Three-Dimensional Polymerization of Fullerite C₆₀ under High Pressure

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We have studied the 3D polymerization of fullerite C₆₀ under high pressure by x-ray diffraction, Raman spectroscopy, measurements of hardness, and annealing experiments. For the first stage of this gradual transformation we have proposed the model, in which the 3D polymers may involve both bonding characters of van der Waals and covalent intermolecular bonds. The pressure of the crossover between 2D and 3D polymerization was estimated near 8 GPa. [fullerite C₆₀, high pressure, polymerization, rigidity percolation, carbon networks]

I. Introduction

Variation of external pressure and temperature leads to different structural transformations in fullerite C₆₀, such as orientational transitions, polymerization, and molecular collapse to amorphous or ordinary microcrystalline carbon phases (see references in [1]). The one- or two-dimensional (1D or 2D) polymerization has been observed under pressures $P \leq 8$ GPa [2–4], and several new polymorphic forms of solid C₆₀ have been synthesized upon heating in this pressure region. The polymerization of fullerite is associated with the formation of covalent sp^3 bonds between molecules via the [2+2] cycloaddition [6]. The polymer phases may be reverted to pristine C₆₀ by heating at ambient pressure [2,3], and hence may be treated as metastable phases of the molecular fullerite crystal.

At higher pressures $P > 8$ GPa the three-dimensional (3D) polymerization was observed [7,8], but the mechanism of such type transformations is not well studied now. We have synthesized a set of crystalline phases, corresponding to different stages of the 3D polymerization, by heating C₆₀ to different temperatures under pressures 8.3, 9.0, and 12.5 GPa with the subsequent quenching to ambient conditions. The detailed study of x-ray diffraction, Raman spectra, thermal stability, and hardness of 3D fullerite polymers has allowed us to propose the model of 3D polymerization.

II. Experimental

The samples were synthesized from fullerite powder produced at Russian Scientific Center “Kurchatov Institute”, with the C₆₀ content not less than 99.9 % and 50–100 μm crystalline grains. A new version of the “toroid” chamber was used for high pressure – high temperature generation (up to 13 GPa in the temperature range 300–2000 K) in a large volume (up to 30 mm^3). The samples were placed into the Pd or Pt cells and heated by passing electric current through the outer graphite container. The density of samples was determined by the Arkhimed method. The structure of samples was investigated by conventional x-ray diffraction (Cu K α). Raman measurements were performed at 300 K using the Jobin-Yvon T64000 triple grating spectrometer with the nitrogen-cooled multichannel CCD detector. The 514.5 nm line of Ar⁺ laser was used for excitation. All the Raman spectra presented here were independent of the excitation intensity, which was typically within the range 0.1–15 mW. The Raman spectra

were taken in the true backscattering configuration with incident and scattered polarizations orthogonal to each other. The hardness was investigated by means of indenting the diamond Vickers pyramids under the loads 1.96 and 5.5 N. The thermal stability was studied using the derivative thermogravimetric apparatus Derivatograph-C (Hungary), the heating rate being 20 K/min.

III. Results and Discussion

The typical x-ray diffraction patterns for C₆₀ samples, obtained after high-pressure-high-temperature treatment, are presented in Fig. 1. The structure of all crystalline phases prepared at 9.0 and 12.5 GPa was identified as fcc. The samples prepared at 8.3 GPa was partially 2D polymerized, but they were also considered as fcc. The lattice parameter a was found to decrease with increasing synthesis temperature T_{syn} . The calculated crystallographic densities are in good agreement with the direct measurements. The identification by 3–5 lines can be hardly considered to be reliable, so the structure of crystalline phases obtained may in fact deviate slightly from the fcc symmetry. Still, the features of the mutual location of molecules and intermolecular distances must be practically the same. We do not exclude the presence of 2D polymerized phases for the samples prepared at $P = 8.3$ GPa.

The calculated and measured intensities of (111), (200), and (220) reflections are compared in Fig. 2. The calculations were made in the uniform sphere approximation for the molecular factor $F_{\text{mol}} \propto \sin(QR)/QR$, where Q is the scattering wave vector and R is the radius of fullerene molecule ($R = 3.5$ Å). The theoretical and experimental intensities are in satisfactory agreement for the phases with the lattice parameter $a \geq 12.3$ Å, when C₆₀ molecules can be regarded as structure-forming units. The samples with $a < 12.3$ Å revealed an essential distortion of the sphere-like C₆₀ molecules in accordance with a high degree of disorder in the corresponding x-ray diffraction patterns (Fig. 1). Thus, the 3D polymerization may be conditionally divided into two stages.

The Raman spectra for pristine C₆₀ and some polymerized phases are presented in Fig. 3. The Raman spectra of slightly polymerized C₆₀ phase ($a = 13.5$ Å) revealed clearly the narrow lines corresponding to the fullerene modes. Apart from the narrow lines, the broad bands (1100–1600 cm^{-1} and 250–600 cm^{-1}) are seen in this Raman spectrum. The samples with a higher polymerization degree ($a < 13$ Å) have broad bands (200–

800 and 1200-1700 cm^{-1}) in their Raman spectra, which are rather typical for amorphous phases, although the x-ray diffraction patterns of these samples definitely reveal their crystalline nature (Fig. 1).

Fig. 1. X-ray diffraction patterns for the initial fullerite and for the samples obtained by heating C_{60} up to different temperatures T_{syn} under pressure 12.5 GPa followed by quenching. The similar fcc reflections are marked by identical symbols.

Fig. 2. Calculated dependences (lines) and experimental data (symbols) for relative intensities of the (111) (solid line and triangles), (200) (dashed line and circles), and (220) (dashed and dotted line and stars) fcc reflections vs lattice parameter.

The dependence of the lattice parameter on the synthesis temperature has a quasicontinuous character for the fcc 3D-polymerized fullerite phases (Fig. 4) in accordance with the published data [2,7,8]. It is natural to suppose the possible existence of fcc polymers with any lattice parameter within the range from 14.17 Å (pristine C_{60}) to ~ 11.6 Å (the strongly-polymerized phases obtained in the current study).

We propose a model for the 3D polymerization. The model considers the lattice parameter of fcc phases as a continuous function of the share of covalently bonded molecular pairs, which is obtained by the averaging over a lattice with disorder in the bond type between molecules and bond length. The 3D-

polymerized fullerite crystal may involve both bonding characters of the van der Waals interaction and covalent intermolecular bond. Analogous to the Vegard's law for solid solutions the lattice parameter of a partially-polymerized phase can be linearly approximated as a function of the proportion of polymerized molecular pairs n_p :

$$a = a_0 + (a_p - a_0) n_p, \quad (1)$$

where a_0 and a_p are the lattice parameters of pristine C_{60} and the completely-polymerized phase with spherical C_{60} units respectively. The previous analysis of x-ray diffraction intensities gives fairly good estimation $a_p \approx 12.3$ Å. This parameter corresponds to the intermolecular distance 8.7 Å which is very close to the sum of the C_{60} molecule diameter (≈ 7 Å) and the bond length between sp^3 carbon atoms (1.54 Å in diamond and ≈ 1.6 Å between polymerized fullerene molecules), and we will use this estimation.

Fig. 3. Raman spectra for 3D-polymerized fcc phases with different lattice parameters prepared from C_{60} under pressure 12.5 GPa.

Fig. 4. Lattice parameter vs synthesis temperature dependences for 3D-polymerized phases prepared under different pressures (diamonds correspond to 8.3 GPa; squares-9 GPa; circles-12.5 GPa). The dashed lines are guides for the eyes.

Static fluctuations in the positions of molecules should be evidently maximum at the intermediate concentrations of van der Waals and covalent intermolecular bonds similarly to substitutional solid solutions. Indeed, the maximum width of x-ray crystalline peaks is observed, when the lattice parameter corresponds to $a \sim 13$ Å or $n_p \sim 0.5$ [see Fig. 5 (a) and Eq. (1)].

Fig. 5. Widths at half height for the (220) reflection (a) and hardness (squares correspond to 9 GPa; circles -12.5 GPa) (b) of 3D polymerized samples as a function of the lattice parameter.

Covalent bonds are much more rigid than the van der Waals bonds. In the framework of the model proposed the mechanical characteristics of 3D-polymerized fullerite phases may be considered in terms of rigidity percolation [10]. If the lattice parameter of fcc polymer is close to that of pristine fullerite, the proportion of polymerized pairs is small, according to Eq. (1), so just a few clusters would be covalently bonded. The phases with $a \rightarrow a_0$ would be as soft as pristine fullerite itself and cannot be treated rigorously as 3D-polymerized phases. For $a \rightarrow a_p$, we, in fact, deal with a rigid covalent network. Experimental data for hardness completely support this approach [Fig. 5 (b)]. We have found that the lattice parameter value ≈ 13.7 Å is the threshold for formation of rigid 3D polymers of fullerite. Practically the same value may be predicted theoretically. The 3D network of covalently bonded atoms becomes rigid, when the average coordination number reaches or exceeds the value $Z_c = 2.4$ [10]. The average coordination number of covalently bonded pairs of C_{60} molecules Z_p would be defined by their share n_p as $Z_p = n_p Z$, where $Z = 12$ is the coordination number of fcc lattice. Assuming the threshold intermolecular coordination number responsible for the appearance of hardness and elasticity in a system of covalently bonded C_{60} molecules to be $Z_c = 2.4$, we obtain the threshold concentration $n_c = 0.2$ and the corresponding lattice period $a_c \approx 13.8$ Å.

We suppose that the first stage of 3D polymerization ($a \geq a_p = 12.3$ Å) occurs via the [2+2] cycloaddition mechanism, which is much more favorable energetically [9]. This means that in the completely polymerized phase ($a = a_p$) the share of sp^3 atomic sites is equal to $2Z/60$, i.e. 40 %. The hardness growth for the phases with $a < a_p$ [Fig. 5 (b)] is probably connected with the further increase of the number of covalent bonds between molecules due to their deformation and partial destruction. The distortion of C_{60} molecules in the fcc phases with $a < a_p$ is caused by the strong repulsion between covalently bonded atoms of adjacent molecules. So, probably the polymerization mechanisms other than the [2+2] cycloaddition, for example, the formation of 4 bonds between molecules [9], become prevalent. The broad amorphous peaks at $Q \approx 3$ and 5.5

Å⁻¹ visible in the x-ray diffraction patterns of polymerized phases (Fig. 1) correspond to the significant amount of sp^3 sites. The detailed discussion of the polymerization mechanism for the second stage will be presented elsewhere [11].

Isochronous annealing of the samples up to 500 °C revealed substantial differences in the thermal stability of fcc phases with different lattice parameters. The sample with $a = 13.5$ Å transformed under heating in the temperature interval 150–200 °C into the initial fullerite (heat release $\Delta H \approx 300$ J/g), similarly to the 1D and 2D polymers [3]. In the case of higher-density fcc phases ($a \leq 12.95$ Å) annealing did not result in any appreciable changes in the structure of samples, in accordance with the idea of the 3D polymer as a rigid covalent sp^2 – sp^3 network.

Comparison of the lattice parameter vs synthesis temperature dependences obtained for different pressures (Fig. 4) clearly shows that the 3D polymerization is a high-pressure phenomenon. The pressure threshold corresponding to the crossover between 2D and 3D polymerization may be estimated near 8 GPa. The temperature of molecular-structure collapse, being approximately constant at lower pressures [4], decreases with pressure at $P > 8$ GPa.

IV. Conclusion

We have studied the 3D polymerization of fullerite C_{60} caused by high-pressure–high-temperature treatment and propose the model of this phenomenon. Further experimental confirmations for this model may be obtained from direct measurements of the proportion of sp^3 atomic sites in different polymers, e.g., using ¹³C NMR or electron loss energy spectroscopy experiments.

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