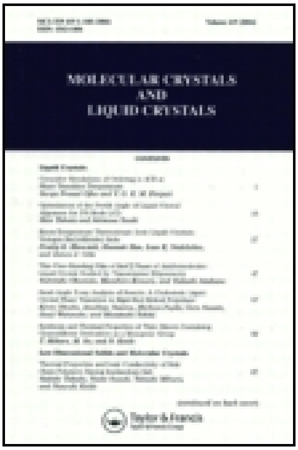

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

High pressure phases of fullerenes, hydrofullerenes, and fluorofullerenes

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Version of record first published: 18 Oct 2010

To cite this article: Shinji Kawasaki, Akifumi Yao, Fujio Okino, Hidekazu Touhara & Kaichi Suito (2002): High pressure phases of fullerenes, hydrofullerenes, and fluorofullerenes, Molecular Crystals and Liquid Crystals, 386:1, 109-114

To link to this article: http://dx.doi.org/10.1080/713738827

Mol. Cryst. Liq. Cryst., Vol. 386, pp. 109–114
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1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113312

HIGH PRESSURE PHASES OF FULLERENES, HYDROFULLERENES, AND FLUOROFULLERENES

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In order to acquire information on the structural and chemical stability of hydrofullerene and fluorofullerene solids, high-pressure XRD study of hydrofullerene $C_{60}H_{36}$, and fluorofullerenes $C_{60}F_{36}$, $C_{60}F_{48}$ has been performed. No structural phase transformation was observed up to about 2.7 GPa and 6.1 GPa for $C_{60}H_{36}$ and $C_{60}F_{36}$, respectively. The bulk moduli of $C_{60}H_{36}$ and $C_{60}F_{36}$ were determined to be 15.7 GPa and 14.3 GPa, respectively.

Keywords: hydrofullerene; fluorofullerene; high pressure; XRD

INTRODUCTION

A variety of phases of polymerized fullerenes have been synthesized by high pressure and high temperature treatments of face centered cubic (fcc) C_{60} solid. The crystal structures of the polymerized C_{60} have been identified as orthorhombic phase with one-dimensional chains, and as tetragonal and rhombohedral (rh-C_{60}) phases with two-dimensional layers. The polymerized fullerenes themselves have interesting properties (surprisingly, Makarova *et al.* have discovered ferromagnetism in rh-C_{60} very recently [1]) and are expected to lead to new functional materials by intercalation technique [2]. Even at room temperature pressure-induced phase transformations of C_{60} occur due to the change of the orientational ordering of the molecular rotation. For example, at about 0.4 GPa, C_{60} transforms from the fcc structure, in which the C_{60} molecules rotate freely, to the simple cubic structure, where the molecular rotation are partially ordered [4].

Hydrofullerenes and fluorofullerenes have attracted considerable interests, particularly in relation to their potential use as hydrogen storage materials and as molecular lubricant, respectively. It is interesting to explore their high pressure induced phase transformation on the analogy of C_{60} case. Recently, Meletov *et al.* [3] have performed a micro-Raman high pressure experiment of $C_{60}H_{36}$ and reported that the anomaly at 0.6 GPa in the pressure dependence of Raman spectra could be attributed to a phase transformation. In order to confirm this transformation, we have performed *in situ* XRD measurements of $C_{60}H_{36}$ under high pressure. To our knowledge, no structural investigation of fluorofullerenes under pressure has been carried out except for our preliminary work using inhomogeneous $C_{60}F_x$ and $C_{70}F_x$ [5]. Recently, isolation of individual fluorofullerenes has been accomplished by optimization of the reaction conditions and a careful choice of the halogen donor. So far, the fluorofullerenes such as $C_{60}F_2$, $C_{60}F_{16}$, $C_{60}F_{18}$, $C_{60}F_{20}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ have been isolated and some of them are well characterized [6]. Among them, $C_{60}F_{36}$ and $C_{60}F_{48}$ are easily produced and are commercially available. Here we also report on high-pressure XRD study of fluorofullerenes $C_{60}F_{36}$ and $C_{60}F_{48}$ in order to acquire information on their structural and chemical stability.

EXPERIMENTAL

Powder samples $C_{60}H_{36}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ were purchased from Tokyo Progress Systems. In order to confirm the homogeneity of the sample, we performed mass spectroscopic and X-ray photoelectron spectroscopic measurements. *In situ* XRD measurements under high pressure were carried out using a conventional powder diffractometer with a MoKα radiation. A diamond anvil pressure cell was used as a high pressure device. A 4:1 mixture of methanol and ethanol was used as a pressure transmitting medium. The pressure inside the cell was determined by ruby fluorescence method.

RESULTS AND DISCUSSION

Figure 1 shows the observed XRD patterns of $C_{60}H_{36}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ samples, which were charged in a silica glass capillary under Ar atmosphere, at room temperature and under atmospheric pressure. Their lattice parameters are summarized in Table 1. In contrast to the earlier report [7], we found that $C_{60}H_{36}$ can not be indexed by an body centered cubic (bcc) lattice. The nearest-neighbor distance between molecular centers along the body diagonal in the bcc structure of $C_{60}H_{36}$ is calculated to be 1.0206 nm using the value of $a = 1.1785$ nm reported by Hall *et al.* [7] and is slightly

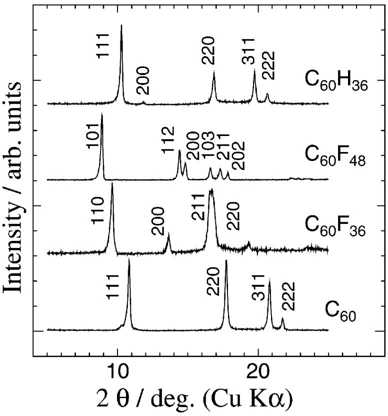

FIGURE 1 XRD diffraction patterns of C_{60}, $C_{60}F_{36}$, $C_{60}F_{48}$ and $C_{60}H_{36}$ at room temperature and under atmospheric pressure.

shorter than that (1.054 nm) of fcc $C_{60}H_{36}$. The volume per a $C_{60}H_{36}$ molecule for the bcc phase is calculated to be 0.8127 nm^3 and is smaller than that of the fcc phase. It indicates that the bcc phase is denser than the fcc phase.

Figures 2–4 show the changes in the diffraction patterns of $C_{60}H_{36}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ with pressure. As shown in Figures 2–4, no structural phase transformation was observed in the present experimental conditions. Although there are many isomers for $C_{60}H_{36}$ molecule, D_{3d} and S_6 isomers are considered to be dominant. $C_{60}F_{48}$ molecule has two isomers having D_3 and S_6 symmetry. Therefore, in both cases of $C_{60}F_{48}$ and $C_{60}H_{36}$, the molecule has an oblate character and cubic crystal structure is allowed only when the polar axes of the molecules are randomly arranged. If the alignment of the axes does occur, then there should be a tendency to form a tetragonal structure. In fact, $C_{60}F_{48}$ crystal transforms from the body centered tetragonal structure to an fcc structure at about 353 K with increasing temperature [8]. On the other hand, in the case of $C_{60}H_{36}$,

TABLE 1 Lattice Parameters and Volume per Molecule of Hydrofullerene and Fluorofullerenes

	Structure	Lattice parameters (nm)	Volume/molecule (nm^3)
$C_{60}H_{36}$	fcc	a = 1.4909(5)	0.8285
$C_{60}F_{36}$	bcc	a = 1.302(1)	1.1035
$C_{60}F_{48}$	bct	a = 1.1852(8), c = 1.791(1)	1.2579
C_{60}*	fcc	a = 1.4166	0.7107

*JCPDS 44-0558.

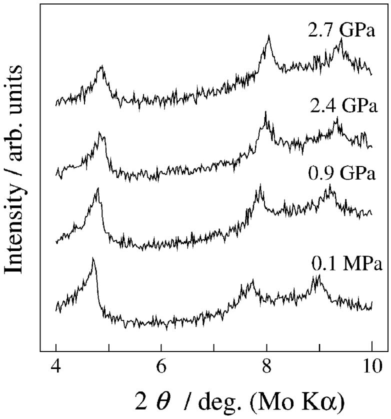

FIGURE 2 Change in XRD diffraction pattern of $C_{60}H_{36}$ with pressure.

Hall *et al.* [7] predicted that at sufficiently low temperatures the cubic crystal structure would be transformed to a tetragonal one. However, their low temperature XRD measurements revealed that the cubic structure is stable even at liquid nitrogen temperature. On the other hand, Meletov *et al.* [3] reported the anomaly at 0.6 GPa in the pressure dependence of Raman spectra could be assigned to such a structural transformation. In the present study, although the crystal structure of $C_{60}H_{36}$ is fcc, the polar axes arrangement is random as in the bcc phase. Therefore, the structural phase transformation from the fcc to a tetragonal phase is also expected, but it was not observed up to 2.7 GPa.

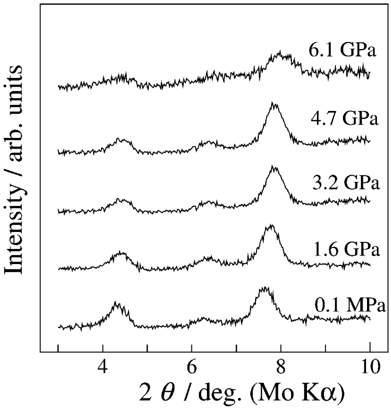

FIGURE 3 Change in XRD diffraction pattern of $C_{60}H_{36}$ with pressure.

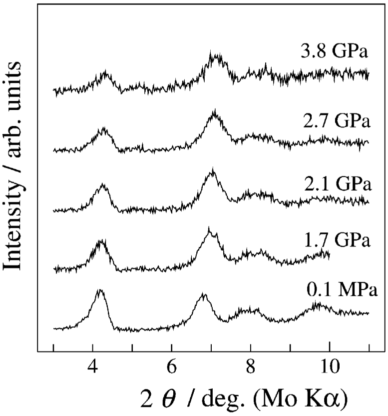

FIGURE 4 Change in XRD diffraction pattern of $C_{60}F_{36}$ with pressure.

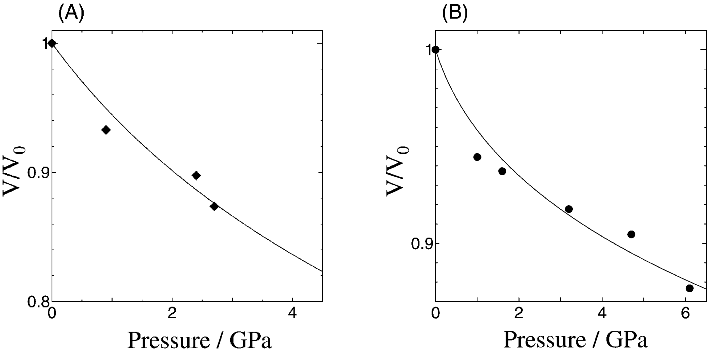

FIGURE 5 Equation of state data for (A) $C_{60}H_{36}$ and (B) $C_{60}F_{36}$. Solid curves are fitted to the Birch-Murnaghan equation of state.

Lattice parameters of $C_{60}H_{36}$ and $C_{60}F_{36}$ under pressure were determined from the XRD patterns. However, we could not obtain reliable lattice parameters of $C_{60}F_{48}$ under pressure because the diffraction lines 112 and 200, and the lines 103, 211 and 202 were overlapped. In order to obtain bulk modulus B_0 at 0.1 MPa and its pressure derivative B'_0, the lattice volume changes shown in Figure 5 were fitted to the Birch-Murnaghan equation of state. As data points of $C_{60}H_{36}$ were too few to determine two parameters, B'_0 was assumed to be 4 and B_0 was determined to be 15.7 (1.1) GPa. B_0 and B'_0 of $C_{60}F_{36}$ were determined to be 14.3 (8.8) GPa and 28.0 (31.8), respectively. These values indicate that $C_{60}H_{36}$ and $C_{60}F_{36}$ are ‘soft’ material as C_{60} ($B_0 = 15.6$ (0.8) GPa).

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