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Abstract: Structural property of a C₆₀-peapod sample under high pressure up to 25 GPa was investigated by in-situ synchrotron X-ray diffraction measurements with a diamond anvil cell. It was observed that C₆₀-C₆₀ distance in a carbon nanotube decreases with pressure from 0.956 nm at 0.1 MPa down to 0.845 nm at 25 GPa. It was also found that the distance value on complete release of pressure after compression remained to be much smaller than the its initial value. These experimental results indicate the polymerization of C₆₀ molecules in a carbon nanotube.

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Pressure-polymerization of C₆₀ molecules in a carbon nanotube

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Abstract

Structural property of a C₆₀-peapod sample under high pressure up to 25 GPa was investigated by in-situ synchrotron X-ray diffraction measurements with a diamond anvil cell. It was observed that C₆₀-C₆₀ distance in a carbon nanotube decreases with pressure from 0.956 nm at 0.1 MPa down to 0.845 nm at 25 GPa. It was

also found that the distance value on complete release of pressure after compression remained to be much smaller than the its initial value. These experimental results indicate the polymerization of C_{60} molecules in a carbon nanotube.

1 Introduction

High-pressure and high-temperature treatment of face centered cubic (fcc-) C_{60} crystal sample leads to various polymerized phases [1–8]. The pressure-polymerized fullerenes consist of hybrid networks of sp^2 and sp^3 carbon atoms and they have quite different physical and chemical properties from those of other crystalline carbon phases such as graphite, diamond, and fcc- C_{60} [9]. Similar polymerization of carbon nanotubes (CNTs) is expected and many high pressure experiments of CNTs have been performed [10–12]. However, the detailed structural property of CNTs is still not well understood.

C_{60} -peapods, a single-walled carbon nanotube (SWNT) including C_{60} molecules inside the tube, is attracting much interest. It is very interesting to investigate how the interactions between (i) tubes, (ii) tube and C_{60} -molecules, (iii) C_{60} -molecules in a tube change by external pressure. In this work, the structural property of C_{60} -peapod sample was investigated by in-situ synchrotron XRD measurements and it was compared with those of solid C_{60} and empty SWNT samples.

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2 Experimental

SWNT samples used in the present study were prepared by laser-ablation method [13]. The tube diameter was estimated to be 1.4-1.5 nm by Raman scattering (JASCO, NRF-2200) measurement of radial breathing modes (RBM), by TEM (JEOL, JEM-2010) and XRD (Rigaku, RINT-2200) measurements. For the preparation of C₆₀-peapod sample, after decapping the SWNTs, C₆₀ molecules were introduced into tubes by heating C₆₀ powders with SWNTs in a sealed quartz tube. The C₆₀-occupancy of the pods was estimated to be more than 80% by TEM observation.

In-situ XRD measurements under high pressure were performed with a diamond anvil cell at a beam line BL-10XU of SPring-8 (proposal number:2004A0448-ND2a-np, 2004B0296-ND2a-np). A 4:1 mixture of methanol and ethanol was used as a pressure transmitting medium. Pressure was determined by ruby fluorescence method. XRD patterns were observed with an imaging plate detector.

3 Results & Discussion

The XRD patterns of the SWNT and C₆₀-peapod samples under atmospheric pressure and at room temperature measured by a conventional powder diffractometer (“Fig. 2” in Ref. [12]) shows that the samples are well crystallized. Since the contribution of the structure factor of C₆₀ chain inside the tube reduces the total structure factor at the 100 peak position [13], the 100 peak intensity of the C₆₀-peapod sample is much lower than that of the SWNT sample, the observed XRD patterns confirmed us that C₆₀ molecules were

well filled in the tubes of the peapod sample. Strong G-band at about 1600 cm^{-1} and weak D-band at about 1330 cm^{-1} in Raman spectra (Fig. 1) indicate the high quality of the used SWNT and C_{60} -peapod samples. As shown in Fig. 1, a weak Ag(2) mode of C_{60} molecule was observed on the shoulder of the strong SWNT G-band peak in the Raman spectrum of the peapod sample. Although the exact position of the Ag(2) mode is an important signal for the polymerization of C_{60} molecules, it was hard to obtain well resolved C_{60} Raman peaks for the pressure treated peapod sample.

First, we describe the pressure-induced structural changes of empty SWNT samples. Two kinds of the empty SWNT samples were used in this work. One was closed-end SWNT (c-SWNT) sample having half fullerene caps at the ends of the tube and the other was decapped open-end SWNT (o-SWNT) sample. As we reported in previous paper [12], diffraction peaks of the c-SWNT sample disappeared above about 2 GPa (Fig. 2-(b)) while those of the o-SWNT sample could be observed at least up to about 10 GPa (Fig. 2-(a)). For the diffraction patterns observed at relatively low pressure in which several diffraction peaks could be clearly observed, we have done pattern fitting (Fig. 3) and determined two dimensional hexagonal lattice parameter a and the tube radius R . The pattern fitting has been done in the range of $0.3 \text{ nm}^{-1} < q$ (scattering vector) $< 1.0 \text{ nm}^{-1}$ where 100, 110, 200, 210 diffractions are separately observed. In the calculation, the SWNT form factor was approximated by the 0th order cylindrical Bessel function $J_0(qR)$. The following equation was used for the fitting to calculate the diffraction intensity.

$$I(q) = Y \sum \exp\left(-\frac{(q-q_i)^2}{(u+vq)^2}\right) S(q) J_0(qR) \exp(-B_0 q^2) + \alpha q^2 + \beta q + \gamma$$

where Y is a scaling factor, q_i is Bragg position for i th diffraction, u and

v are peak width parameters, B_0 is a thermal factor, $S(q)$ is carbon atomic scattering factor, α , β and γ are background parameters, respectively. With assumed a and R values, other parameters can be determined by least squares method. In this work, we have performed least squares calculation with some trial combinations of a (from 16.5 to 17.5 nm, step by 0.005 nm) and R (from 0.65 to 0.75 nm, step by 0.001 nm) values and determined optimum combination of a and R values which gives the least residual. The optimized a and R values are summarized in Table 1. As shown in Table 1, the tube radius R of c-SWNT drastically changes by compression comparing with that of o-SWNT. This drastic change of c-SWNT tube may cause the lowering of crystallinity at high pressure. The stability of o-SWNT is considered to be due to the internal pressure of the penetrated liquid pressure medium. Since both o-SWNT and c-SWNT samples recover their initial XRD patterns on complete release of pressure, polymerization between tubes does not occur by the high pressure treatment at room temperature.

In the diffraction pattern of the peapod sample (Fig. 2-(c)), the diffraction peaks (marked “C₆₀(100)”, “C₆₀(200)” in Fig. 2-(c)) from one dimensional C₆₀ crystals inside the pods are observed. The diffractions of the two dimensional hexagonal SWNT (pod) lattice were also observed and they could be observed at relatively high pressure as those of the o-SWNT sample. So, structural property of the SWNT (pod) lattice of the peapod sample may be similar with that of the o-SWNT sample. However, since 100 diffraction of the SWNT (pod) lattice of the peapod sample was not able to be observed because of its low intensity and 110 peak was overlapped with “C₆₀(100)”, we gave up pattern fitting analysis of the SWNT (pod) lattice of the peapod sample. It was observed that center-to-center distance of the nearest C₆₀ molecules

($D_{C_{60}}$) in the pods decreases with pressure from 0.956 nm at 0.1 MPa down to 0.855 nm at 10 GPa, 0.845 nm at 25 GPa (Fig. 4). The decreasing rate is very great up to 10 GPa while the slope becomes to be gentle from 10 GPa. It was also found that the distance value on complete release of pressure after compression up to 25 GPa remained to be much smaller than the its initial value. These experimental results indicate that the polymerization of C_{60} molecules in a carbon nanotube can occur even at room temperature.

Rhee et al. [14] reported that solid fcc- C_{60} is transformed into a polymer phase by compression at room temperature, although their ex-situ XRD measurement could not determine the transformation pressure. So, we have conducted the in-situ XRD measurement of fcc- C_{60} up to 35.7 GPa at room temperature (Fig. 5-(a)). As shown in Fig. 5-(a), it was confirmed that fcc- C_{60} is transformed into a polymer phase because the XRD pattern remained to be much smaller than the initial pattern on complete release of pressure. Unfortunately, however, since no remarkable change was observed in the diffraction pattern with increasing pressure (Fig. 5-(a)), it is still hard to determine the transformation pressure. One may find a change that 200 diffraction peak which is absent at atmospheric pressure appears at relatively low pressure. However, such phenomenon was already reported by Duclos et al. [15] and the appearance of 200 peak is explained as follows. The scattering factor of fcc- C_{60} depends on the ratio of lattice constant a and the molecular radius R_C and the scattering factor at 200 peak position is accidentally almost 0 at atmospheric pressure. However, since the intramolecular bonds are significantly less compressible than the intermolecular bonding, the ratio a/R_C changes with pressure and the accidental absence of 200 line is eliminated at high pressure (Fig. 5-(b)). We determined lattice constant a up to 35.7 GPa assuming that

cubic lattice is kept under high pressure and the determined values well reproduce the data reported by Duclos et al. [15] up to their highest pressure of about 20 GPa. The $D_{C_{60}}$ derived from the determined a are plotted in Fig. 4. Although $D_{C_{60}}$ of fcc- C_{60} decreases with pressure down to 0.845 nm at 35.7 GPa, it is always greater than that of the peapod sample at the same pressure. However, since the $D_{C_{60}}$ decreasing rate of the peapod sample becomes to be small from 10 GPa, it is estimated that the two $D_{C_{60}}$ values might be almost the same (~ 0.845 nm) at about 35 GPa. Assuming the compressibility of C_{60} molecule itself is quite little, the $D_{C_{60}}$ value of 0.845 nm corresponds to the intermolecular distance of about 0.145 nm which is comparable with the intramolecular bonds. Therefore, it is considered that 0.845 nm is short enough to be polymerized. It is plausible that polymerization of C_{60} molecules in a pod may occur at around 10 GPa where the $D_{C_{60}}$ decreasing rate drastically changes.

4 Acknowledgement

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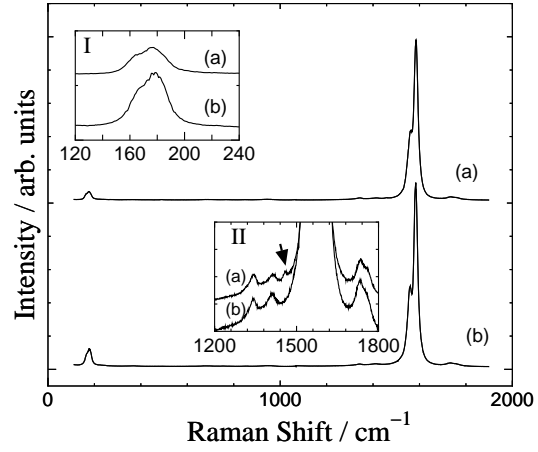


Fig. 1. Observed Raman spectra of (a) C₆₀-peapod and (b) empty SWNT samples. Inset I shows the RBM peaks. The arrow in Inset II indicates Ag(2) mode of C₆₀ molecules in C₆₀-peapods.

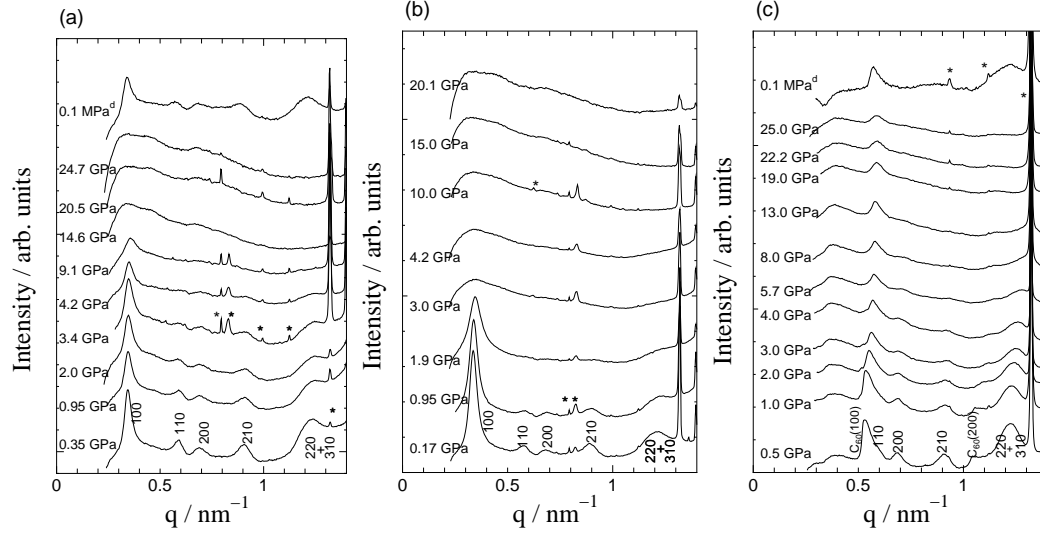


Fig. 2. Change in XRD patterns of (a) o-SWNT, (b) c-SWNT, (c) C₆₀-peapod samples with pressure at room temperature. Asterisks indicate unidentified scattering lines from diamond anvils. The patterns marked 0.1 MPa^d were observed after complete release of pressure. The wavelength of the incident beam was 0.0618 nm. C₆₀(100), (200) in (c) indicate the diffraction peaks of 1D C₆₀ crystals inside the SWNTs.

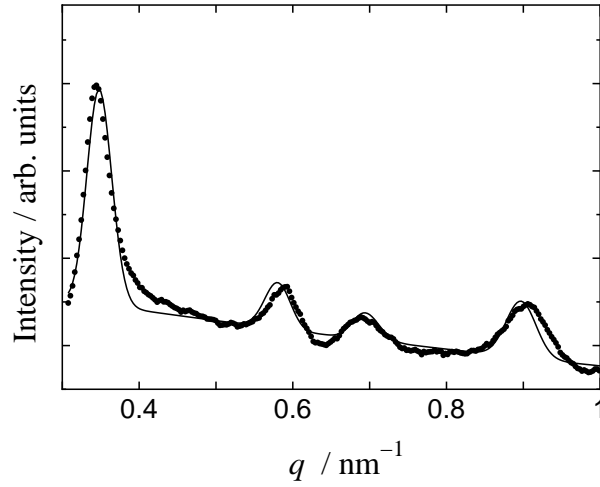


Fig. 3. Observed (dots) and calculated (solid line) diffraction patterns.

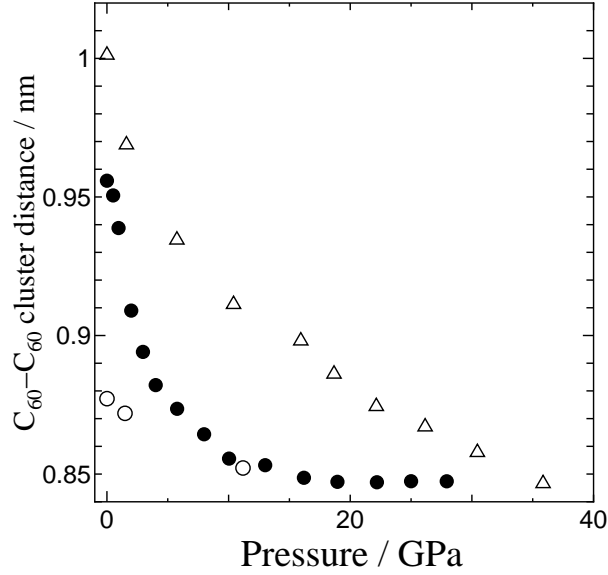


Fig. 4. The center-to-center distance of the nearest C_{60} molecules in C_{60} -peapods (circles) and fcc- C_{60} (triangles) samples as a function of pressure. Filled and open circles represent data with increasing and decreasing pressure, respectively.

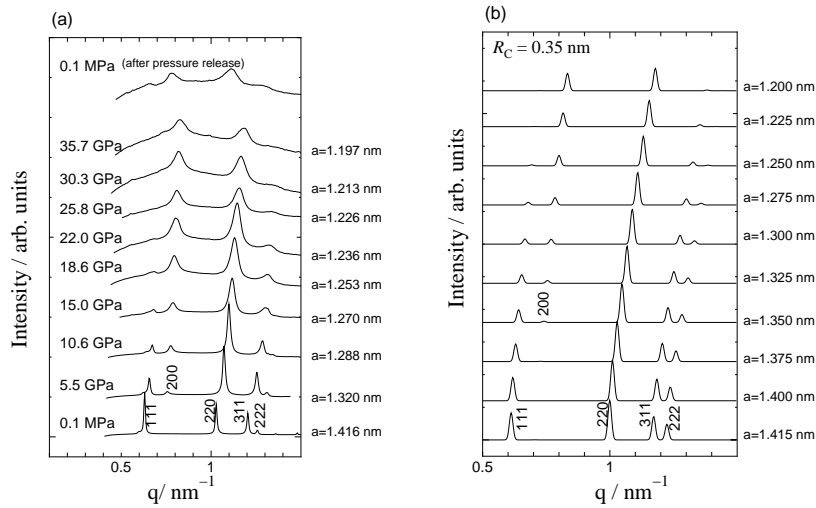


Fig. 5. (a) Observed and (b) simulated XRD patterns of fcc- C_{60} sample with pressure at room temperature. Simulation was done with a fixed molecular radius of 0.35 nm and an indicated lattice constant a in the figure.

Table 1

Optimized a and R values.

| sample | pressure | a (nm) | R (nm) |
|--------|----------|----------|----------|
| o-SWNT | 0.1 MPa | 1.74 | 0.706 |
| | 0.35 GPa | 1.695 | 0.694 |
| | 0.95 GPa | 1.685 | 0.698 |
| | 2.00 GPa | 1.680 | 0.698 |
| c-SWNT | 0.1 MPa | 1.74 | 0.706 |
| | 0.95 GPa | 1.70 | 0.674 |

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