

Nanoindentation and x-ray diffraction studies of pressure-induced amorphization in C-70 fullerene

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We have carried out high-pressure studies on a C-70 fullerene sample in a diamond anvil cell to 46 GPa at room temperature. Synchrotron energy dispersive x-ray diffraction studies were carried out to monitor the irreversible amorphization transformation followed by nanoindentation studies of the pressure-quenched samples. Micro-Raman studies indicate broad bands at 1570 and 1422 cm^{-1} indicative of an amorphous phase with a mixture of sp^2 - and sp^3 -bonded carbon. Nanoindentation studies on the quenched amorphous phase shows an elastic loading behavior with a hardness of 18 GPa, which is 2–3 times that of the surrounding steel gasket. Our results conclusively establish that the hard carbon phases can be produced from C-70 fullerene by application of pressure at room temperature. © 2000 American Institute of Physics. [S0003-6951(00)03832-8]

High-pressure high temperature (HPHT) studies on C-60 and C-70 fullerenes have gained a new impetus recently because of the synthesis of novel superhard amorphous phases, composites, and nanoscale networks based on carbon. A recent summary¹ of the mechanical properties of polymeric fullerenes prepared by high-pressure high temperature synthesis has shown that most polymeric phases of C-60 have Vicker's hardness of about 1 GPa while the amorphous phases can have hardness as high as 40 GPa (about 40% of the hardness of the bulk crystalline diamond of 100 GPa). Most of the earlier HPHT studies have focused on the bulk synthesis from C-60 and C-70 below 12 GPa using a large volume press followed by bulk hardness measurements of the quenched samples. However, the extended pressure and temperature regime offered by diamond anvil cell devices ($P=400$ GPa and $T=4000$ K) combined with nanoindentation studies on quenched samples offer new opportunities in characterization of pressure and temperature synthesized phases. Earlier structural and spectroscopic studies² on C-70 samples have shown formation of intermolecular bonds with the occurrence of polymerized phases at temperature above 100 °C at a pressure of 5 GPa. Pressurization of C-70 at 5 GPa and 800 °C resulted in an amorphous carbon phase² suggesting that the C-70 cage is less stable than C-60 at this condition. A recent Raman-scattering study³ of C-70 fullerene in a diamond anvil cell to 51 GPa has documented formation of an irreversible amorphous phase on compression starting at a pressure as low as 12 GPa. However, *in situ* x-ray diffraction data on C-70 fullerene is required to precisely monitor the change in crystalline structure and eventual completion of the amorphization transformation. Also, the mechanical properties of the pressure quenched amorphous phase produced by compression at room temperature need to be characterized for comparison with other superhard amorphous phases⁴ produced by the HPHT techniques. It should be pointed out that hardness measurements on pressure-temperature quenched samples in a diamond cell

device is a challenging endeavor as the sample size is limited to 25–150 μm in diameter depending on the highest pressure required in a study. We report a new experimental study of nanoindentation hardness measurements on samples of 150 μm in diameter that have been pressure treated in a diamond anvil cell device. These studies can be extended to a variety of new materials synthesized by application of high pressures and high temperatures in diamond anvil cell devices.

C-70 fullerene of sample purity 99% was purchased from Alfa AESAR. Prior to loading in a diamond anvil cell, C-70 sample was annealed at 400 °C in an argon atmosphere for 2 h to minimize the amount of solvent present in the sample before experiments. Three different high-pressure experiments in a diamond anvil cell were carried out to investigate the effect of nonhydrostatic pressure conditions on the amorphization transition in C-70 fullerene. All high-pressure experiments employed diamonds with culet size of 600 μm and sample was placed in a chamber of 150 μm in diameter drilled in a spring steel gasket. Two experiments were carried out without the use of any pressure medium and a third experiment employed 4:1 methanol: ethanol hydrostatic pressure medium. Energy dispersive x-ray diffraction spectra were recorded at the superconducting wiggler beamline X-17C at National Synchrotron Light Source, Brookhaven National Laboratory. The x-ray diffraction experiments were performed with a microcollimated x-ray beam with a beam size of 30 $\mu\text{m}\times 30$ μm . Micro-Raman studies on pressure-quenched samples were carried out with a 514.5 nm green excitation from an argon ion laser employing a 0.6 m spectrometer fitted with a super-notch filter. Nanoindentation studies were carried out using a Materials Testing System-Nano Instruments XP with a continuous stiffness option and an atomic force microscope attachment.

Figure 1 shows energy dispersive x-ray diffraction pattern of a C-70 sample in a diamond anvil cell at a pressure of 4 GPa, 17 GPa, 27 GPa, 43 GPa, and at ambient condition after release of pressure. The starting C-70 sample at room pressure shows a mixture of face centered cubic phase ($a = 14.95 \pm 0.04$ Å) and hexagonal close packed phase ($a = 10.67 \pm 0.03$ Å, $c = 16.75 \pm 0.04$ Å). On increasing pres-

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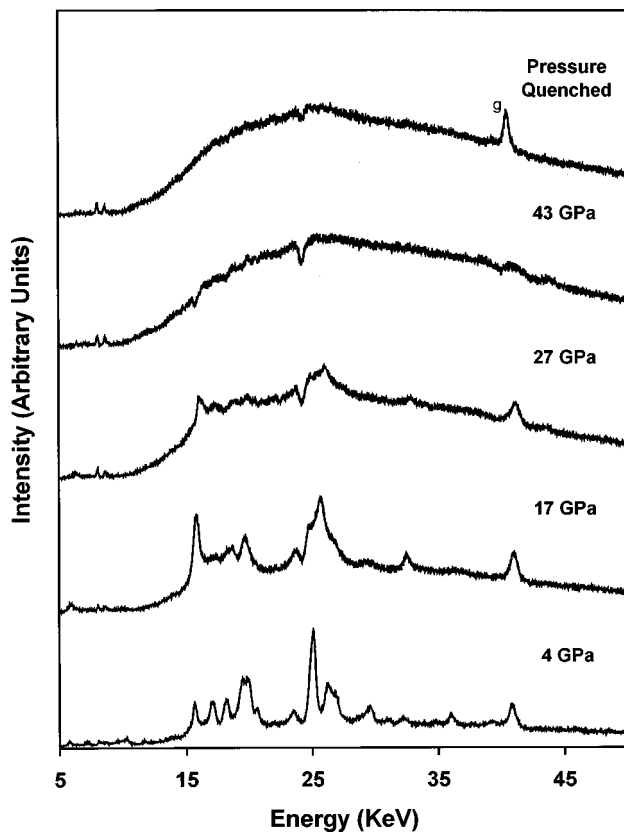


FIG. 1. Energy dispersive x-ray diffraction spectrum of C-70 in a diamond anvil cell on increasing and decreasing pressure. The product of Energy and Interplanar spacing $Ed = 81.799 \pm 0.005$ keV Å. The diffraction peaks gradually broaden and sample transforms into a pure amorphous state above 35 GPa. The amorphous phase is retained on decreasing pressure at ambient conditions. Peak marked "g" is from the surrounding steel gasket.

sure, we see a general broadening of diffraction peaks above 12 GPa and with an eventual loss of diffraction pattern above 35 GPa. In the highest-pressure diffraction pattern recorded at 43 GPa, no residual crystalline phase could be detected. The amorphous phase is retained on decreasing pressure as shown in the diffraction pattern of the pressure-quenched

sample in Fig. 1. The x-ray diffraction patterns were similar in all three experiments with or without the use of pressure medium. The pressure-volume curve or equation of state of C-70 is sensitive to state of stress in the sample; however, the eventual transformation to the amorphous state is observed in all three experiments. As shown later in this letter, amorphous carbon phase formed at high pressure is a high strength material and would support significant shear stresses in the sample under nonhydrostatic conditions. Further high pressure experiments with a truly hydrostatic medium like helium may be needed to investigate the role of nonhydrostatic stresses on the onset of amorphization in C-70 fullerene under high compressions.

Figure 2 shows the micro-Raman spectra of the pressure quenched C-70 sample using a green laser excitation of 514.5 nm from an argon ion laser. It shows a broad band centered at 1570 cm^{-1} with a shoulder band at 1420 cm^{-1} . We do not observe any significant intensity at 1332 cm^{-1} typical of a crystalline diamond phase or at 1350 cm^{-1} typical of the *D* band of the nanocrystalline graphite. We can clearly say that the amount of crystalline diamond phase in the quenched samples is below the detection limit of 1% of Raman and x-ray diffraction. The observation of a single broad band between 1550 and 1570 cm^{-1} range is typical of a class of amorphous carbon phases produced by a variety of other techniques such as pulsed laser deposition, cathodic arc deposition, ion beam methods, and chemical vapor deposition methods. The amorphous carbon phase with this characteristic Raman signature is believed to contain some fraction of sp^3 -bonded carbon and leads to hard and optically transparent films. Our pressure-quenched sample is not optically transparent as our starting sample was a polycrystalline C-70 and optical response may be complicated by the slight amount of impurities present in the sample.

Figure 3 shows the results of nanoindentation study on a pressure quenched C-70 sample from a peak pressure of 35 GPa without any hydrostatic pressure medium. The load displacement curve is shown both for the surrounding steel gas-

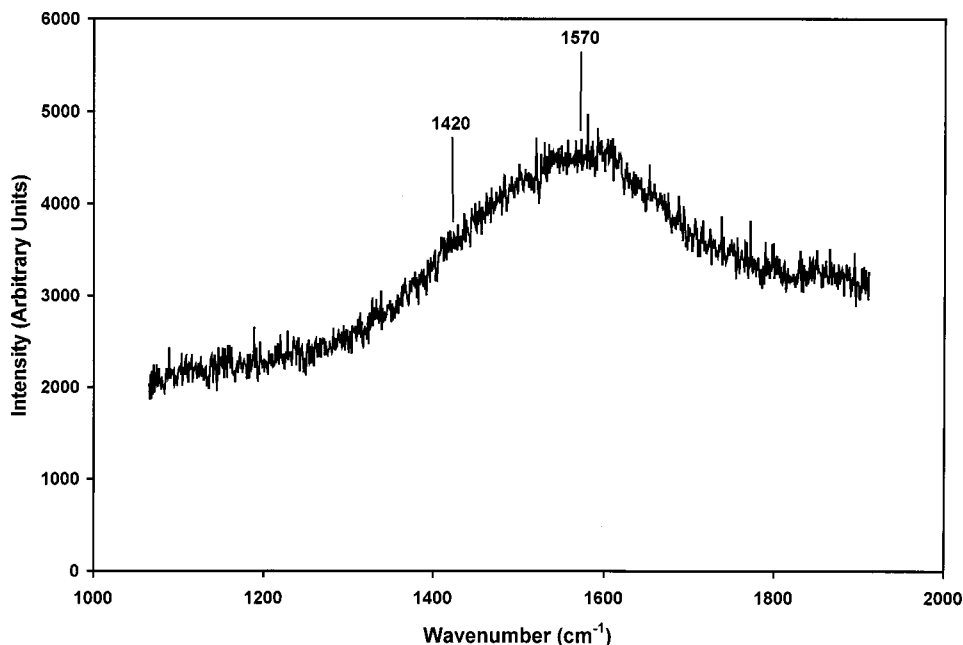


FIG. 2. Micro-Raman spectrum from an amorphous phase after compression to 46 GPa in a diamond anvil cell. The laser excitation was 514.5 nm from an argon ion laser. The broad peak from the amorphous carbon can be fitted as a doublet with components at 1570 and 1420 cm^{-1} as indicated.

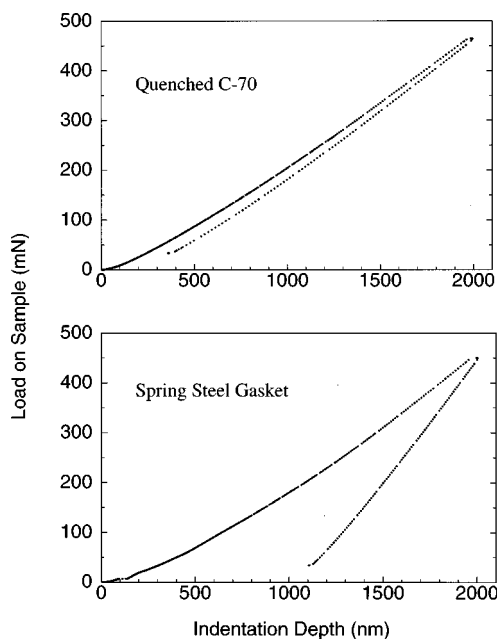


FIG. 3. Load displacement curves for the spring steel gasket (lower panel) and pressure quenched C-70 sample (upper panel) as a function of penetration depth into the sample. C-70 sample was quenched from a pressure of 35 GPa. The steel gasket shows quite a large plastic deformation while the quenched C-70 sample showing mostly elastic behavior characteristic of a hard material.

ket and pressure quenched C-70 sample. This data was obtained by locating the diamond indenter (Berkovich diamond tip radius less than 50 nm) on top of the gasket and sample regions, respectively. It is clear from Fig. 3 that the steel gasket exhibits a large amount of plastic flow as shown by the large hysteresis in the loading and unloading curves. The final depth of the indentation once the load is removed is approximately 56% of the maximum indent depth. In contrast, the loading and unloading curves for the pressure-quenched C-70 sample exhibit a small amount of hysteresis typical of a highly elastic material. In this case, the final depth of indentation is only about 20% of the maximum indent depth.

Figure 4 shows nanoindentation hardness data with increasing depth to 2000 nm for the spring steel gasket as well as for the pressure-quenched C-70 sample. Calibration of the indenter tip area function was obtained using a silica standard with a known hardness of 9.5 GPa. The measured average hardness for nine indentations made on the C-70 sample is 18.3 ± 1.2 GPa, whereas the average measured hardness of the spring steel gasket was 7.3 ± 0.3 GPa.

It is important to note that this hard amorphous carbon phase synthesized at high pressure of 46 GPa from C-70 is synthesized at room temperature without any thermal activation. All previous hard amorphous carbon phases from C-60 and C-70 fullerenes required temperatures in excess of 800 °C and pressure in the range of 5–12 GPa. This pressure quenched amorphous phase from C-70 sample is distinct from the HPHT synthesized amorphous phases^{1,4} and tetrahedral amorphous carbon⁵ in terms of its Raman and x-ray diffraction spectra. Also, the hardness value of 18 GPa in our case is lower than the hardness value of 40–90 GPa for a

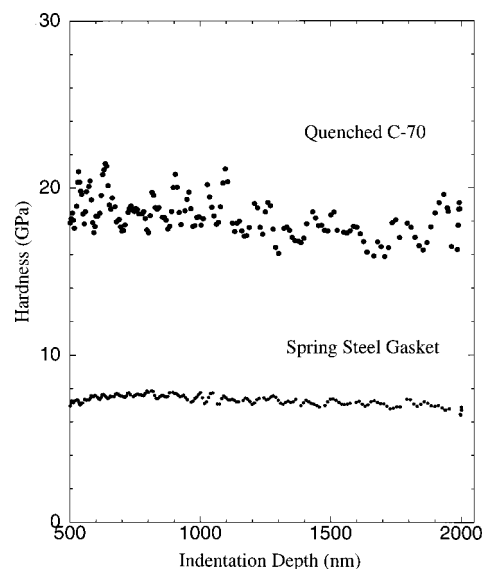


FIG. 4. The measured hardness as a function of indentation depth using the continuous stiffness measurement method. The hardness value for quenched C-70 sample is about 2–3 times that of the surrounding spring steel gasket.

variety of other hard amorphous carbon phases.^{1,4,5} The hardness of amorphous carbon in this work is 50–100 times greater than that of graphite and is 2–3 times the hardness value of the work hardened steel gasket surrounding the quenched sample.

In conclusion, our high-pressure x-ray diffraction study on C-70 has clearly documented a gradual amorphization phenomenon with the transformation to amorphous phase completed above 35 GPa. The amorphous phase is retained on decreasing pressure as confirmed also by micro-Raman spectroscopy and x-ray diffraction. Nanoindentation study on pressure-quenched samples have revealed hardness of 18.3 GPa which is 2–3 times the hardness of surrounding steel gasket. Nanoindentation studies demonstrated in this letter can be applied to other novel materials quenched from high-pressure high temperature conditions in diamond anvil cell devices.

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