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Pressure-induced phase transitions of C₇₀ nanotubes

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Abstract

Single crystalline C₇₀ nanotubes having a face-centered-cubic (fcc) structure with diameters in the nanometer scale were synthesized by a facile solution method. *In-situ* high pressure Raman spectroscopy and X-ray diffraction have been employed to study the structural stability and phase transitions of the pristine sample. We show that the molecular orientation related phase transition from the fcc structure to a rhombohedral structure occurs at about 1.5 GPa, which is ~1 GPa higher than in bulk C₇₀. Also, the C₇₀ molecules themselves are more stable in the nanotubes than in bulk crystals, manifested by a partial amorphization at ~20 GPa. The crystal structure of C₇₀ nanotubes could partially return to the initial structure after a pressure cycle above 30.8 GPa, and the C₇₀ molecules were intact up to 43 GPa. The bulk modulus of C₇₀ nanotubes is measured to be ~50 GPa, which is twice larger than that of bulk C₇₀.

Keywords: Fullerene, nanocrystal, size effect, amorphization.

Introduction

As an important member of the carbon family, fullerenes have attracted much attention from both chemists and physicists due to their extraordinary properties.^{1,2} The compressibility of the single buckminsterfullerene molecule has been calculated to be 700-900 GPa, much higher than that of diamond (~440 GPa).^{3,4} However, high pressure studies show that in fcc C₆₀ crystals amorphization occurs due to a collapse of the C₆₀ molecules at ~22 GPa, possibly due to the intermolecular interaction under high pressure.⁵⁻⁷ C₇₀ is the second most abundant fullerene and has many properties which are superior to those of C₆₀, such as conductivity, photoconductivity and optical limiting performance.⁸⁻¹¹ Above room temperature, the freely rotating C₇₀ molecules form a close-packed lattice. The structure is usually face centered cubic (fcc), but may sometimes be hexagonal (hcp). On compression or cooling the molecules minimize the lattice volume by aligning the molecular axes perpendicular to the close-packed planes, changing the free rotation to uniaxial rotation and distorting the fcc lattice into a rhombohedral structure. The pressure-temperature phase diagram of C₇₀ has been mapped,¹²⁻¹⁸ but many questions remain. The fcc-rhombohedral phase line was identified by Kawamura et al.,¹⁵ and anomalies associated with changes in molecular rotation or structure have found in compression,¹⁶ transport,¹⁸ and spectroscopic^{12,13} studies. In addition to these properties, previous high pressure studies found that the cage structure of C₇₀ can be maintained even after a cycling of 31 GPa,¹² indicating a higher pressure stability for C₇₀ than for C₆₀. This is probably connected with its low molecular reactivity. An amorphization of the C₇₀ lattice is observed at high pressures. Chandrabhas *et al.* found that the amorphous phase of C₇₀ was reversible when released from 31.1 GPa,¹³ while Wasa *et al.* found that the transition was irreversible after treatment above 35 GPa.¹⁴ However, both the low pressure structural phase diagram and the reversibility of the high pressure amorphization in C₇₀ are still under discussion and further high pressure studies on C₇₀ are necessary.

From another perspective, our recent studies have shown that in nano-scale C₆₀ crystals, some properties are influenced by the decrease in crystallite size, such that, for example, the bulk modulus and

phase transition pressure increase.^{19,20} For C₇₀ nanocrystals, such comparative high pressure studies are still missing. In a recent study, we found that we could prepare C₇₀ nano-sized crystals with different shapes by a solution method similar to that reported for C₆₀ nano-crystals. We now want to extend this study and investigate how the size effect plays a role for the high pressure properties of C₇₀ nanocrystals.

C₇₀ nanotubes were synthesized by introducing isopropyl alcohol into a saturated C₇₀ solution in m-xylene, following by a high pressure treatment in vacuum. The outer diameters of these tubes range from 500 to 800 nm and the wall thickness was in the range of 100 to 200 nm. The as-synthesized C₇₀ nanotubes have an fcc structure. We have carried out *in-situ* Raman scattering measurements on C₇₀ nanotubes under pressure up to 38 GPa. An orientational ordering phase transition was observed at a pressure between 1.59 and 2.26 GPa. Raman spectra measured on C₇₀ nanotubes released from different high pressures suggested that the cage structure of C₇₀ molecule persist to at least 43 GPa, which is significantly higher than for the bulk C₇₀ counterpart. The C₇₀ nanotubes transformed to amorphous carbon at pressure ~51 GPa. *In-situ* high pressure XRD measurements were carried out up to 30.8 GPa. A phase transition from the fcc to the rhombohedral structure was observed at about 1.43 GPa. The rhombohedral structure then transformed reversibly into an amorphous structure at 20 GPa. And this pressure-induced amorphization of C₇₀ nanotubes could recover to the initial fcc structure after the cycling of 30.8 GPa. From the in situ XRD measurements the bulk modulus of the C₇₀ nanotubes was found to be much larger than that of bulk crystals.

Experimental section

C₇₀ nanotubes were fabricated by introducing isopropyl alcohol into a saturated solution of C₇₀ in m-xylene with the volume ratio of 1:10, following by heat treatment on the as-grown samples at 150°C in vacuum for 5 hours.²⁰ The morphologies of samples were characterized by scanning electron microscopy (SEM, JEOL JSM-6700F). X-ray diffraction (XRD, Rigaku D/max-RA, CuK α 1 radiations $\lambda=1.5406$ Å) showed that the pristine C₇₀ nanotubes crystallize in the fcc structure.

For high pressure studies, samples were loaded into a T301 stainless steel gasket with a 100 μm diameter hole. Silicone oil was used as pressure medium, *in-situ* high pressure Raman spectra were carried out at pressures up to 38 GPa using a Renishaw inVia Raman Microscope with a 514.5 nm Ar^+ laser line as excitation. *In-situ* high pressure angle-dispersive x-ray diffraction (ADXRD) measurements up to about 30.8 GPa were performed at Beijing Synchrotron Radiation Facility at ambient temperature. To find the pressure for the irreversible amorphization of C_{70} nanotubes caused by the collapse of C_{70} molecular cages, we also recorded Raman spectra on samples decompressed from different pressures. Another pressure medium, 4: 1 methanol-ethanol mixture has also been used for comparison purpose and to clarify the influence of the pressure medium on the Raman peaks for the C_{70} nanotubes decompressed from high pressure.

Figure 1. (a) SEM and TEM (insert) images, (b) XRD patterns and (c) Raman spectra for pristine C_{70} nanotubes.

Results and discussion

A representative SEM image of as-grown nanotubes is shown in Figure 1a. The image shows that the as-grown samples have tubular shapes, with outer diameters in the range of 500-800 nm. The insert in Figure 1a shows the TEM image of one single C_{70} nanotube. From the TEM image, we can observe its hollow morphology clearly, which further confirm its tubular shape. To study the structure of the heat-treated C_{70} nanotubes, an XRD measurement was carried out in the 2θ range of 5-30°. The XRD pattern is shown in Figure 1b. There are four diffraction peaks indexed as the (111), (220), (311) and (024) reflections of an fcc structure, respectively. The lattice constant is $a = 1.492$ nm, which is similar to

that of bulk crystals measured at room temperature.^{21,22} And the small peak near 10 degree (marked with *) probably arise from the presence of a slight stacking fault, which was also observed in previous report on C₇₀ bulk crystals.²⁷

Raman spectroscopy is a powerful tool to characterize C₇₀. For pristine C₇₀ at room temperature, 53 Raman active modes are predicted (12A'₁+22E'₂+19E'₁) from the D_{5h} point group according to group theory.^{23, 24} Upon polymerization, one of the most characteristic feature is the split of the E'₂ mode (located at 1567 cm⁻¹ for pristine C₇₀) into two peaks due to the reduced symmetry.^{25, 26} The Raman spectrum of the pristine sample was shown in Figure 1c, from the insert in it we can observe a single Raman peak centered at 1567 cm⁻¹, thus indicating that the C₇₀ nanotubes are in a monomeric state, as indicated by the fcc structure.

Figure 2. *In-situ* Raman scattering spectra of C₇₀ nanotubes at high pressures.

In-situ high pressure Raman spectra obtained under pressure up to 38 GPa are shown in Figure 2. The Raman spectrum recorded at 0.44 GPa shows more than 10 peaks, and all peaks shift towards higher frequency with increasing pressure. At pressures higher than 10.2 GPa, most of the peaks become broad or too weak to be observed and only the strongest broad peak at ~1567 cm⁻¹ can be observed clearly. This peak persisted to 18.2 GPa, which indicates that the C₇₀ structure still remained up to this pressure. At higher pressures up to 26.8 GPa, the Raman peaks became broader and diffuse, and the spectra showed a broad band around 1700 cm⁻¹, which has been identified as an evidence for the

amorphization of C_{70} under pressure.¹⁴ This characteristic “amorphous” band becomes more evident at 38 GPa.

To study the phase transition in C_{70} nanotubes, the pressure dependence of the three strongest Raman modes below 9 GPa is shown in Figure 3a. As shown in the spectra, these three characteristic peaks (one E_1 mode and two E_2 modes) persist to the highest pressure. Detailed studies of the pressure dependence $d\omega/dp$ were carried out on these three peaks which at atmospheric pressure were found at from 1229 cm^{-1} , 1470 cm^{-1} and 1567 cm^{-1} , respectively. A very clear change occurs in $d\omega/dp$ between 1.59 and 2.26 GPa, indicating a phase transition. In addition, to further study the orientation ordering transition pressure of C_{70} nanotubes, we have also investigated the dependence of the full width half at maximum (FWHM) of the strongest peak initially located at 1567 cm^{-1} . As shown in Figure 3b, a rapid decrease in $\Delta\omega_0/\Delta\omega_p$ (ratio of FWHM for the E_2 mode at ambient pressure to that under high pressure) also occurs between the pressure of 1.59 GPa and 2.26 GPa, which is consistent with the results of the pressure dependence of the Raman peaks shown above. The large change in the slopes $d\omega/dp$ of the three modes confirms the orientational ordering transition in this pressure range.

A similar anomaly in $d\omega/dp$ at about 1 GPa was also observed for several C_{70} Raman lines by Sood

Figure 3. (a) Pressure dependence of the peak positions of the Raman spectra for C_{70} nanotubes. The three peaks had initial positions of 1229 cm^{-1} (●), 1470 cm^{-1} (▲) and 1567 cm^{-1} (■), respectively. The unit of $d\omega/dp$ is $\text{cm}^{-1}/\text{GPa}$. (b) Pressure dependence of the inverse of the full width at half maximum (FWHM) for the 1567 cm^{-1} peak.

et al.,¹³ and attributed to an orientational ordering phase transition from fcc to rhombohedral structure as observed by x-ray diffraction.²⁷ In contrast, Maksimov and co-workers found two anomalies at about 2 and 5.5 GPa, respectively.¹² They assigned these two anomalies to phase transitions corresponding to a freezing of the rotation around the short and long axes of the C₇₀ molecules, respectively. In our studies on C₇₀ nanotubes, only a single anomaly was observed in the pressure dependence of the peak positions and the peak width, which is consistent with that of Raman studies by Sood *et al.*¹³ and the XRD studies by Christides *et al.*²⁷ Therefore, we interpret our Raman results as signs for an orientational ordering phase transition from fcc to rhombohedral in our C₇₀ samples. The slightly higher transition pressure in our study (1.59 compared to 1 GPa) of C₇₀ nano crystals compared to C₇₀ bulk crystals is probably due to the nanometer size of our sample. This also agrees with earlier comparative studies on C₆₀ nano crystals and bulk crystals.

To investigate at which pressure irreversible amorphization of C₇₀ nanotubes occurs, Raman scattering spectra were recorded on C₇₀ nanotubes released from different pressures. As shown in Figure 4, the samples were measured after removal from the diamond anvil to avoid the Raman signal from diamond. The Raman spectra for the samples released from a maximum pressure 18.2 GPa shows features practically identical to those for pristine C₇₀ nanotubes. We thus conclude that the amorphization observed at this or lower pressure is almost fully reversible. In the spectrum of C₇₀ nanotubes released from 43 GPa, most of the peaks from pristine C₇₀ disappear. However, the peak at

Figure 4. Raman scattering spectra of C₇₀ nanotubes taken at ambient pressure after decompression from various pressures, using (a) silicon oil and (b) 4: 1 methanol-ethanol mixture as pressure transmitting medium, respectively. The peaks marked with “*” are from the pressure medium.

1567 cm^{-1} characteristic for C_{70} molecules can still be observed, although it broadens significantly in comparison to the peak for pristine C_{70} nanotubes. This result indicates that the amorphization of our C_{70} nanotubes was still partially reversible up to this pressure. Finally, for the C_{70} nanotubes released from the maximum pressure 51.1 GPa, all the characteristic Raman peaks for C_{70} disappeared, and a broad and asymmetric band around 1600 cm^{-1} is observed in the Raman spectrum. This Raman spectrum was very similar to that of amorphous carbon containing sp^3 bonded atoms, indicating amorphization of C_{70} nanotubes after such high pressure treatment.^{28, 29} The pressure of 51.1 GPa needed for the full and irreversible amorphization of C_{70} nanotubes in our experiments is significantly higher than that at which bulk C_{70} crystals (35.1 GPa), indicating that the size effect in our sample possibly plays an important role.

In addition, in the Raman spectra of C_{70} nanotubes decompressed from 43 and 51.1 GPa in silicone oil, several new wide peaks were observed at 190 cm^{-1} , 491 cm^{-1} , 688 cm^{-1} , 699 cm^{-1} and 790 cm^{-1} (see Figure 4a, marked with *). To investigate if these peaks arise from pressure-induced transformations in our sample or as an effect of the pressure medium, we performed similar high pressure experiments but replacing the silicone oil with a 4: 1 methanol-ethanol mixture. In this experiment none of the peaks mentioned above can be detected in the Raman spectra (see Figure 4b). We conclude that the peaks probably stem from silicone oil that has been polymerized under high pressure. However, except for the difference noted above concerning the silicone oil Raman peaks, the experiments with methanol-ethanol as pressure medium for the samples decompressed from ~20, 43 and 51 GPa verify clearly the results obtained using silicone oil as pressure medium. These results further confirm that the pressures needed for irreversible amorphization of C_{70} nanotubes were much higher than that needed for bulk crystals, independent of the pressure medium used.

To further investigate the nature of C_{70} nanotubes under high-pressure, ADXD patterns were recorded at ambient temperature. As shown in Figure 5a, the structure is fcc with a lattice constant $a = 14.9 \text{ \AA}$ at the pressure 0.22 GPa, which is similar to that at ambient pressure. As the pressure reaches 1.43 GPa, the fcc (311) peak splits into two peaks. The d-spacings are shown as functions of pressure in

Figure 5. (a) In-situ ADXD patterns of C₇₀ nanotubes under different pressures, (b) pressure dependence of the XRD peaks for C₇₀ nanotubes, (c) XRD diffraction patterns of C₇₀ taken at ambient pressure after decompression from 30.8 GPa, and the insert shows the SEM images of C₇₀ nanotubes decompressed after the cycling of this presser (d) equation of state of C₇₀ nanotubes.

Figure 5b. Both the (220) and (311) shift with pressure. Furthermore, it is found that an obvious anomaly was observed at the same pressure for both the (202) and (311) peaks. This phenomenon indicated an occurrence of a phase transition, in agreement with previous work and our Raman results. The new phase could be indexed as a rhombohedral unit cell, and the observed three peaks were indexed to be the (202), (311) and (113) peaks of a rhombohedral phase. In the previous literature on C₇₀ bulk crystals, this fcc-rhombohedral phase transition was reported to be due to the molecular orientation with respect to the (111) direction.²⁷ When the pressure was increased to ~18.39 GPa, most of the peaks became too weak to be observed, and only the strongest (202) peak from the rhombohedral structure remained broad peak. This peak persisted until the pressure of 26.2 GPa, which indicated that the pressure-induced amorphization was completed at this pressure. After pressure cycling to 30.8 GPa, the XRD patterns was recorded at ambient pressure. The XRD patterns for C₇₀ nanotubes decompressed from 30.8 GPa are shown in Figure 5c. The two peaks assigned as the (220) and (311) peaks were again observed, and were almost identical to those for the pristine C₇₀ nanotubes. This result suggested that

the structural phase transition is reversible up to 30.8 GPa. Also, the SEM images of C₇₀ nanotubes decompressed from this pressure were shown in the insert in Figure 3c. Because of the influence of silicone oil remained on the surface of the samples, the images were not very clear, however, we can observe that the nanotubes still maintain their one-dimensional morphologies and well dispersed. We thus believe that the nanometer size was affecting the high pressure behavior up to this pressure.

High pressure XRD investigations by Christides *et al.* showed that an irreversible phase transition to an amorphous carbon phase occurred in C₇₀ bulk crystals when the pressure is up to 11 GPa.²⁷ In the high pressure Raman studies up to 31.1 GPa, Chandrabhas *et al.* reported that amorphization of C₇₀ bulk crystals was reversible,¹³ while an irreversible amorphization of C₇₀ was observed in the high pressure. Raman studies of Wasa *et al.*,¹⁴ indicating the collapse of C₇₀ molecular cages. In the present work, both the crystal structure and the molecular structure of our C₇₀ nanotubes persisted to much higher pressures than in bulk crystals.

The pressure-volume for the rhombohedral phase up to 9.5 GPa is shown in Figure 5d. The data were fitted using the Birch-Murnaghan equation of state:³⁰

$$P(V)=1.5B_0[(V_0/V)^{7/3}-(V_0/V)^{5/3}]*\{1+0.75(B_0'-4)[(V_0/V)^{2/3}-1]\}.$$

where B₀ is the bulk modulus, B₀' is its pressure derivative (dB₀/dP), and V₀ is the unit cell volume at ambient pressure. The fitted values for the bulk modulus (B₀) and its pressure derivative (B₀') were 49.3±1.5 and 1.5±0.2 GPa, respectively. A comparison of these values with data from earlier high-pressure experiment on C₇₀ bulk crystals,²⁷ shows that the bulk modulus of the C₇₀ nanotubes is significantly elevated. This result is probably due to the small crystallite sizes, which is similar to our former results on C₆₀ nanosheets.¹⁹

Previous theoretical calculations indicated that fullerene crystals will transformed to amorphous carbon, when the fraction of the pressure-induced *sp*³ intermolecular bonds increased to a certain value.^{31, 32} The reversibility of the high pressure phase C₇₀s on decompression is believed to be related to the relative strengths of the intermolecular (*sp*³) versus intramolecular interactions (*sp*²).¹³ If the former is sufficiently stronger, the molecules will be permanently distorted and/or destroyed, and the high

pressure amorphous phase will be irreversible on decompression.¹³ In addition, it was known that the intermolecular interaction depends strongly on the distance of the nearest C₇₀ molecules. In our sample, the bulk modulus of C₇₀ nanotubes is much larger than that of bulk materials, which indicates the molecular distance in C₇₀ nanotubes is much less compressible. Thus, under identical pressures, the intermolecular interaction of carbon atoms in C₇₀ nanotubes is thus much weaker than that in bulk crystals. It is now reasonable that it is more difficult to form irreversible amorphization in C₇₀ nanotubes, and C₇₀ molecule cages can persist to a higher pressure. Therefore, we believe that the nanosize effect of C₇₀ nanotubes is the crucial reason for the higher phase transition pressure.

Conclusion

In summary, to investigate the phase transitions and structural stabilities of single crystalline C₇₀ nanotubes with fcc structure, *in-situ* Raman spectra and X-ray diffraction patterns were recorded under high pressure. Both Raman and XRD indicate that a molecular orientation related phase transition, from the fcc structure to the rhombohedral structure, occurred in C₇₀ nanotubes at ~1.5 pressures. This pressure is about 1 GPa higher than that for C₇₀ bulk crystals. Raman and XRD results also revealed an amorphization of C₇₀ nanotubes at about 20 GPa. The C₇₀ nanotubes could partly retain to their initial crystal structure after a pressure cycle of 30.8 GPa. The cage structure of the C₇₀ molecules was preserved under pressures up to 43 GPa. Detailed investigation revealed that the bulk modulus of C₇₀ nanotubes was about 50 GPa, twice larger than that of a bulk crystal. The higher stability of both the crystal structure and the molecular structure of C₇₀ nanotubes is probably due to the higher bulk modulus induced by the nano size effect.

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