Size-dependent phase transition of diamond to graphite under high pressures and temperatures

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Size-dependent phase transition of diamond to graphite was detected by studies of pressure-temperature-induced transformations of diamond nanosized particles and characterization of the products by X-ray diffraction, Raman spectroscopy, scanning and transmission electron microscopy.

Studies of the effects of pressure and temperature on the size of diamond nanoparticles have shown that the increase of treatment temperature at 8 GPa from 873 to 1573 K results in a gradual enlargement of diamond nanoparticles from the initial mean size of 4.5 nm to 10.2 nm. At 1573 K, when the mean size of diamond nanoparticles reaches 10.2 nm, the system undergoes diamond-to-graphite phase transition. Taking into account the p,T-parameters of this transition, 8 GPa and 1573 K, it is obvious that the observed phase transition occurs in the region of thermodynamic stability of the bulk macroscale diamond. Based on the mean size of diamond nanoparticles – treatment temperature relationship and using the Arrenius equation, the activation energy for the diamond solid phase growth at 8 GPa in the nanoscale size range was calculated to be 112 ± 8 kJ/mol.

The mechanism of solid phase growth of diamond nanoparticles at high pressures and temperatures has been proposed in this work. Possible effect of the size-dependent phase transition of diamond to graphite on the processes of bulk diamond synthesis and creation of superhard composites on the basis of diamond nanoparticles is also discussed. In particular, in light of the discovered existence of size-dependent diamond-to-graphite phase transition under pressure the problem of formation of critical seeds for growth of macroscale diamond crystals has received a new clarification.

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Electrotransport properties of novel polymerized phases of C₆₀

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Recently it was found [1] that the polymerization of carbon phases leads to hopping transport with a number of peculiarities which can not be understood in the framework of conventional Mott-Shklovskii-Efros theory of electron mobility in disordered media. This includes a crossover between various Mott laws with different exponents and discrepancies between the temperature dependency of low-field magnetoresistance coefficient and the theoretically predicted one.

The electronic transport of polymerized phases of C_{60} obtained under high pressure was thoroughly studied but the whole picture is controversial and far from being complete [2]. It was observed that a small variation in the synthesis condition lead to drastic changes in the charge transfer causing the transition from insulating state to either Mott-like law or critical behaviour (σ -*const*+ \sqrt{T}). It was also reported that the polymerized phases C_{60} exhibit quite uncommon negative magneto-resistance as well as the positive one which is observed in other carbon phases such as carbynes and fullerenes' mixtures.

The synthesis of new C_{60} phases under relatively small pressures P≤1 GPa [3] provides an interesting model object which has unusual mechanical and electrical properties. We found that these phases are in the critical region in the vicinity of the metal-insulator transition. The synthesis conditions were controllable enough to enable us to study the influence of synthesis conditions on structural properties of the obtained phases and theirs electro- and magnetotransport coefficients.

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Shock-induced phase transitions of C₇₀ fullerite

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Shock-induced phase transitions of C_{70} fullerite were studied with use of recovery assemblies of planar geometry. Two types of starting material were investigated: polyphase material consisting of a phases with hexagonal close-packed (hcp) and with rhombohedral structures [1] and monophase C_{70} fullerite with hcp-structure. In the specimens, maximal shock pressures were reached after several reverberations of the waves between the steel walls of the recovery ampoule and were 8, 9, 14, 19, 23.5, 26, 36 and 52 GPa. With the purpose of examination of influence of a temperature schedule of shock compression on characteristics of phase transitions, experiments with thin (20 microns) specimens in massive copper plates were executed for low (up to 19 GPa) pressures. Microstructure of the material, recovered after shock-wave loading, was examined by means of X-ray diffractometry.

We have found that the results of a shock-wave compression of fullerite C_{70} with a various initial phase composition qualitatively coincide in all explored pressure range. Rhombohedral modification of fullerite C_{70} completely disappears already at pressure 9 GPa. At the same time, crystalline modification of fullerite C₇₀ with hcp-structure in conditions of step-like shock-wave compression does not undergo phase changes down to pressure 9 GPa and practically completely disappears from the recovered material only at pressure 23.5 GPa. Shock-induced transformation of hcp into fcc structure was fixed at pressures in the range 9 to 23.5 GPa. Depth of this transformation is increasing with growth of shock pressure. In the specimens recovered from 23.5 GPa, the only crystalline phase of fullerite C_{70} with fcc structure is observed (about 5 %) and for the first time formation of a graphite-like carbon is fixed (about 95 %). Influence of a temperature schedule of a shock compression on phase changes in conditions of our experiments is not so great - as a rule a discrepancy of phase compositions of "thin" and "massive" recovered specimens of C₇₀ did not exceed 3 %. With growth of shock pressure up to 26 GPa and higher (up to 52 GPa), destruction of C_{70} molecules occurs. This destruction is accompanying with a formation of graphite-like carbon.

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New pentafluoroethyl derivatives of [60]fullerene, three isomers of $C_{60}(C_2F_5)_{10}$

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While a large number of trifluoromethyl derivatives of fullerenes was synthesized and structurally characterized, higher perfluoroalkylated fullerenes were scarcely investigated. There are some reports concerning the preparation of pentafluoroehtyl and undecafluorohexyl derivatives of [60]fullerene [1, 2]. Two hexakis-, six octakix-, and two decakis(pentafluoroehtyl) [60]fullerenes have been structurally investigated already [2,3]. Herein we report the synthesis, isolation, and X-ray crystallographic characterization of three new isomers of $C_{60}(C_2F_5)_{10}$.

A mixture of pentafluoroehtyl [60]fullerenes was synthesized by reaction of C₆₀ with C₂F₅I carried out in sealed glass ampoules at ca. 380°C. MALDI mass spectrometric analysis showed the presence of $C_{60}(C_2F_5)_n$ compounds with n = 8 and 10. The mixture was solved in hexane and subjected to separation by means of High Performance Liquid Chromatography (HPLC) using a Buckyprep column and hexane as an eluent. The HPLC fractions eluted at 3.35, 5.06, and 5.40 min were collected and slowly concentrated to give deepbrown colored crystals. X-ray single crystal diffraction study revealed the structure of three isomers, 1,6,11,16,18,24,27,36,54,60-, 1,6,11,16,18,26,36,41,44,57-, and $1,6,11,16,18,28,31,36,43,55-C_{60}(C_2F_5)_{10}$ Addition patterns of these isomers can be also described as chains of edgesharing para or meta $C_6(C_2F_5)_2$ hexagons: $[p^3(mp)^2p^2]$, $[p(mp)^4]$, and $[p(mp)^3,p]$ respectively. The addition patterns of the new isomers are compared with those of the known $C_{60}(C_2F_5)_{10}$ isomers [3] and the previously reported $C_{60}(C_2F_5)_8$ isomers as possible precursors [2, 3]. Relative energy of the five so far known $C_{60}(C_2F_5)_{10}$ isomers was calculated by the DFT method.

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Ultrasonic study of fullerite C₆₀ under pressure

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Fullerite C_{60} is an archetype among all-carbon molecular solids bonding by the van der Waals forces. The knowledge of elastic constants is crucial to verify and develop force potentials for interaction between C_{60} clusters. Nevertheless, there is a lack of information on shear modulus of C_{60} under pressure, whereas the data on bulk modulus are contradictory [1]. In this respect the ultrasonic technique is a powerful method to study elastic properties under pressure.

Here we present the ultrasonic study of elastic moduli of polycrystalline fullerite C_{60} in the temperature range from liquid nitrogen to room conditions at pressures up to 1.4 GPa, including areas of the fcc-to-sc and glass orientational transitions. The combination of the ultrasonic study with the direct density measurements provides reliable identification of the phase transitions. The temperature dependences of elastic moduli at ambient pressure are in good accordance with previous studies. For the first time we have determined the pressure dependences of shear modulus and Poisson's ratio. Particularly, the Poisson's ratio was found to increase from ? 0.3 at ambient pressures to ? 0.38 at P= 1 GPa. The observed high values of the Poisson's ratio, as well as the high values of pressure derivatives of bulk modulus B'_p? 25–27, are discussed in terms of the central intermolecular potential and contribution of the non-central forces due to a molecular deformations.

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