Phase Transformations of C_{70} Fullerite under High Pressure of 6.5-12.5 GPa and Temperature 300-1720 K : Comparison with C_{60}

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High-pressure high-temperature polymerization of C_{70} fullerite obtained at first time. New crystal structures of rhombohedrally distorted fcc type and bct type are found for the samples quenched after treatment at $p = 6.5-12.5$ GPa and $T = 500-900$ K. In the temperature range of $900-1720$ K a disordered cross-linked layered structures are found. Samples with bct type crystal structure and with disordered structure have hardness in the range of $30-90$ GPa and their density varies in the range of $2.1-2.8$ GPa. These data are compared with the data for materials obtained from C_{60} fullerite under the same conditions.

[C_{70} , high pressure, structure, hardness, C_{60}]

1. Introduction

Discovery of phase transformations in solid C_{60} under high pressure and combined high-pressure-high-temperature treatment those lead to formation of various new metastable at ambient conditions carbon states [1-14] causes great interest to the behaviour of other type fullerites under the same p-T conditions. Of particular interest is the opportunity to obtain a new forms of superhard and ultrahard (harder than diamond) fullerites analogous to those we have synthesized at first time from pure C_{60} [7-14]. The most available fullerene material after C_{60} is the C_{70} fullerite and very recently it was communicated about creation of dimers of C_{70} molecules under pressure of 5 GPa and temperature about 500°C [15]. Destruction of C_{70} was also observed [16], however in both studies [15,16] no ultrahard or superhard materials were obtained. Superhard and ultrahard properties of the materials synthesized from C_{60} under pressure higher than 8 GPa are associated with their peculiar crystal or amorphous structure. However many details of the phase transformations in solid C_{60} and structure of the phases still not clear completely. Many peculiarities of the phase transformations of C_{60} may be understood in comparison with the behaviour of C_{70} under similar treatment conditions. Physical properties of polymerized C_{70} phases may differ from analogous materials on the basis of C_{60} molecules due to strong anisotropy of C_{70} fullerene.

In this paper we present the first results of the X-ray study of the structure of quenched carbon states obtained from C_{70} fullerite after pressure and temperature treatment in the range of 6.5-12.5 GPa; 300-1830 K and compare them with the data for C_{60} . Hardness and densities of the obtained materials are also measured and will be discussed.

2. Samples.

We have used the same toroid-type high-pressure apparatus for the synthesis of metastable phases of C_{70} as for the treatment of C_{60} samples [8,9]. Bulk samples up to 30 mg weight were synthesized from the pristine C_{70} fullerites (99,2 %) manufactured in the Institute of Metalorganic Chemistry RAS, Russia and in the Ecole Polytechnique Federale de Losanne, Switzerland. C_{70} powders were stored in a sealed vacuum tubes and preparations for the synthesis were done in a dry argon

atmosphere. Structure of the quenched samples was investigated by X-ray powder diffraction method by use of X-ray diffractometer KARD-6 with a flat proportional detector on the fast delay lines. Filtered Cu $K\alpha$ -radiation was used.

3. Results and discussion

Two states (amorphous and crystalline) are found in the samples of both C_{60} and C_{70} quenched fullerites. After treatment under pressure up to 8 GPa the crystal structures of both fullerites are very much alike (Fig. 1).

Fig. 1. X-ray diagrams of the C_{60} and C_{70} samples after treatment at 8 GPa pressure and different temperatures.

The crystal structures are face-centred with a small rhombohedral distortion ($\sim 4^\circ$) for the both fullerites. The unit-cell parameters of C_{70} lattices obtained after treatment under $p = 6.5$ GPa, $T = 920$ K are: $a = 10.09\text{\AA}$, $c = 26.79\text{\AA}$ (hexagonal

aspect), $\rho = 1.77 \text{ g/cm}^3$ and at $p = 8 \text{ GPa}$, $T = 770 \text{ K}$ they are: $a = 9.85 \text{ \AA}$, $c = 26.80 \text{ \AA}$, $\rho = 1.86 \text{ g/cm}^3$. The distortion decreases with the increase of temperature and disorder increases respectively. The diffraction peaks are getting broader, particularly for C_{70} . These structures have polymerized planes formed by fullerene molecules. They are soft like a pristine material, but insoluble in toluene. Crystalline state remains up to about 750–800 K (C_{70}) and 950–1000 K (C_{60}). Then fullerene cages are deformed with a formation of different three-dimensionally polymerized disordered structures. This transformation is accompanied with a sharp growth of density from about 1.8 g/cm^3 to 2.2 g/cm^3 (Fig. 2) and growth of hardness to 30–40 GPa depending on synthesis conditions. Density of the samples was measured by flotation method using a mixtures of diiodomethane and acetone liquids of different concentrations. Hardness was measured by a sclerometric method using a specially designed “NanoScan” device on the basis of the contact scanning force microscope attached with a diamond and ultrahard fullerite probe tips [17].

Fig. 2. Density (ρ) of quenched samples as a function of the treatment temperature (T) for three different treatment pressures.

The cross-linked layered polymerized structure type is observed for both fullerites up to 9.5 GPa and in the 900–2000 K temperature range (Figures 1,3,4).

The diffraction pattern is similar to that of graphite, but the peaks of our samples are broader, (100) and (101) are undistinguished and (hkl)'s are absent. A diffuse (002) peak has a maximum corresponding to interlayer spacing of 3.14–3.3 Å, that is less than in graphite. This structure is getting more ordered and closer to a graphite structure at $T > 1820 \text{ K}$. Fig. 1 shows the graphite diffraction pattern for the comparison.

We obtained new crystalline structures of C_{60} and C_{70} in the higher pressure range 9.5–13 GPa [11,12]. Fig. 3 (pattern of the sample obtained at 770 K) shows this new structure. We have proposed that this phase has cubic body-centred structure with a small orthorhombic distortion [12]. The fullerene molecules are remain and the structure is three-dimensionally polymerised. A bend on the $\rho(T)$ curve at about 620 K for the C_{70} samples synthesized under pressure of 9.5 GPa (Fig. 2) reflects the transformation from rhombohedral phase ($a = 9.35 \text{ \AA}$, $c = 26.74 \text{ \AA}$, $\rho = 2.07 \text{ g/cm}^3$) to bct type structure at higher temperatures.

It should be noted that this crystal structure may be identified only tentatively because of poor diffraction patterns (Fig. 4).

Fig. 3. X-ray diagrams of C_{60} after treatment at 9.5 GPa pressure and different temperatures.

Fig. 4. X-ray diagrams of the C_{70} samples treated under pressure of 9.5 GPa and different temperatures.

The temperature interval for the formation of bcc-like structure of C_{70} is very narrow, only about 100 K. At temperatures of 720–900 K a dense disordered structure forms and the decrease of density takes place under $T > 1000 \text{ K}$.

More distinct bct type structure was obtained under pressure of about 12.5 GPa and temperatures in the range 750–900 K (Fig. 5). The diffraction peaks of C_{70} structures more diffuse than for C_{60} synthesized at the same p-T conditions and they are shifted to smaller angles. Unit-cell parameters of this structure are: $a = 9.51 \text{ \AA}$, $c = 14.56 \text{ \AA}$, $\rho = 2.12 \text{ g/cm}^3$. The experimentally defined density is higher - about 2.45 g/cm^3 , probably due to the presence of dense disordered phase.

Density of the samples obtained from C_{70} under $p = 12.5$ GPa increases slowly with an increase of temperature of the synthesis more than 1000 K and the attained maximum of density was 2.8 g/cm^3 , that is less than in the case of C_{60} under the same conditions: about 3.1 g/cm^3 .

Fig. 5. X-ray diagrams of C_{60} and C_{70} samples after treatment at 12.5 GPa pressure and different temperatures.

As the X-ray diagrams (Fig. 5) show, samples obtained from C_{60} and C_{70} at $p=12.5$ GPa, $T=1720$ K have different disordered structures. Sample obtained from C_{70} has disordered strongly cross-linked layered structure with interlayer spacing of about $3.0 \text{ \AA}$, while the other one may be considered as an intermediate structure between layered structure and ultrahard amorphous cage nanostructure [12,13] that is characterized by intensive diffuse peaks with the maximums at d -spacings 2.14 – $2.18 \text{ \AA}$ and $1.2 \text{ \AA}$. Difference in the structures and densities causes a difference in the hardness of these materials: 90 ± 10 GPa in the case of C_{70} and 120 ± 10 GPa in the case of C_{60} .

Conclusion

Although transformations of C_{70} in the studied P-T region have much resemblance with the transformations of C_{60} , many differences are observed too. Different crystal structures of high-pressure phases, different short-range and probably different medium-range order of disordered states are distinguish C_{60} and C_{70} .

With an increase of pressure in the range of 6.5 – 12.5 GPa a linear, planar and bulk polymerization of C_{70} molecules takes place at temperatures higher of about 450 – 500 K. Polymerized crystal structures are found in the range up to about 800 K. At $T > 800$ K a cross-linked disordered structures with different densities in the range of 2.2 – 2.8 g/cm^3 are synthesized.

Transformations of C_{70} fullerite into an ultrahard cage amorphous nanostructure analogous to the case of C_{60} or into a diamond structure were not observed in the studied pressure range. Further investigations at higher pressure level are needed to make clear whether it is possible to create an ultrahard material from C_{70} or not.

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