Elastic and microstructural properties of $C_{60}$-and $C_{70}$-based polymerized fullerites exposed to high pressure (15 GPa) and elevated temperatures



2002 J. Phys.: Condens. Matter 14 11305

(http://iopscience.iop.org/0953-8984/14/44/472)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 11305–11310 PII: S0953-8984(02)39621-8

# Elastic and microstructural properties of $C_{60}$- and $C_{70}$-based polymerized fullerites exposed to high pressure (15 GPa) and elevated temperatures

**V M Prokhorov**[1], **V D Blank**[1], **G A Dubitsky**[1], **S Berezina**[1,2] **and V M Levin**[1,3]

[1] Technological Institute for Superhard and Novel Carbon Materials, Centralnaya St. 7a, Troitsk 142190, Russia
[2] Department of Physics, University of Zilina, 010 26 Zilina, Slovakia
[3] Centre for Acoustic Microscopy, Russian Academy of Sciences, Kosygin St. 4, Moscow 117334, Russia

Received 1 June 2002
Published 25 October 2002
Online at stacks.iop.org/JPhysCM/14/11305

**Abstract**

Bulk samples of superhard phases of fullerites were prepared by high-pressure (15 GPa) and high-temperature treatment of pure pristine $C_{60}$ and $C_{70}$ for the first time. We applied the acoustic microscopy technique to measure the longitudinal and shear sound velocities and determine the elastic constants of the fullerite specimens. Acoustic microscopy images reflecting the microstructure of the fullerite specimens were obtained.

## 1. Introduction

It is well known that high-pressure high-temperature (HPHT) treatment of solid $C_{60}$ leads to the formation (depending on parameters and conditions of treatment) of several 2D and 3D polymeric phases [1–3]. Certain of them are superhard, ultrahard and ultrahigh-modulus materials [3, 4]. The specimen interior is therefore of great interest. HPHT-sintered specimens are small (1–3 mm) and sometimes have inner cracks due to stress relaxation during cooling. Acoustic microscopy is known to be a method uniquely suited for studying small opaque specimens [5]. It allows one not only to 'screen' a sample and thereby to control the presence of defects but also to follow the mapping of the local elastic properties. The elastic properties are specified by the intermolecular bonding and nanostructural organization of a substance. Their determination can provide a designation for the specimen's microstructure. The first experiments involving measurement of the elastic properties were carried out with $C_{60}$ and $C_{70}$ phases created using HPHT at a pressure of 15 GPa and in the temperature interval 670–1820 K.

  

## 2. Experimental details

HPHT synthesis of the samples was carried out from the $C_{60}$ (99.98%) and $C_{70}$ (99.2%) original powders for a time ∼1 min using an improved toroid-type apparatus. Prior to the experiments, the apparatus was pressure calibrated on the basis of the polymorphic transitions in Ba (12 GPa), Pb (13 GPa), ZnSe (13.7 GPa) and ZnS (15 GPa). Temperature was measured directly by Pt/Pt–Rh thermocouples. The bulk hard samples of $C_{60}$ and $C_{70}$ were obtained under a pressure of 15 GPa at a variety of temperatures (670, 820, 1120, 1470 and 1820 K). The dimensions of the specimens were up to 3 mm in diameter and 3 mm in height. To carry out ultrasonic studies, the upper and lower faces of the cylindrical specimens were polished after the synthesis.

The density of the specimens was measured by the flotation method using mixtures of di-iodomethane and acetone liquids of different concentrations.

A wide-field pulse scanning acoustic microscope (WFPAM) was used in a reflection mode at the driving frequency $f = 50$ MHz to measure local values of the ultrasonic velocities and elastic moduli (microacoustic technique) and to visualize the bulk microstructure of a specimen (scanning acoustic microscopy). The method makes it possible to measure elastic characteristics of small specimens and inclusions. The mean diameter of the acoustic spot on the specimen face was below 100 $\mu$m. The experimental procedure was described in detail previously [6].

We measured longitudinal and shear sound velocities, recording echo–signal oscillograms (A scans). The time interval $\tau_L$ between the signals reflected at the front (B signal) and the back (L signal) faces of the sample determines the magnitude of the longitudinal sound velocity $V_L$:$V_L = 2d/\tau_L$, where $d$ is the specimen thickness (the time-of-flight method). The transverse wave velocity magnitude was derived from measurements of the time intervals $\tau_L$ for the longitudinal wave and $\tau_{LT}$ for the mixed propagation mode: $V_t = d/(\tau_{LT} - \tau_L/2)$.

Local and mean elastic moduli were calculated from the measured velocities and densities of the polymerized fullerite samples. Some of $C_{60}$ samples had values of the local bulk and Young's moduli much higher than those of diamond, but the single $C_{70}$ samples had moduli comparable to those of diamond.

Acoustic microscopy images of the fullerite specimen microstructures were obtained (B and C scans). The B-scan mode was used to obtain the transverse sections of the objects.

B-scan images of plane-parallel samples reveal significant changes of the echo's arrival time along the scanning line for both the longitudinal and the shear waves. These time variations depend on the spatial distribution of the elastic properties of the samples.

## 3. Results and discussion

The bulk density $\rho$ of the specimens was measured with an accuracy of $\pm 0.05$ g cm$^{-3}$. It varied in the range 2.55–3.28 g cm$^{-3}$ for the $C_{60}$ samples and 2.34–2.90 g cm$^{-3}$ for the $C_{70}$ samples according to the synthesis parameters (figure 1). The maximum value of $\rho$ is evident for the $C_{70}$ specimen sintered at $T = 1120$ K.

Sound velocity data for $V_L$ and $V_t$ were obtained from A-scan profiles with an accuracy of ∼3%. The data were used to calculate elastic moduli, such as the bulk modulus $K$, the shear modulus $G$ and Young's modulus $E$. The local values of both longitudinal and transverse wave velocities as well as the values of the density increase significantly at $T > 1100$ K for the $C_{60}$ specimens while for the $C_{70}$ specimens the same elastic parameters lead to maximum values at identical temperatures. Figure 2 depicts the mean values of the sound velocities for hard $C_{60}$ and $C_{70}$ samples. The dependences of the elastic moduli on treatment temperature for hard $C_{60}$ and $C_{70}$ are presented in figures 3 and 4.

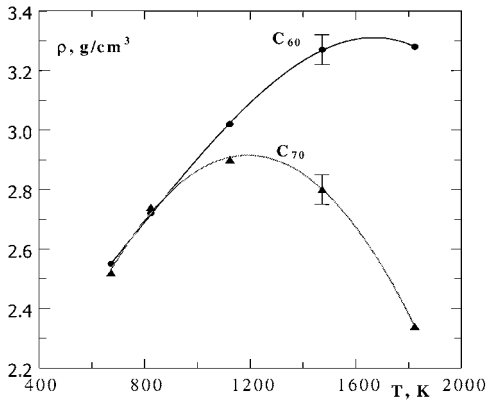


**Figure 1.** The treatment temperature dependence of the mean densities for hard $C_{60}$ and $C_{70}$.

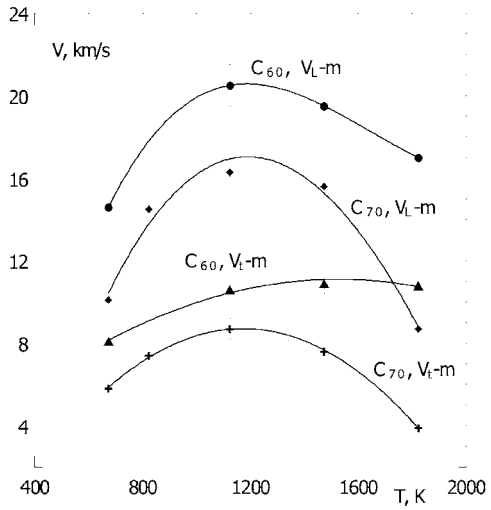


**Figure 2.** The treatment temperature dependence of the mean sound velocities for hard $C_{60}$ and $C_{70}$.

All the values of elastic parameters for the samples represented in the figures are averaged ones. However, we observed a large sound velocity variation along the scan direction line. The sound velocity has the highest value near the specimen periphery and the lowest one in the central part. It should be noted that the radial variation of the sound velocity was not symmetric. It varied with the angular variation of the scanning line in the B scans.

Figure 5 presents a typical B-scan image for fullerite samples, namely for the $C_{70}$ one created at 1470 K. The echoes from the front face of the sample give the upper straight bright line in the image. The reflections of the longitudinal and the shear waves from the bottom of the sample are depicted by the downward-flexed lines. We can conclude that these curved and discontinuous lines relate to the echoes of the ultrasonic waves reflected from the sample bottom. Their curvature indicates decrease of propagation time—that is, the rise of the sound velocity—towards the edges.

As was reported in [6], B scans also reveal defects inside the specimens. The disruption of the bottom reflections in figure 5 may indicate cracks or an internal boundary making a big angle with the specimen face. They are very much evident also in the ordinary acoustic

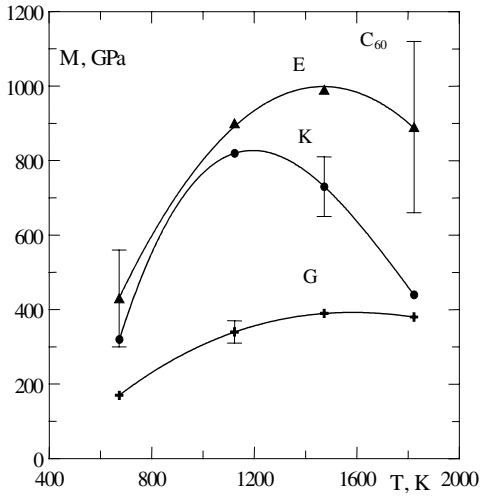


**Figure 3.** The elastic moduli of HPHT-prepared $C_{60}$.

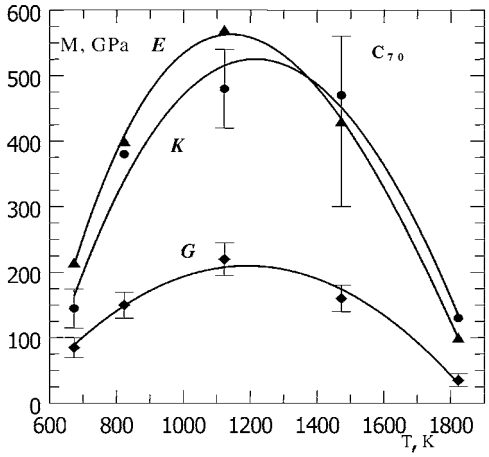


**Figure 4.** The elastic moduli of HPHT-prepared $C_{70}$.

images (C scans) for this sample (figure 6). While the image of the front surface reflects only the grinding traces, the image formed by the bottom echo shows heterogeneity of the interior. The extended crack (the breach in the B-scan lines) originated from relaxation of the stressed state during sample quenching.

## 4. Conclusions

Ultrahard and superhard fullerites are a new class of carbon materials produced recently by bulk polymerization of $C_{60}$ fullerenes under HPHT treatment. Elastic properties of solid $C_{60}$ in different metastable phases synthesized under HPHT conditions (within a wide range of pressure $P = 5$–$13$ GPa and temperature $T = 500$–$1870$ K) have been measured by us previously [1–4, 6, 7].

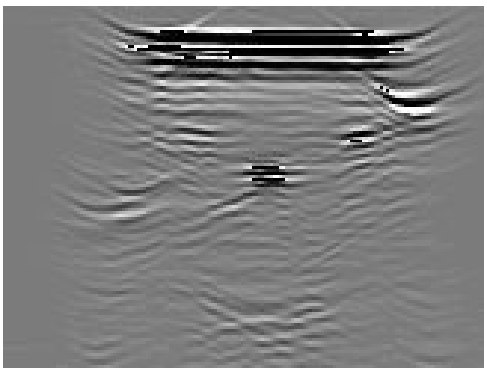

**Figure 5.** A B-scan image for $C_{70}$ created at 1473 K.

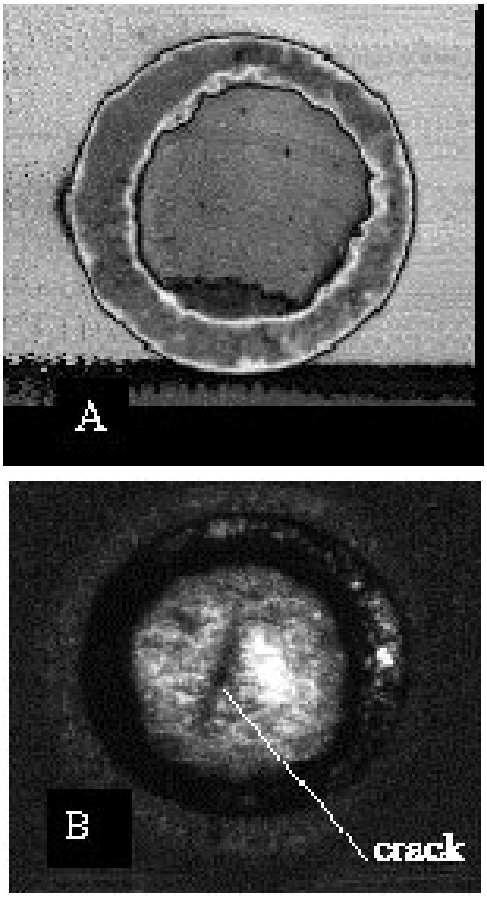


**Figure 6.** C-scan images of front (A) and bottom (B) surfaces of a $C_{60}$ sample.

The bulk elastic moduli $K$ and the shear moduli $G$ for 3D polymerized $C_{60}$ and $C_{70}$ under a pressure of 15 GPa were compared with those of diamond. The samples of $C_{60}$ produced at the temperatures $T = 1120$–$1820$ K possess unique mechanical properties including the

highest value of the longitudinal sound velocity ($V_L = 22$ km s$^{-1}$). The values of the bulk modulus ($K \approx 600$–$900$ GPa) are substantially greater than the bulk elastic moduli of diamond ($K \approx 440$–$490$ GPa). The essential elastic heterogeneity of most HPHT states has been demonstrated.

We consider the structure of the samples synthesized in the temperature range of 900–2000 K as a highly $sp^3$-linked bulk polymer on the basis of fullerene molecules (perhaps deformed). We call it an ultrahard (for $C_{60}$ polymer) or hard (for $C_{70}$ polymer) amorphous cage nanostructure and have described it in [1–4].

The elastic heterogeneity results from the non-uniform distribution of pressure and temperature during the synthesis. Experimental results as well as model calculations indicate that the elastic properties correlate with the state of the fullerene molecules, the character and number of covalent bonds and the nanostructure of the material [7]. One of the effective ways to get information on the nanostructure of solid $C_{60}$, to allow classification and identification its diverse phases, is to measure the elastic properties.

## Acknowledgment

This work was supported by the National Foundation for Intellectual Collaboration 'Fullerenes and Atomic Clusters' (grant No 95-076).

## References

[1] Blank V D *et al* 1995 *Phys. Lett.* A **205** 208
[2] Blank V D *et al* 1996 *Mol. Mater.* **7** 251
[3] Blank V D *et al* 1998 *Rev. High Pressure Sci. Technol.* **7** 814
[4] Blank V D *et al* 1998 *Carbon* **36** 319
[5] Briggs A *et al* (ed) 1992 *Acoustic Microscopy* (Oxford: Oxford University Press)
[6] Prokhorov V M, Blank V D, Buga S G and Levin V M 1999 *Synth. Met.* **103** 2439
[7] Levin V M *et al* 2000 *J. Phys. Chem. Solids.* **61** 1017