

PRODUCTION AND INVESTIGATION OF FULLERITE C₆₀ INTERCALATED WITH SMALL MOLECULES

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Introduction

It is well known that fullerene C₆₀ can exist as a gas (at temperature ≥ 450 °C) or solid. Liquid phase for C₆₀ was not established still now. At normal conditions C₆₀ molecules form fullerite – solid state of fullerene. The fullerite can be amorphous or crystalline. Transitions between amorphous and crystalline states are not possible as a rule. It is related with low temperature of C₆₀ sublimation (~ 450 °C). Ratio between amorphous and crystalline parts of solid C₆₀ formed in process of its production.

C₆₀ molecules are crystallized in face-centered cubic (*fcc*) lattice. Van der Waals forces bond molecules in fullerite. One octahedral ($R_{oh} = 2.06$ Å) and two tetrahedral ($R_{th} = 1.13$ Å) sites per one C₆₀ are in *fcc* lattice [1]. Small molecules can be placed in octahedral sites of fullerite if its van der Waals diameters are not substantial higher than the diameter of the site. Distance between the center of C₆₀ molecules is increased then the sites are occupied.

We find new method of fullerite doping [2] in process of its salting out from solution in organic solvent [3]. Such doping can be performed at room or lower temperature. By this method were obtained fullerites C₆₀ intercalated with Ar [4], CH₄ [5], CH₂F₂ [6-7] and O₂ [1, 8, 9]. The main peculiarity of our samples is more high stability in compare with that of same samples obtained by means of hot pressing [10]. High stability of our samples is connecting with its more large crystalline size.

New data on the properties of our fullerites, which were obtained in last two years, are present in my report.

Ar_xC₆₀

Fullerite with composition Ar_xC₆₀ ($0.60 < x < 0.75$) was obtained in accordance with [2] from solvents saturated with argon gas. It was established that constant a_0 for *fcc* lattice is equal to 1.422 nm and temperature of the phase transition from *fcc* (Fm3m) lattice to a simple cubic (*sc* or Pa3) lattice is equal to -26 °C. These values differ substantial from the same values for

clean fullerite (1.416 nm and -13 °C correspondently). Heating of Ar_xC₆₀ leads to loss of argon and returns to the structure that is characteristic for clean fullerite.

(CH₂F₂)_xC₆₀

Fullerite C₆₀ with intercalated CH₂F₂ (Freon-32) was prepared for the first time. The sample was studied by elemental analysis, X-ray powder diffraction, mass spectrometry, and IR spectroscopy. The composition of the sample was found to be (CH₂F₂)C₆₀. The sample had a *fcc* lattice with $a_0 = 1.4284$ nm that is much larger than that for pure fullerite. The gas released from the sample during heating in a vacuum to 450° C largely consisted of initial Freon (mass spectrometry data); no Freon destruction products were observed at this temperature. The C–F stretching vibration frequency (1058 cm⁻¹) was shifted in (CH₂F₂)C₆₀ by 30 cm⁻¹ toward lower wave numbers compared with the gas phase. The absorption bands at 1182 and 1428 cm⁻¹ (IR active modes (F_{1u}) of high-symmetry (I_h) C₆₀ molecules) did not change their positions in the intercalate.

(O₂)_xC₆₀

For fullerite C₆₀ with intercalated oxygen, a sharp (by three orders of magnitude) increase in the intensity of the EPR signal with a *g*-factor of 2.0024 was observed at ~ 200 ° C. The conclusion was drawn that the products of oxygen interaction with fullerene rather than the concentration of oxygen in the sample determined the intensity of the EPR signal.

Processes inside of (O₂)_xC₆₀ induced by the heating are also analyzed using mass-spectrometry, thermogravimetry, differential scanning calorimetry, and so on. It was found that the primary product at heating temperatures below 100° C is oxygen. At higher heating temperatures up to 200° C, carbon oxides CO and CO₂ were also observed. Our DSC measurements showed an intense peak at +193° C that indicates a rather unusual interaction of fullerite with intercalated oxygen. Enthalpy of the phase transition from *fcc* lattice to *sc* lattice is found to decrease by 23% as a

result of heating of fullerite samples up to 300 °C in the dry argon atmosphere. This finding can be explained by the formation of oxygen containing products of C₆₀ that exhibit no free rotation inside the crystalline fullerite. In order to gain insight in possible oxidation mechanisms, density functional theory computations were performed for the C₅₈O_n (n=0-4) and C₅₉O_m (m=0-2) species. Total energies of the optimized states are used for estimating the energetic of different oxidation channels. The lowest total energy states of C₅₉ and C₅₈O₃ are found to be triplets. Thus, these states may contribute to the ESR intensity as well as to be a source of paramagnetism observed previously in C₆₀ fullerite irradiated by oxygen.

Fullerite C₆₀ intercalated with isopropyl alcohol

A highly defect fullerite was obtained by adding of isopropyl alcohol (IPA) in the solution of C₆₀ in 1,2-dichlorobenzene (DCB) [11]. It was shown that molecules of IPA and DCB are placed in the large size defects. At heating up to 200 °C IPA molecules are evolved from the fullerite, and acetone molecules are evolved at more high temperature (200-350 °C). Products of DCB thermal decomposition are not established at all temperature intervals. Quantum chemistry calculation of possible products of reaction between IPS and C₆₀ were performed. New data on properties of such highly defect fullerite were obtained by means of transmittance electron microscopy, powder pattern, mass spectrometry and infrared spectroscopy. One of possible mechanism of transformation of IPS to acetone in intrinsic pores of the fullerite was proposed.

References

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