SALTING OUT AS A NEW LOW TEMPERATURE METHOD PRODUCTION FULLERENE INTERSTITIAL COMPOUNDS

Yu.M.Shulga[1], S.A. Baskakov[1], V.M.Martynenko[1], Yu. G. Morozov [1], V.N. Vasilets [1], A.F.Shestakov[1], A.V.Kulikov[1],D.V.Schur[2]

[1]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia;

[2]Institute for Problems of Materials Science of NAS of Ukraine, Krzhizhanovsky str., 3, Kiev-142, 03680, Ukraine

Introduction

Assink et al [1] have pointed out that fullerenes may provide an efficient way for gas storage. Usually gas C_{60} interstitial compounds are produced by hot pressing the fullerene solid (fullerite) at temperatures between 200 – 550°C and under gas pressures in the range 170 –200MPa for set periods from 12 to 60h. With this method Ar, Kr and Xe as well as CO, CO_2 and N_2O fullerene compounds were produced.

In this paper we report the formation and characterization of the gas interstitial fullerenes of C_{60} with argon, nitrogen or oxygen molecules produced from the solution of C_{60} in 1,2 dichlorobenzene saturated with these gases at room temperature. We used isopropyl alcohol adding for the precipitation of fullerenes from the solution. The choice of this system was dictated by the following reasons: a) the solubility of C_{60} in 1,2 dichlorobenzene is high enough (27 mg/ml), and therefore we do not need too much alcohol for precipitation of fullerenes; b) according to the preliminary experiments isopropyl alcohol was selected for precipitation since it has shown a more stable yield of perfect fullerene microcrystals in comparison with other precipitators like methyl alcohol, ethyl alcohol and the mixture of ethyl alcohol with water. The influence of gas molecules dissolved in solution on the process of fullerene crystallization for the solution is not still clear. The structure and chemical composition of the precipitations was characterized by X-ray powder diffraction analysis, FTIR spectroscopy, thermal desorption mass spectrometry, differential scanning calorimetric and chemical analysis. Thermal desorption mass spectrometry analysis confirmed the presence of Ar, N and O atoms in C_{60} specimens. We discuss the effects of gas intercalation on the lattice parameters and phase transition temperature of precipitated fullerene microcrystals.

Experimental

The solution of the fullerene (1mg C_{60} per 1ml 1,2 dichlorobenzene) in a glass retort was fasten on the massive stand to avoid any vibration, and left for 10 days in air, nitrogen, oxygen or argon atmosphere at room temperature (295K). After that the isopropyl alcohol in five times higher volume was slowly added to the solution without shaking. Isopropyl alcohol was previously saturated with appropriate gas by intensive bubbling during 20 minutes. The mixture was then kept for several days at room temperature in darken place. The black bright crystals precipitated from the solution were finally separated by filtration.

Results

Fig.1 shows scanning electron microscopy (SEM) photograph of microcrystals precipitated from C_{60} solution in 1,2 dichlorobenzene. The mixture of perfect crystals with the size up to 100μ with sub-micron microcrystals and amorphous clusters represent the typical structure of precipitated fullerenes. It was found that the ratio of the crystalline and amorphous phases depends on the precipitation rate and the temperature of C_{60} solution. The higher crystalline fraction was obtained at lower temperatures and lower rate of precipitation.

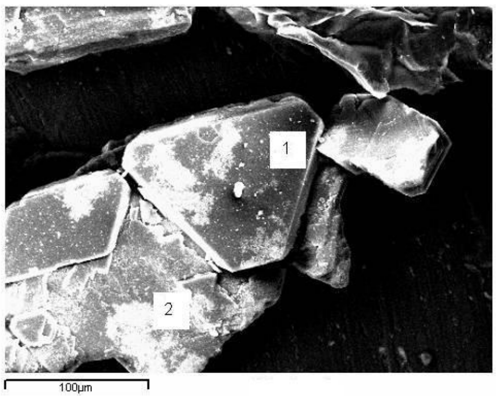

Fig.1. Scanning electron microscopy image of fullerene microcrystals precipitated from C_{60} 1,2 dichlorobenzene solution saturated with argon.

The results of EDS analysis obtained at two different points marked in the Fig. 1 are presented in the table 1. The first point was selected in the crystalline region and the second one in the amorphous fraction. It is clear that Ar molecules are mainly concentrated in the crystalline region while DCB molecules containing Cl atoms are located preferably in amorphous phase.

Table 1. X-ray energy dispersive analysis of Ar interstitial fullerene

Analyzing area (Fig.1)	C at%	Cl at%	Ar at%
1	99.86	0.10	0.04
2	99.64	0.36	0.00

Fig. 2 shows the room temperature diffraction pattern for pure C_{60} and for fullerenes precipitated from air and Ar saturated solutions. It is clear that the X-ray diffraction patterns of fullerens contain the entire narrow peaks characteristic for face centered cubic lattice of C_{60}. The intensities of the diffraction peaks for fullerenes are nearly the same as for pure C_{60}.

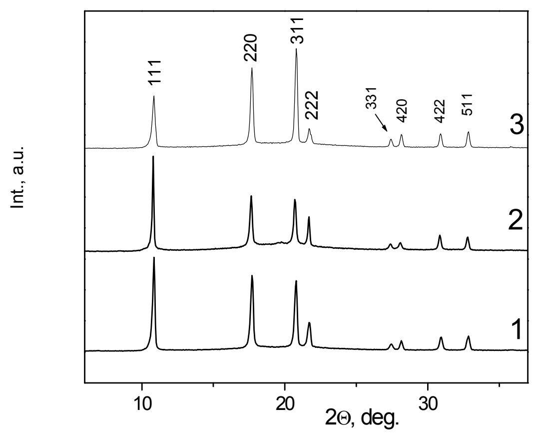

Fig.2. X-ray diffraction patterns from pure C_{60} obtained by vacuum sublimation (1), and precipitated from C_{60} 1,2 dichlorobenzene solutions saturated with air (2) and argon (3).

Weak Van der Waals (VDW) forces do not prevent the C_{60} molecules from freely rotating at room temperature. However, cooling and reducing of the thermal energy to the value comparative with VDW interaction allows locking of C_{60} molecules into fixed orientation with respect to each other. Thus, the C_{60} lattice undergoing an orientational ordering phase transition from face centered cubic Fm3m to simple cubic (sc) Pa3 [2]. Intercalation of gas molecules into C_{60} lattice would influence the VDW forces and, as a result, decrease the temperature at which orientation ordering takes place. Fig. 3 shows the DSC curves obtained for pure C_{60} and C_{60} precipitated in the presence of air, oxygen and Ar. The gas intercalation causes the shift of order-disorder transition peak detected for pure C_{60} at 263K to the lower temperatures for precipitated fullerenes. This effect implies that lower temperatures are required to bring about orientation ordering when the lattice is expanded by intercalation of different gases. The decrease of the enthalpy value normalized to the weight of the sample for intercalated fullerenes in comparison with pure C_{60} may be due to the presence of amorphous phase in precipitated fullerenes.

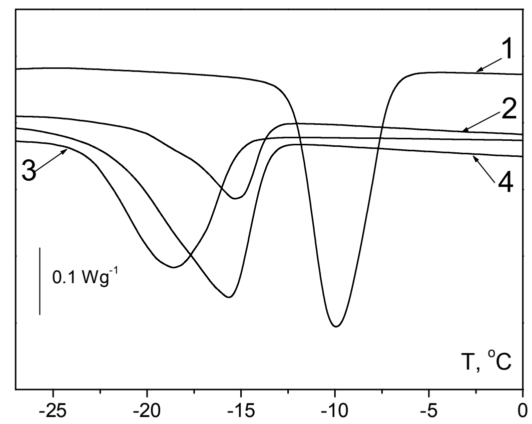

Fig.3. DSC curves for pure C_{60}, (1) and fullerenes precipitated from the solution saturated with air (2), Ar (3) and O_2 (4).

The wet procedure described and based on precipitation of microcrystals from the solution makes possible to introduce gas molecules in the lattice of C_{60} at room temperature and atmospheric pressure. In contrast to hot pressing method, which could be used only for incorporation of chemically inert molecules to the fullerenes, low temperature technique allow us to synthesize for the first time fullerene microcrystals containing chemically active molecules like oxygen. Ar interstitial fullerene obtained by precipitation was found to exhibit much higher thermal stability then that produced by hot isostatically pressing method.

The work was supported by RFBR (project 03-03-32796) grant.

References

1. R.H.Assink, J.E.Shirber, D.A.Loy, B.Morosin, G.Carlson «Intercalation of molecular species into the interstitial sites of fullerene» J.Mater.Res., 1992; v.7(8), p.2136.
2. E. Grivei, M. Cassart, J.–P. Issi, L. Langer, B. Nysten, J.–P. Michenaud, C. Fabre, A. Rassat "Anomalous specific heat of C_{60}" Phys.Rev.B: 1993, vol.48, No 11, p. 8514-8516.