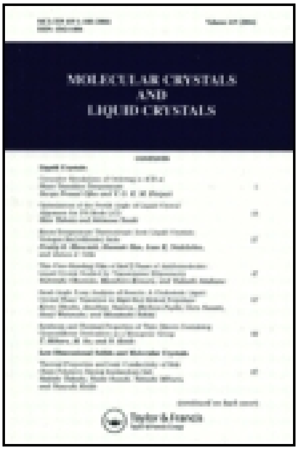

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Crystal Structures and Phase Transformations of the Fluorinated Fullerenes

Shinji Kawsaki [a] , Fujio Okino [a] & Hidekazu Touhara [a]
[a] Faculty of Textile Science and Technology, Shinshu University, Ueda, 386-8567, Japan

Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 629-633
Reprints available directly from the publisher
Photocopying permitted by license only

Crystal Structures and Phase Transformations of the Fluorinated Fullerenes

SHINJI KAWSAKI, FUJIO OKINO and HIDEKAZU TOUHARA

Faculty of Textile Science and Technology, Shinshu University, Ueda 386–8567, Japan

(Received May 30, 1999; In final form June 22, 1999)

In situ x-ray diffraction experiments of the fluorinated fullerenes, $C_{60}F_x$ ($x = 0$, 36 and 48) at high temperatures have been undertaken. The structural phase transformation of $C_{60}F_{48}$ was observed at about 358 K. It was also found that the lattice parameters of the low temperature phase of $C_{60}F_{48}$ show anomalous change at about 310 K. The thermal expansion coefficients of the fluorinated fullerenes were determined by using the change of the lattice parameters with temperature.

Keywords: fullerene; fluorine; x-ray diffraction; high temperature

INTRODUCTION

The discoveries of synthesizing methods for high purity fluorinated fullerenes have inspired many studies in the physical and chemical properties of these materials. [1, 2] Recently, we have found that the stable phases of $C_{60}F_{36}$ and $C_{60}F_{48}$ under ambient conditions are a body centered cubic (bcc) and a body centered tetragonal (bct) phases, respectively and that the bct phase of $C_{60}F_{48}$ transforms into a face centered cubic (fcc) phase at about 353 K. [3] However, the mechanism of the phase transformation is not still well understood. In this study, in order to clarify the mechanism, the temperature dependence of the lattice parameters at temperatures from 292 to 419 K was measured by x-ray diffraction experiments. The temperature dependence of the lattice parameters yields information about phase transformation, e.g., whether the transition is of first or second order. We have also carried out the same experiments on C_{60} and $C_{60}F_{36}$ to compare their high temperature behavior with that of $C_{60}F_{48}$.

EXPERIMENTAL

Powder x-ray diffraction measurements were performed on a Rigaku RINT-2200 using Cu Kα radiation. Pyrolytic graphite was used as a counter monochromator. The powder was sealed in a 0.3 mm diameter silica glass capillary. High temperature experiments were done with a home-made small furnace of a 10 mm diameter ceramic tube wound by a Pt wire with windows for incident and diffracted beams. The sample in the capillary was set in the furnace. The sample temperature was monitored by a thermocouple at the top of the furnace. The distance from the sample to the thermocouple was about 20 mm. Prior to the experiments, the sample temperature was calibrated by setting another thermocouple at the sample position.

RESULTS & DISCUSSION

Figures 1 and 2 show the change in the diffraction pattern of $C_{60}F_{36}$ and $C_{60}F_{48}$ with temperature. As shown in Fig. 1, no remarkable change was observed in the diagrams of $C_{60}F_{36}$. On the other hand, the diffraction pattern of $C_{60}F_{48}$ begins to change at about 358 K (Fig. 2). The lower and higher temperature phases are bct and fcc phases, respectively. This bcc to fcc transition of $C_{60}F_{48}$ is reversible since the sample after the high temperature measurements showed the same pattern as that of the starting sample.

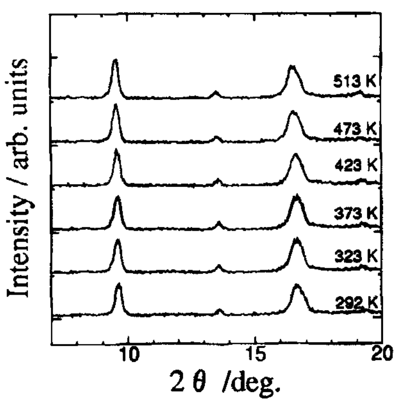

FIGURE 1 Change in XRD diffraction pattern of $C_{60}F_{36}$ with temperature.

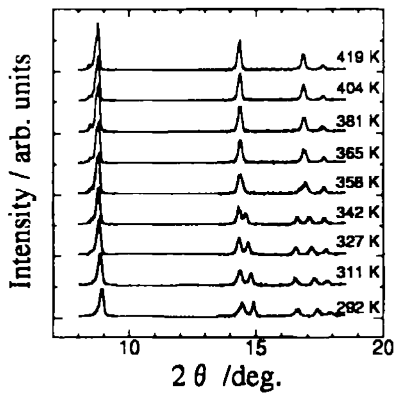

FIGURE 2 Change in XRD diffraction pattern of $C_{60}F_{48}$ with temperature.

The extended cell of bct can be treated as a face centered tetragonal (fct) cell that is derived by the elongation of an fcc cell along the c-axis with the new choice of a-axis coinciding with the C-face diagonal of the initial bct cell. For convenience sake, we treat the lower temperature phase of $C_{60}F_{48}$ as fct. The observed lattice parameters a and c of the fct phase and a of the fcc phase of $C_{60}F_{48}$ are plotted in Fig. 3 as a function of temperature. The lattice parameters were determined by the least-square method using 6 and 4 reflections for the fct and the fcc phases, respectively. A small jump is observed at 358 K. This behavior shows that the phase transformation of $C_{60}F_{48}$ from fct to fcc is a first-order transition. Furthermore, it is shown in Fig. 3 that c parameter of the fct phase increases with temperature up to 310 K and then decreases while the a parameter increases linearly.

Figure 4 shows the observed lattice parameters of C_{60} and $C_{60}F_{36}$ as a function of temperature. In contrast to the drastic change of the lattice parameters of $C_{60}F_{48}$, the changes of the parameters of C_{60} and $C_{60}F_{36}$ are quite small. The evaluated thermal expansion coefficients at 330 K are 2.54×10^{-4}, 4.39×10^{-5}, 5.30×10^{-5} and 4.25×10^{-5} K^{-1} for fct $C_{60}F_{48}$, fcc $C_{60}F_{48}$ (by extrapolation), bcc $C_{60}F_{36}$ and fcc C_{60}, respectively.

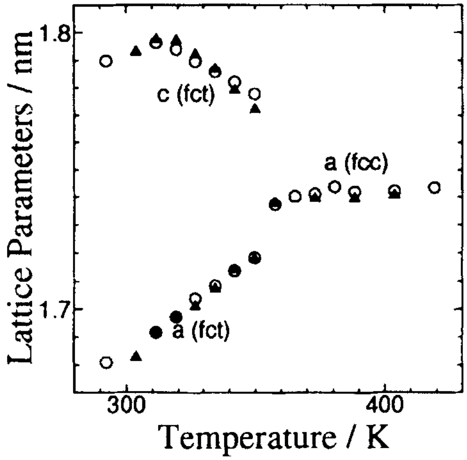

FIGURE 3 Temperature dependence of lattice parameters, a and c, in $C_{60}F_{48}$. Solid circles and open triangles indicate the parameters determined with increasing and decreasing temperature, respectively.

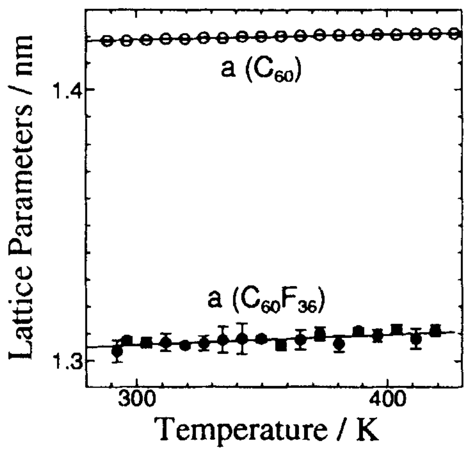

FIGURE 4 Temperature dependence of lattice parameters, a, of C_{60} (open circles) and $C_{60}F_{36}$ (solid circles). Solid straight lines are least squares fits to the observed data.

References

[1] A. A. Gakh *et al., J. Am. Chem. Soc.,* **116,** 819 (1994).
[2] O.V. Boltalina *et al., J. Chem. Soc., Perkin Trans. 2,* 2275 (1996).
[3] S. Kawasaki *et al., J. Phys. Chem. B,* **103,** 1223 (1999).
[4] F. Okino *et al., Fullerene Science & Technology,* **4,** 873 (1996).