

## Syntheses and characterization of nanonetworked carbon materials

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### Abstract

Several forms of nanonetworked carbon materials were synthesized by high pressure and high temperature treatments of fullerene C<sub>60</sub> and single-walled carbon nanotube bundles. Structural properties (e.g. thermal expansion coefficients and compressibilities) of the synthesized materials were investigated by XRD measurements using synchrotron X-ray. Their formation mechanisms are also discussed.

### Introduction

High pressure and high temperature (HPHT) treatments of solid C<sub>60</sub> (fcc-C<sub>60</sub>), in which C<sub>60</sub> molecules are bound together by weak van der Waals forces, produce a variety of phases of polymerized C<sub>60</sub> known as "fullerene polymers". So far, three crystalline phases (orthorhombic, rhombohedral and tetragonal phases) and some amorphous phases of polymerized fullerenes were synthesized. For convenience, we use abbreviations such as o-C<sub>60</sub>, rh-C<sub>60</sub> and t-C<sub>60</sub> to denote orthorhombic, rhombohedral and tetragonal polymers, respectively. o-C<sub>60</sub>, rh-C<sub>60</sub> and t-C<sub>60</sub> are suggested to be formed by the polymerization of C<sub>60</sub> molecules via [2+2] cycloaddition in the direction [110] or planes (111) and (001) of fcc-C<sub>60</sub>, respectively. The polymerized fullerenes consists of hybrid networks of sp<sup>2</sup> and sp<sup>3</sup> carbon atoms and are classified as a new family of crystalline carbon. Therefore, they are expected to have different properties from those of other crystalline carbon phases such as graphite, diamond and fcc-C<sub>60</sub>.

Single-walled carbon nanotube (SWNT) bundles are also expected to be transformed into polymerized phases by HPHT treatment. However, so far structural properties of SWNT bundles under high pressure have not been understood well.

In the present paper, we discuss syntheses of new forms of nanonetworked carbon materials and characterization of their properties.

### (1) Selective syntheses of rh-C<sub>60</sub> and t-C<sub>60</sub> polymers

rh-C<sub>60</sub> and t-C<sub>60</sub> (Fig. 1) are often obtained as a mixed phase. We have investigated synthesis conditions to obtain rh-C<sub>60</sub> and t-C<sub>60</sub> as a single phase. By exploring their stability region in pressure-temperature diagram, we have found that rh-C<sub>60</sub> and t-C<sub>60</sub> can be obtained by HPHT treatments at 5.5 GPa - 800 K and at 1.6 GPa - 900 K, respectively. Figure 2 shows the observed XRD patterns of pristine C<sub>60</sub>, rh-C<sub>60</sub> and t-C<sub>60</sub>.

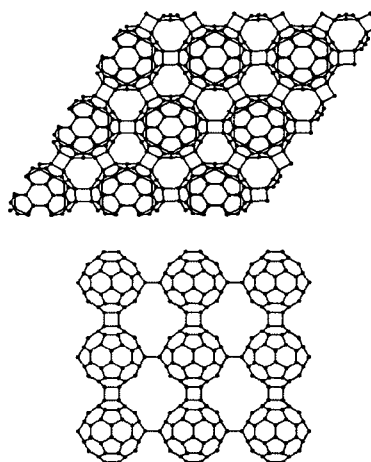


Fig. 1 Polymerized planes of rh-C<sub>60</sub> (upper) and t-C<sub>60</sub> (lower).

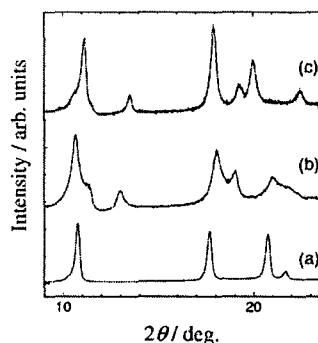


Fig. 2 The observed XRD patterns of (a) pristine C<sub>60</sub>, (b) rh-C<sub>60</sub> and (c) t-C<sub>60</sub>.

## (2) Thermal expansion of rh-C<sub>60</sub> and t-C<sub>60</sub> polymers

In order to confirm the difference between the bonding natures of inter- and intra-polymerized planes, the thermal expansion coefficients of rh-C<sub>60</sub> and t-C<sub>60</sub> polymers were investigated by in situ XRD measurements at high temperature. Figure 3 shows the lattice parameters of rh-C<sub>60</sub> (hexagonal cell) as a function of temperature. The linear expansion coefficients along the *a*- and *c*-axes are determined to be  $4.0 \times 10^{-6} \text{ K}^{-1}$  and  $1.5 \times 10^{-5} \text{ K}^{-1}$ , respectively. The facile expansion along the *c*-axis is confirmed by the positive slope of the temperature dependence of *c/a*. Similar phenomena were also observed for t-C<sub>60</sub>. The linear expansion coefficients of t-C<sub>60</sub> along the *a*- and *c*-axes are determined to be  $7.0 \times 10^{-6} \text{ K}^{-1}$  and  $1.5 \times 10^{-5} \text{ K}^{-1}$ , respectively.

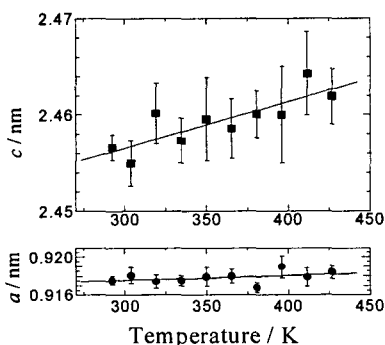


Fig. 3 The temperature dependence of the lattice parameters of rh-C<sub>60</sub>

## (3) In situ XRD measurements of SWNT bundles and C<sub>60</sub> polymers

New forms of nanonetworked carbon materials are expected to be synthesized by HPHT treatments of SWNT bundles and C<sub>60</sub> polymers. In order to explore them, we have performed in situ synchrotron XRD measurements of SWNT bundles and C<sub>60</sub> polymers under high pressure with a cubic anvil press (MAX80) at a beam line AR-NE5C of High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. Figure 4 shows the change in XRD pattern of t-C<sub>60</sub> at 11.2 GPa as a function of temperature. As shown in Fig. 4, a new peak appeared in high energy side of 110 diffraction line at around 573 K with increasing temperature. It indicates a transformation from 2-dimensionally (2D) polymerized t-C<sub>60</sub> to a 3D polymerized phase which is predicted by theoretical calculation.

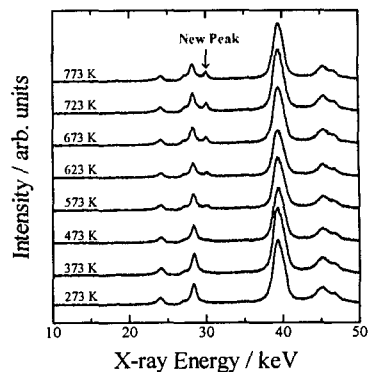


Fig. 4 Change in XRD pattern of t-C<sub>60</sub> with increasing temperature at 11.2 GPa

Figure 5 shows the diffraction patterns of SWNT bundles under high pressure. Four single diffraction lines and one doublet line were observed under relatively low pressure. The higher order diffractions lose their intensity with pressure increase and only 100 line was observed beyond 6 GPa. On complete release of pressure after heat treatment at about 800 K for 20 min at 11.2 GPa, the diffraction pattern did not recover the initial pattern. We will discuss the structural properties of the transformed phase.

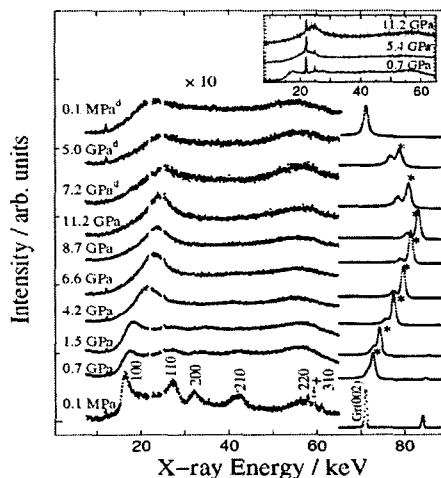


Fig. 5 Change in XRD pattern of SWNT as a function of pressure. The pressure labeled with "d" denotes the pressure on decreasing pressure. Gr(002) and asterisks denote the diffraction line of graphite-like impurity and BN in pressure cell, respectively. The energy region containing the strong Ag characteristic x-ray emission lines are excluded. The Ag lines are shown in the inset.