first time that the velocity of the compressional sound wave in ultrahard fullerites is higher than that in diamond and the bulk elastic modulus of ultrahard fullerites is essentially higher than that for diamond and all the other solids.

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