

CRYSTAL STRUCTURE OF HARD PHASES OF C₆₀ AND C₇₀

V.D.Blank^{***}, N.R.Serebryanaya^{***}, G.A.Dubitsky^{**}, S.G.Buga^{***}, S.N.Sulyanov^{***}

^{*}Institute of Spectroscopy RAS, 142092 Troitsk, Moscow region, Russia

^{**}Research Center for Superhard Materials of State Committee for Science & Technologies of Russia

^{***}Shubnikov Institute of Crystallography RAS, Leninskii pr. 59, Moscow, 117333 Russia

Introduction

The structural investigations of fullerite new phases obtained from pure solid C₆₀ and C₇₀ at static pressure up to 13 GPa and temperatures in the interval 300-2100 K are presented. Earlier [1] it was found that the new carbon states on basis of C₆₀ have polymerized structures and exhibit very interesting physical properties like as hardness exceeding hardness of diamond, semiconductor electrical properties and some others. A search of new superhard fullerene derivates forces to pay attention to C₇₀ as the closest to C₆₀.

Experimental

The toroid-type high-pressure apparatus were used for the synthesis of the hard phases of C₇₀ as for the treatment of C₆₀ samples [1]. Bulk samples up to 30 mg of weight were synthesized from the pristine C₇₀ (99.2%). C₇₀ powders were stored in a sealed vacuum tubes and preparations for the synthesis were done in a dry argon and air atmosphere. The structure of superhard and ultrahard phases, obtained under these conditions, has been investigated by X-ray powder diffraction method by using X-ray diffractometer Kard-6 with a flat proportional chamber on the fast delay lines. Cu K α -radiation was used.

Results and Discussion

Two states (amorphous and crystalline) are found in samples of both quenched fullerites. At the low pressure up to 8 GPa crystal structures of both fullerites are very much alike (Fig.1, the two upper diffraction patterns). The crystal structures are face-centered with a small rhombohedral distortion ($\sim 4^\circ$) for the both fullerites. The distortion is decreasing with the increase of temperature and the disorder is increasing respectively. The diffraction peaks are getting broader, particularly for C₇₀. These structures have two-dimensional polymerized planes formed by fullerene molecules. Diffraction patterns are just the same at the air and dry argon atmospheres. These new phases are insoluble in toluene. Crystalline state is remained up to 900-1000 K then fullerene cages are deformed with a formation of different three-dimensional polymerized disordered structures. The cross-linked layer

polymerized structure-type is observed for both fullerites up to 9 GPa and the 900-2000 K temperature range (Fig.1).

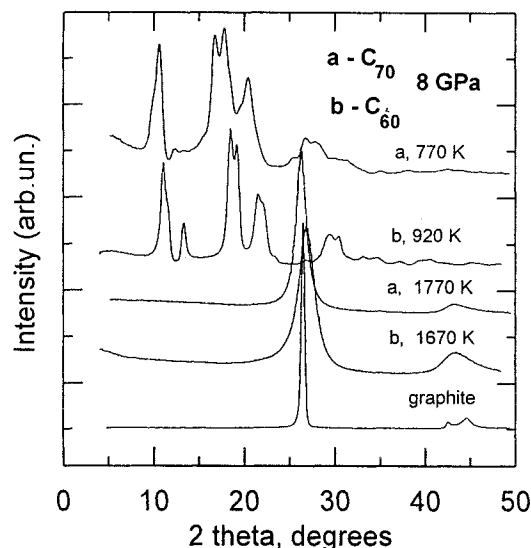


Figure 1. The diffraction patterns of C₆₀ and C₇₀ at 8 GPa and different temperatures.

The diffraction pattern is similar to that of graphite, but the peaks of our samples are broader, (hk0) and (h0l) are undistinguished and (hkl)'s are absent. The hardness of the samples with cross-linked disordered structure is in the range between sapphire and cubic BN. This structure is getting more ordered and closer to a graphite structure at $T > 1820$ K. Fig.1 shows the graphite diffraction pattern for the comparison.

There are new crystalline structures for C₆₀ in the higher pressure range 9.5-13 GPa [1]. Fig.2 (pattern of the sample obtained at 770 K) shows this new structure. It was proposed that this phase has cubic body-centered structure with a different small orthorhombic distortion [1]. The fullerene molecules are remained and the structure is a three-dimensional polymerised, the hardness of these structures changes in the range 70-150 GPa. Structure of these phases is stable upon annealing up to 1000 K. At 870K (Fig. 2) fullerene cages are beginning to destroy and the disordered cross-linked structure is forming. Fig. 3. shows the same pictures for the C₇₀. However, the stability interval of bcc-like structure of C₇₀ is very small, less than

100 K. At 720 K the cross-linked structure is forming. The highest temperature structures at 9.5 GPa are alike for the both fullerites and are just the same as at 8 GPa (Fig.1).

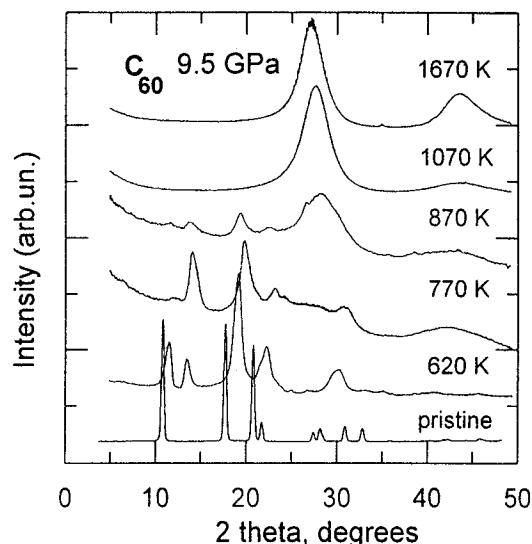


Figure 2. The diffraction patterns of C_{60} at 9.5 GPa and different temperatures.

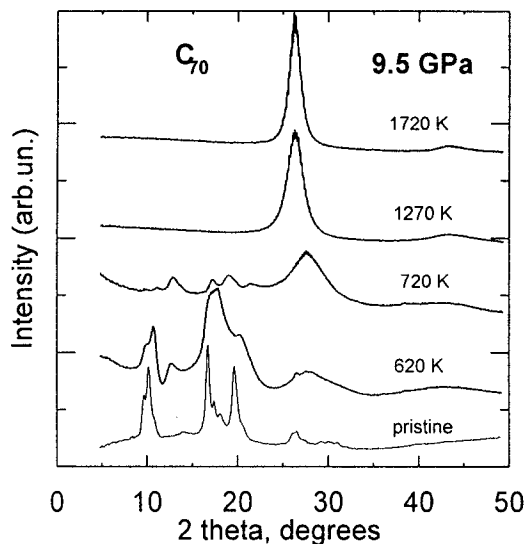


Figure 3. The diffraction patterns of C_{70} at 9.5 GPa and different temperatures.

It should be noted that crystal structure of P-T-treated C_{70} may be identified only tentatively because of poor diffraction patterns. However the experimental density of quenched phases is in a good accordance with the X-ray-calculated one. The observed growth of the density with the temperature-increase (Fig.4) indicates the formation of the denser crystalline phases, and the decrease

of density takes place at the high-temperature-amorphization.

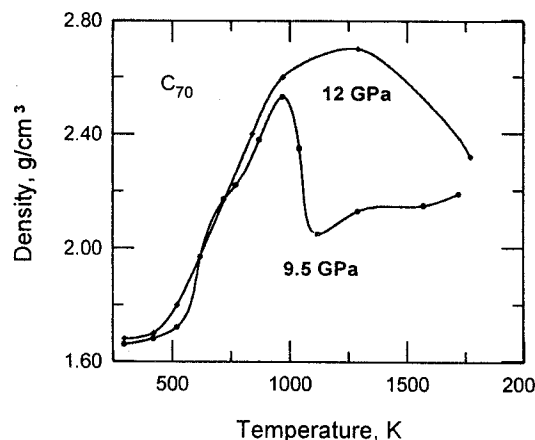


Figure 4. The temperature-dependence of the density of C_{70} -samples.

At the highest pressure 13 GPa and the temperature >1000 K the second type of disordered structure is found for C_{60} [1]. The diffraction pattern of this structure has one halo at 2.18-2.16 Å. This hardest phase, called ultrahard fullerite, in addition to sp^3 -bonds contains an essential quantity of sp^2 -bonds, and, probably, has a carcass disordered structure.

Conclusions

The hard phases of C_{60} and C_{70} are found at high pressures and high temperatures by using of X-ray powder diffraction method. These phases have 1D, 2D and 3D-polymerized structures. Two types of states (crystalline and disordered) in polymerized phases of both fullerites are found. The diffraction patterns of all obtained phases with unit-cell parameters are represented. The P-T phase diagram of C_{70} will be plotted by using X-ray diffraction data. It is found that C_{60} -crystalline-polymerized-phases are more stable than such C_{70} -phases.

Acknowledgments

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References

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