

Time-resolved x-ray diffraction measurement of C_{60} under high pressure and temperature using synchrotron radiation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 10483

(<http://iopscience.iop.org/0953-8984/14/44/319>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 18/05/2010 at 15:21

Please note that [terms and conditions apply](#).

Time-resolved x-ray diffraction measurement of C₆₀ under high pressure and temperature using synchrotron radiation

T Horikawa¹, K Suito¹, M Kobayashi¹ and A Onodera^{1,2}

¹ Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

² University of Marketing and Distribution Sciences, Nishi-ku, Kobe 651-2188, Japan

E-mail: horikawa@xrd.mp.es.osaka-u.ac.jp

Received 21 June 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/10483

Abstract

C₆₀ has been studied by means of time-resolved x-ray diffraction measurements using synchrotron radiation. Diffraction patterns were recorded at intervals of 1–10 min for samples under high pressure (12.5 and 14.3 GPa) and high temperature (up to 800 °C) for, at the longest, 3 h. Time, pressure, and temperature dependences of the C₆₀ structure are presented and the relevance to the hardness of materials derived from C₆₀ is discussed.

1. Introduction

Various high-pressure studies have been performed on fullerene (C₆₀) to investigate the effects of pressure on the fullerene cages. For example, very hard materials comparable to, or even harder than, diamond can be produced [1–15]. The structures of such materials are interpreted using different models such as an amorphous state consisting of $sp^2 + sp^3$ bondings [1–4, 6, 9, 11–13], a nanocrystalline mixture of diamond and graphite [5, 7, 8, 10, 14], and a mixture of amorphous carbon and nanocrystalline graphite [15]. These interpretations have been all derived from post-compression investigations. *In situ* observation is required to establish the structure of hard materials derived from fullerene in more detail and, furthermore, to find the mechanism for producing hard materials.

2. Experimental details

Powder C₆₀ (99.9% purity, MER Co.), after being dried at 200 °C and 10⁻³ Torr for 24 h, was used as a starting material. The sample was pressurized with a cubic anvil press (MAX80) [16] installed at the AR-NE5C beamline of the High Energy Accelerator Research Organization (KEK), Tsukuba. Polycrystalline NaCl was used as a pressure marker. High temperature was attained by passing a direct current through a pair of graphite discs. Energy-dispersive x-ray diffraction study was undertaken with a diffraction angle chosen at 6°. Time-resolved measurements were carried out at 400, 500, 600, 650, and 800 °C (12.5 GPa) and 200,

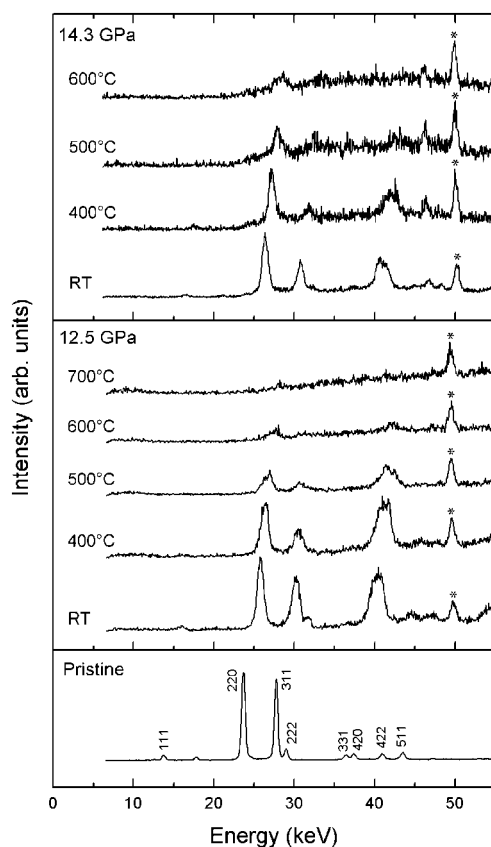


Figure 1. X-ray diffraction patterns of samples. The asterisked peaks are from the MgO tube used for the sample capsule.

300, 400, and 600 °C (14.3 GPa). For each P , T -condition, diffraction patterns were recorded at intervals of 1–10 min, for 3 h in most cases. After the high-pressure–high-temperature experiments, the samples were retrieved and subjected to Raman scattering investigation and scratch tests. The scratch tests were performed by using sintered compacts of SiC and WC.

3. Results and discussion

X-ray diffraction patterns taken at room temperature indicated that the pristine fcc structure persisted to at least 14.3 GPa. Upon heating to 900 °C (at 12.5 GPa) or to 600 °C (at 14.3 GPa), there occurred significant changes in the diffraction patterns. Typical examples are shown in figure 1. In this case, each pattern was recorded every 100 °C with an acquisition time of 200 s. In figure 1, amorphization starts at about 400–600 °C (12.5 GPa) and at about 400–500 °C (14.3 GPa), as evidenced by a significant broadening of each peak. According to the Raman scattering spectra of samples retrieved from 12.5 GPa, the A_g mode vibration peaked at around 1460 cm^{-1} has disappeared around these temperatures. This fact suggests that the five-membered rings of the C_{60} molecule break and the cage structure collapses. At temperature higher than 700 °C (at 12.5 GPa) all the reflections from the fcc phase finally disappear and the sample becomes completely amorphous.

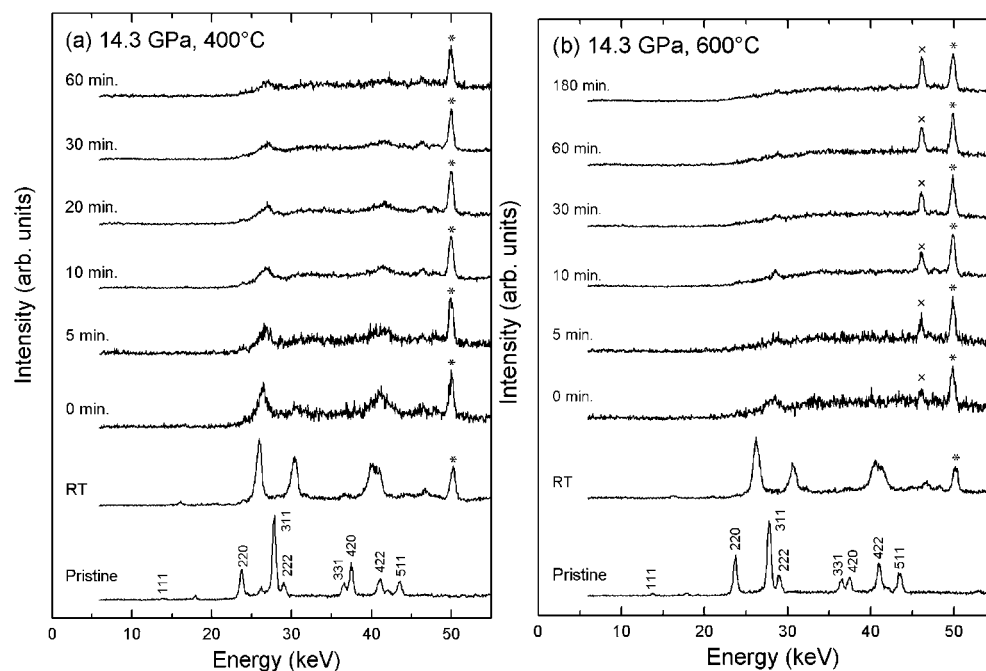


Figure 2. Representative time-resolved x-ray diffraction patterns recorded at 14.3 GPa: (a) at 400 °C; (b) at 600 °C. The asterisked peaks are from the MgO used for the capsule and the crossed peak is from the NaCl used for the pressure marker.

Results of time-resolved measurements recorded at 14.3 GPa are shown in figure 2. At 400 °C, figure 2(a), the intensities of reflections from the fcc phase clearly decrease during the period spent at this temperature. At 0 min (i.e., just after the temperature 400 °C is reached), the (220), (331)/(420), and weak (311)/(222) peaks are present. After 5 min, the (311)/(222) peak disappears, and broadening of the widths of the (220) and the (331)/(420) peaks takes place over a 30 min period. After 60 min, only the (220) remains but is very weak, indicating the amorphization of the sample. When the temperature was held at 600 °C, figure 2(b), the sample almost became amorphous from the start of the period, and only the weak (220) peak is observable. After 60 min, this peak also disappears and the amorphization has been completed. The diffraction patterns after 30 min at 600 °C are similar to that for 700 °C under 12.5 GPa.

During the time-resolved measurements a continuous decrease of the lattice parameter of residual fcc phase was observed both at 12.5 and 14.3 GPa (figure 3). This indicates that the distance between the C₆₀ molecules is shortened significantly while the pressure and temperature were held constant. The amount of the decrease becomes larger when the investigation temperature is raised. At 14.3 GPa, the decrease is essentially completed within the first 30 min.

The scratch tests revealed that products harder than SiC were obtained over the range 500–650 °C (12.5 GPa) and from 400 °C (14.3 GPa). The product retrieved from 600 °C at 14.3 GPa was partly harder than WC. These *P*, *T*-conditions overlap the range where the cage structure of the C₆₀ molecule is broken and amorphization occurs, as studied by x-ray diffraction and Raman scattering measurements. Our analysis showed that the lattice parameter in the range of 11.6–12.6 Å is relevant to the hardness of the sample. In order to reach this range of lattice parameter, heating of the C₆₀ sample beyond 400 °C is needed at 12.5 GPa and the lowest temperature bound is lowered by about 100 °C with elevation of pressure to 14.3 GPa.

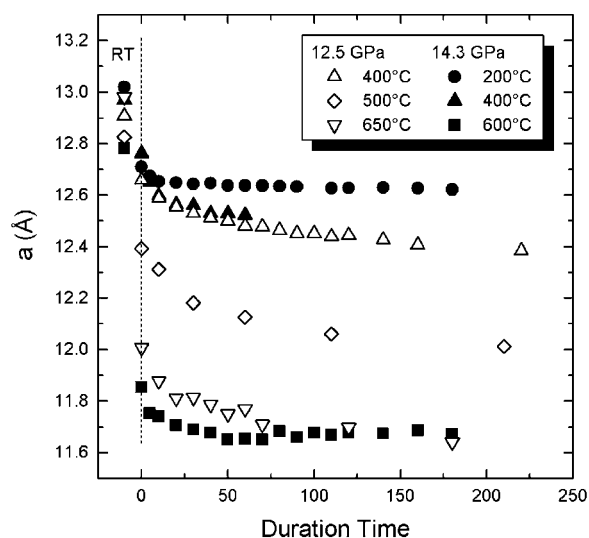


Figure 3. Change of the lattice parameter of the residual fcc phase with time at 12.5 and 14.3 GPa. Symbols to the left of the dashed line represent values at room temperature.

Acknowledgments

We thank Taku Kinoshita for helping us with the experiment. This work was performed by approval of the Photon Factory Advisory Committee (00G216).

References

- [1] Blank V D, Popov M, Buga S, Davydov V, Denisov V N, Ivlev A N, Mavrin B N, Agafonov V, Ceolin R, Szwarc H and Rassat A 1994 *Phys. Lett. A* **118** 281
- [2] Blank V D, Kulnitskiy B A and Tatyaniin Ye V 1995 *Phys. Lett. A* **204** 151
- [3] Blank V D, Buga S G, Serebryanaya N R, Denisov V N, Dubitskiy G A, Ivlev A N, Mavrin B N and Popov M Yu 1995 *Phys. Lett. A* **205** 208
- [4] Blank V D, Buga S G, Serebryanaya N R, Dubitskiy G A, Sulyanov S N, Popov M Yu, Denisov V N, Ivlev A N and Mavrin B N 1996 *Phys. Lett. A* **220** 149
- [5] Brazhkin V V, Lyapin A G, Popova S V, Voloshin R N, Antonov Yu A, Lyapin S G, Kluev Y A, Naletov A M and Mel'nik N N 1997 *Phys. Rev. B* **56** 11 465
- [6] Blank V, Popov M, Pivovarov G, Lvova N, Gogolinsky K and Reshetov V 1997 *J. Mater. Res.* **12** 3109
- [7] Lyapin A G, Brazhkin V V, Lyapin S G and Popova S V 1998 *Rev. High Pressure Sci. Technol.* **7** 811
- [8] Brazhkin V V, Lyapin A G, Lyapin S G, Popova S V, Voloshin R N and Antonov Yu N 1998 *Rev. High Pressure Sci. Technol.* **7** 817
- [9] Blank V D, Buga S G, Serebryanaya N R, Dubitskiy G A, Popov M Yu, Prokhorov V M, Lvova N A and Sulyanov S N 1998 *Rev. High Pressure Sci. Technol.* **7** 972
- [10] Brazhkin V V, Lyapin A G, Popova S V, Antonov Yu N, Kluev Yu A and Naletov A M 1998 *Rev. High Pressure Sci. Technol.* **7** 989
- [11] Blank V D, Buga S G, Serebryanaya N R, Dubitskiy G A, Mavrin B N, Popov M Yu, Bagramov R H, Prokhorov V M, Sulyanov S N, Kulnitskiy B A and Tatyaniin Ye V 1998 *Carbon* **36** 665
- [12] Blank V D, Serebryanaya N R, Dubitskiy G A, Buga S G, Denisov V N, Mavrin B N, Ivlev A N, Sulyanov S N and Lvova N A 1998 *Phys. Lett. A* **248** 415
- [13] Blank V, Popov M, Pivovarov G, Lvova N, Gogolinsky K and Reshetov V 1998 *Diam. Relat. Mater.* **7** 427
- [14] Lyapin A G, Brazhkin V V, Lyapin S G, Popova S V, Varfolomeeva T D, Voloshin R N, Pronin A A, Sluchanko N E, Gavriilyuk A G and Trojan I A 1999 *Phys. Status Solidi b* **211** 401
- [15] Horikawa T, Suito K, Kobayashi M, Oshima R and Onodera A, in preparation
- [16] Shimomura O 1986 *Physica B* **139+140** 292