A DSC STUDY OF C_{60} FULLERITE OXIDATION BY INTERSTITIAL OXYGEN

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Introduction

Fullerites C_{60} intercalated with oxygen $(O_2)_xC_{60}$ were obtained by method described previously [1]. Oxidation of the samples by interstitial oxygen was detected at a relatively low temperature around 100°C [2]. As a result of oxidation, an intensive peak indicating the heat release was observed in the DSC curve.

It was also found [3] that the C_{60} fullerite lattice is undergoing the phase transition (PT) from a face centered cubic (fcc) Fm3m lattice to a simple cubic (sc) Pa3 lattice at approximately -12 °C. Fullerite intercalation by gas molecules usually decreases the phase transition temperature, and the downshift ΔT_{PT} ranges from 10° C to 20° C [4]. Enthalpy of the phase transition (ΔH_{PT}) in the pure fullerite is usually inside the range from 3 to 8 J/g [5]. In this work, we report the phase behavior of fullerite $(O_2)_{0.69}C_{60}$ studied by the DSC technique.

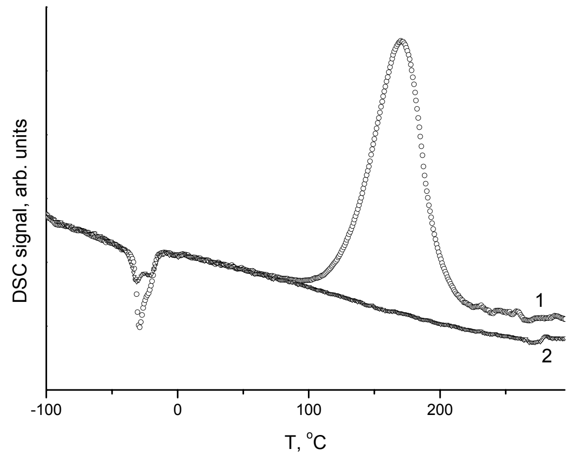

Fig. 1. DSC curves for $(O_2)_{0.69}C_{60}$ C_{60} obtained in the dry Ar atmosphere in the range from -100 °C to +300 °C with the heating rate 10K/min. The first pass corresponds to curve 1, the second pass corresponds to curve 2.

Experimental

The sample was kept on air at room temperature during 1 month before measurements were performed. The oxygen content was measured by Vario-MICRO "CUBE" (Elementar, Germany). The DSC analysis was performed using a DSC 822 (Mettler-Toledo) instrument. Samples of 3-10 mg weight were placed in aluminum pans with perforated lids under flowing dry argon (50 ml•min^{-1}). The temperature range selected for these measurements was from – 150 °C to +300 °C, and the heating rate is 10°K/min.

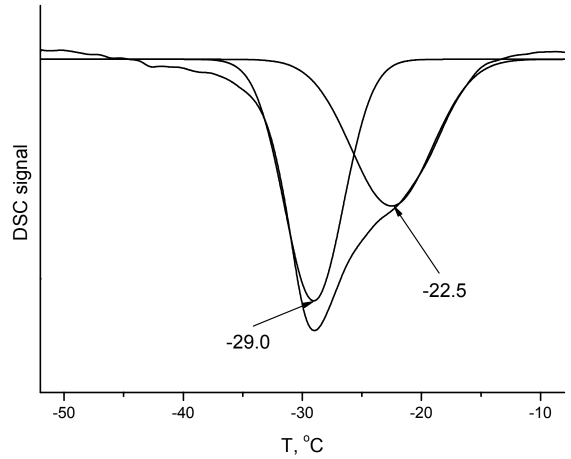

Fig. 2. Fitting of the first pass DSC curve (see Figure 1, curve 1) by two Gaussian functions.

Results and discussion

The first pass DSC curve contains two peaks at -29.0 °C and +169.8 °C (see Fig. 1, curve 1). The peak at +169.8 °C was attributed [2] to fullerite oxidation by interstitial oxygen. After heating the sample up to 300 °C, this peak disappears (see Figure 1, curve 2).

In addition to the peak at -29.0 °C, there is a shoulder at -22.5 °C on the DSC curve in the fcc → sc phase transition region (see Fig. 2). The temperature values of the peak and shoulder are in the range of phase transitions observed [1, 4] in the C_{60} fullerite intercalated by small species like Ar, N_2, CO.

Fitting the experimental DSC curve by Gaussian functions, we found that two Gaussians are enough for fitting the curve (see Fig. 2). The area of the Gaussian fitting of the first peak at -29.0 °C comprises of 56% and that of the second peak at -29.0 °C comprises of 44% of the total area of the DSC curve, respectively. It is worth to mention that the half-width of the main peak at -29.0°C (4.8°C) is appreciably smaller than the half-width of the second peak at -22.5°C (6.7°C). The total enthalpy is 6.8 J/g, which is a typical value for the phase transitions in intercalated fullerites [1, 4].

Two peaks at -13°C and -33°C on the DSC curve of the fullerite intercalated by oxygen was described earlier in the literature [6]. The first peak at -13°C was attributed to the part of the sample without oxygen and the second peak at -33°C was attributed to the oxygen containing regions. As a result of the first pass heating of the sample, the second peak shifted that indicates a partial reversibility of the process of charging the fullerite by oxygen. According to the model of Schirber et al. [6], there are two different parts of a sample: one part (corresponding to the peak at -29°C) with 83% of octahedral interstitial sites containing oxygen and the second part (peak at -22,5°C) with 50% of oxygen containing octahedral interstitial sites. It is likely that other parts with low oxygen concentrations were formed as a result of oxygen elimination during one-month storage.

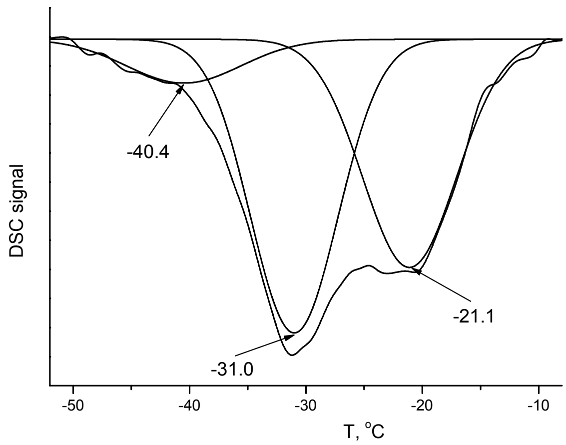

Fig. 3. Deconvolution of the second pass DSC curve(see Figure 1, curve 2) by three Gaussian functions.

The DSC curve of the sample after its heating up to 300°C (see Fig. 1, curve 2) is not fitted by two Gaussians. The curve deconvolution shows that one needs three Gaussians with the peaks at -40.4, -31.0 и -21.1 °C and relative intensities of 9.5, 47.4 и 41.1% in this case. One of these peaks (at -21.1 °C) exhibits a low temperature shift corresponding to the model of reversible oxygen charging described above. Two other peaks (at -31.0 °C и -40.4 °C) do not follow this model. The downshift should indicate the increase in observation of molecular oxygen elimination and formation of carbon oxides during the heating in an argon atmosphere. Moreover, there was no charging of the fullerite sample by Ar atoms after the heating as follows from our mass spectroscopy measurements. A possible explanation of this controversy may be related to an enlargement of octahedral interstitial sites due to the formation of carbon oxides in the course of the oxidation process. Similar behavior was previously observed during the C_{60} fullerite intercalation with different species such as Ar, N_2 and CH_2F_2 [4, 7]. This effect should be more pronounced in the formation of two CO molecules in octahedral interstitial sites. Elimination of oxides and a short time annealing of the sample at 300°C are probably not sufficient for a reconstruction of the octahedral interstitial sites to the initial state, which is characteristic for the non-intercalated fullerite. In order to quench free rotations in the enlarged octahedral interstitial sites, one needs to freeze the sample to lower temperatures than that characteristic for the pure fullerite.

The second pass DSC curve is also characterized by the 23% decrease in enthalpy of the phase transition observed for the first pass curve. This likely means that free rotation for about 23% of C_{60} molecules becomes impossible. Locked species are likely C_{60} fullerenes with holes (C_{59} and C_{58}), C_{60} oxides ($C_{59}O$ and $C_{58}O$), dimers $C_{120}O_n$ or other products of C_{60} oxidation by intercalated oxygen. Most likely, the presence of these products of partial oxidation irreversibly disturbs the lattice of C_{60}.

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References

1. Shulga Y.M., Martynenko V.M., Shestakov A.F., Baskakov S.A., Kulikov A.V., Vasilets V. N. et. al. Russian Chem. Bull. **55** (4), 687-696 (2006).
2. Shulga Y.M., Martynenko V.M., Open'ko V.V., Kulikov A. V. et. al. J. Phys. Chem. C **112** (32), 12096-12103 (2008).
3. Heiney P.A., Fischer J.E., McGhie A.R., Romanow W.J., Denenstein A.M., McCauley J.P. Jr., Smith A.B. Phys. Rev. Lett. **66** (22), 2911 - 2914 (1991).
4. Sundqvist B., Low Temperature Physics, **29** (5), 440-444 (2003).
5. Gadd G.E., Moricca S., Kennedy S.J., Elcombe M.M., Evans P.J., Blackford M., Cassidy D., Howard C.J., Prasad P., Hanna J.V., Burchwood A., Levy D. J. Phys. Chem. Solids, **58** (11), 1823-1832 (1997).
6. Schirber J.E., Assink R.A., Samara G.A., Morosin B., Loy D., Phys. Rev. B **51** (21), 15552-15554 (1995).