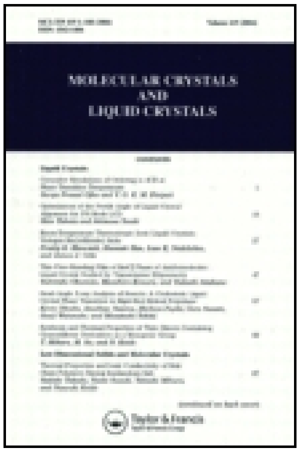

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# Calorimetry and X-ray Powder Diffraction Studies of Carbolite - a New Carbon Phase

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We report on the specific heat, *C*(*T*), measurements of a new carbon phase synthesized by condensation of high temperature carbon gas. For the adequate description of the *C*(*T*) dependence, the model of specific heat for quasi-one-dimensional crystals has been applied. By means of X-ray and specific heat measurements it has been found that the material is a metastable phase under the normal conditions, undergoing the transformations to the amorphous state upon heating above $T \approx 350$ K.

Keywords: carbon deposit; specific heat; X-ray diffraction;

## INTRODUCTION

Recently, a new carbon form has been synthesized by condensation of high-temperature carbon gas on a room temperature copper substrate[1]. Due to the low value of the specific weight, 1.46 g/cm$^3$, the material has been named carbolite. Although its crystal structure has not been studied in detail, it is assumed hypothetically to consist of quasi-one-dimensional carbon chains oriented along the *c*-axis of the hexagonal crystal lattice and interacting with the van der Waals forces [1].

The goal of this study is to explore the low-temperature specific heat of the material and to study the temperature range of metastability of the material by means of calorimetric and X-ray diffraction measurements.

## EXPERIMENT AND DISCUSSION

The samples studied have been synthesized in an argon atmosphere by method of fast condensation of high temperature (4000 K-5000 K) concentrated carbon gas onto room temperature copper substrate[1].

By means of electron energyloss spectroscopy, electron diffraction, infrared optical absorption and high resolution transmission electron microscopy measurements it has been found that the material synthesized is unrelated to graphite, cubic or hexagonal diamond, fullerides, and oriented carbon nanotubes[2]. A typical scanning electron microscope view of the sample is shown in Figure 1(a). The synthesized material is in the form of a film which is built up from the parallel columns aligned perpendicular to the film plane.

The temperature dependences of the specific heat, $C(T)$, have been measured by means of a homemade highly sensitive relaxation microcalorimeter over the temperature range from 4.5 K to 30 K. The masses of two measured samples were 0.085 mg and 0.074 mg.

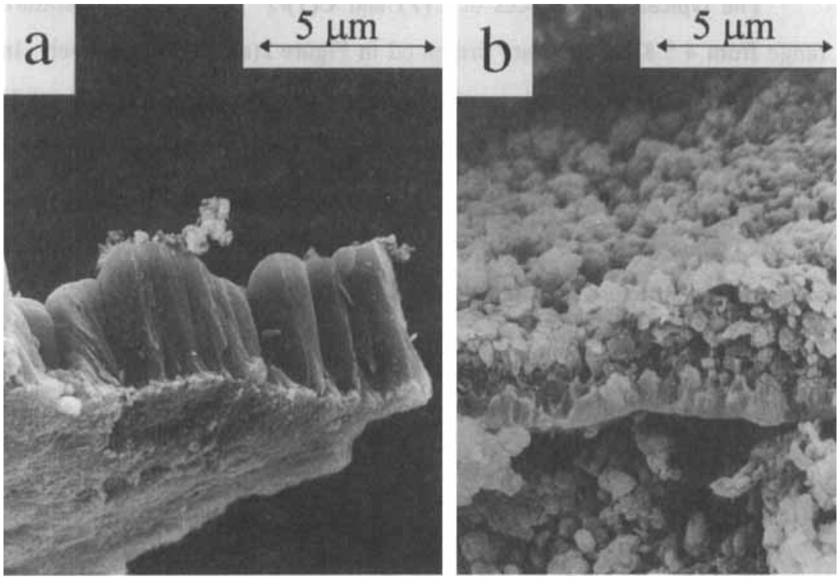

FIGURE 1 (a) A scanning electron microscope view of the carbon crystals synthesized. (b) A scanning electron microscope view of the same sample annealed at 600 K in vacuum followed by subsequent 24 h exposure of the sample under the normal conditions.

For the measurements of the temperature dependences of the specific heat over the temperature range from 130 K to 730 K, a scanning Perkin-Elmer 7 calorimeter has been used. Three samples of the masses from 4 mg to 7 mg were chosen for these measurements.

For the X-ray powder diffraction measurements, a $\theta$ - $2\theta$ mode has been used. An X-ray source was operated at 0.9 kW using a Ni filtered Cu $K_\alpha$ radiation. The sample was crushed and spread on a single-crystal quartz holder which gives no X-ray diffraction lines in the $\theta$ - $2\theta$ mode.

The typical dependences of $C(T)$ and $C(T)/T^3$ over the temperature range from 4.5 K to 30 K are presented in Figure 2(a), (b), respectively. In Figure 2(b), a broad smooth anomaly of the $C(T)$ dependence at 6 K – 8 K and an abrupt steplike one at 11.5 K are clearly seen. These anomalies have been reproducible from scan to scan for the samples studied. The anomaly of the $C(T)$ dependence at 11.5 K has a well-defined edge and may be attributed to the crystal structure transition.

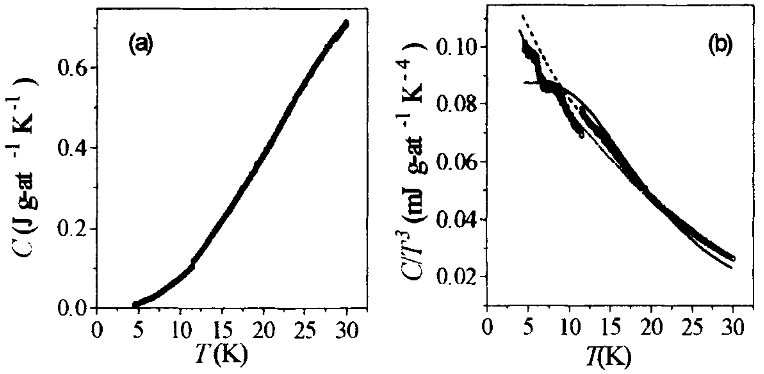

FIGURE 2 (a) The temperature dependence of the specific heat, $C(T)$, of the carbon sample. (b) The dependences of $C/T^3$ on the temperature $T$ of the carbon sample. The open circles are the experimental data. The dashed and dotted lines correspond to the two independent fits to the experimental $C(T)$ dependence at $T$>11.5 K and $T$<11.5 K using the model described in Refs. [3,4], respectively. The solid line is the best fit to the experimental $C(T)$ dependence using a standard Debye model with $\Theta_D$=100 K.

Since, at the temperature of the transition, the specific heat increases drastically with temperature, the transition will probably be due to the effect of freezing of some vibration or rotation degrees of freedom of carbon molecules or gaseous impurities, absorbed in the sample from normal atmosphere rather than a lattice-driven-type phase transition.

As seen in Figure 2(b), the experimental $C(T)$ dependence does not follow the $C(T) \sim T^3$ law down to 4.5 K, and the best fit to the experimental $C(T)$ dependence, using a standard Debye model with $\Theta_D = 100$ K, is unusable to describe the observed $C(T)$ dependence over the studied temperature range. For this reason, for analysis of the measured $C(T)$ dependence of carbolite, a model for the heat capacity of the chain-molecule quasi-one-dimensional crystals has been used[3,4].

Since the experimental $C(T)$ dependence exhibits an abrupt anomaly at 11.5 K, the two independent fits to the $C(T)$ at $T<11.5$ K and $T>11.5$ K have been performed. The calculated $C(T)/T^3$ dependences for $T < 11.5$ K and $T > 11.5$ K are shown by dotted and dashed lines in Figure 2(b), respectively. A comprehensive explanation of these calculations is given in Ref. 5.

The high temperature dependences of the effective specific heat, $C_{\mathrm{eff}}$, for one of the samples studied are shown in Figure 3. The negative $C_{\mathrm{eff}}$ values correspond to the heat removed from the sample and indicate to the exothermic transformations upon heating.

In Figure 3, the curves 1-3 correspond to the three consecutive $C_{\mathrm{eff}}(T)$ scans over the same sample. In order to demonstrate the resolution of the measurements, the $C_{\mathrm{eff}}(T)$ scan of the empty calorimeter is represented by curve 4. As seen from curve 1, in the first scan, the sample undergoes the exothermic process starting from $T \approx 350$ K, which is still not terminated at

$T=730$ K, the upper experimental temperature limit. Against the background of the exothermic process, the relatively narrow anomaly is observed at $T\approx650$ K. The consecutive scans, shown in curves 2 and 3, do not exhibit this anomaly but still contain the broad anomaly, remaining from the exothermic process, which is diminished from scan to scan.

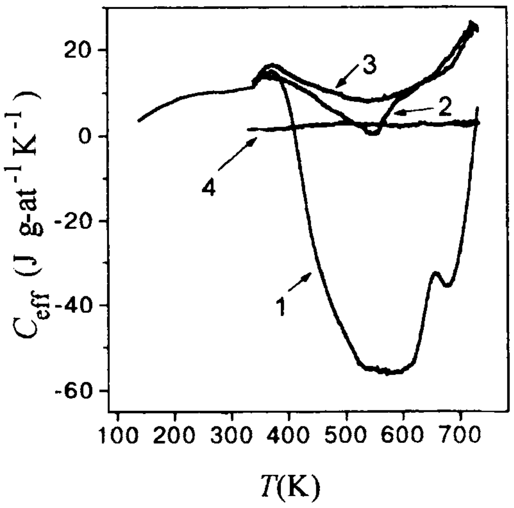

FIGURE 3 The high-temperature dependences of the specific heat, $C_{eff}(T)$, of the carbon sample. The curves 1-3 correspond to the three consecutive $C_{eff}(T)$ scans over the same sample. In order to demonstrate the resolution of the measurements, the $C_{eff}(T)$ scan of the empty calorimeter is represented by curve 4.

In order to explore the anomalies, found in the $C_{eff}(T)$ dependences of the material upon heating, the consecutive procedures of the sample annealing followed by the X-ray powder diffraction measurements have been performed. The annealing procedures were conducted within 1 h at fixed temperatures under $10^{-6}$ Torr vacuum degassing. The X-ray powder diffraction measurements of the annealed sample were carried out under the normal conditions. For the X-ray measurements, it has been found that mechanical or ultrasonic sample grinding has resulted in amorphization of the sample. On the other hand, due to the unfavorable geometry and crystal texture of the samples studied, involving a redistribution of X-ray powder diffraction intensities, the detailed crystal structure analysis by intensities refining has not been performed.

The X-ray powder diffraction pattern of the starting sample is shown in Figure 4(a) and is in agreement with previous data [1].

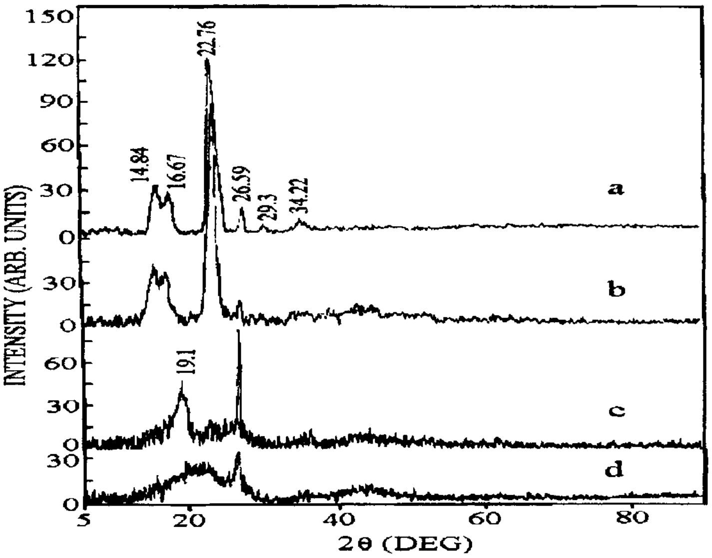

FIGURE 4 (a) X-ray powder diffraction patterns of the started carbon sample, (b) The sample annealed at 450 K, (c) The sample annealed at 600 K, (d) The same sample after subsequent 24 h of exposure under the normal conditions. The $2\theta$ values, corresponding to the peaks, are shown directly above the peaks.

Figures 4(b) and 4(c) correspond to the X-ray powder diffraction patterns of the sample annealed at 450 K and 600 K, respectively. The subsequent 24 h of exposure of the sample under the normal conditions has transformed the sample to the amorphous state, as illustrated in Figure 4(d). A scanning electron microscope view of this sample is shown in Figure 1(b). From Figures 1(a) and 1(b), a distinct change of the carbon sample upon heating can be seen.

On the basis of the high-temperature specific heat and the X-ray powder diffraction measurements, it is evident that the material is a metastable phase under the normal conditions, which undergoes the amorphous state at the temperatures above $T \approx 350$ K.

## Acknowledgments

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