

High pressure X-ray diffraction study on a graphite using Synchrotron Radiation

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ABSTRACT : High pressure X-ray diffraction study was carried out on a graphite to investigate its compressibility as well as any possible phase transition to the hexagonal diamond structure at room temperature. Energy dispersive X-ray diffraction method was introduced using a Mao-Bell type diamond anvil cell with Synchrotron Radiation. Polycrystalline sodium chloride was compressed together with graphite for the high pressure determinations. Because of the poor resolution of the X-ray diffraction pattern of graphite, its compressibility was estimated to be almost same as that of NaCl by graphite (002) X-ray diffraction peak only. An observation of any new peak from a possible hexagonal diamond phase seems very unpalusible for its definite identification based on the present data. Alternative approaches such as an Wiggler Radiation source as well as a Large Volume high pressure apparatus will be necessary for the detailed studies on a graphite in future.

Key Words : Energy dispersive X-ray diffraction (EDXRD), diamond anvil cell (DAC), synchrotron radiation (SR), phase transition, hexagonal diamond phase

INTRODUCTION

Graphite is one of the most familiar materials to mankind. Carbon has been known to show the polymorphisms of graphite, charcoal and diamond depending upon its formation conditions. This means when the stability conditions on any polymorphs of carbon are changed, the material state(s) can be transformed to the desired phase.

Numerous studies have been performed on graphite under high pressure and/or high temperature conditions, especially to synthesize any diamond phase. It was observed for graphite that the electrical resistivity increases above 15 GPa (i.e., 1 GPa=10 kbar, 1 bar \cong 1 atmospheric pressure) at room temperature, which is reversible on release of pressure (Aust and Drickamer, 1963). However, when graphite was heated at the temperature higher than 1000°C under high pressure, a new phase was appeared and this phase was turned out to have an irreversible

'hexagonal diamond structure' (Bundy and Kasper, 1967). This new hexagonal diamond phase was also discovered in meteorite and has been known Lonsdaleite to mineralogists. This kind of pressure-induced phase transition of graphite in the diamond anvil cell (DAC) was observed by a sudden drop of an optical reflectivity (Hanfland *et al.*, 1989). Recently, there have been some researches to clarify the crystal structure of the high pressure phase of graphite (i.e., hexagonal structure of carbon) at room temperature (Utsumi and Yagi, 1991; Yagi *et al.*, 1992).

The purpose of this study is twofold: one is to introduce the experimental methods of the energy dispersive X-ray diffraction (EDXRD) with Synchrotron Radiation (SR) using DAC, and the other is to report some preliminary experimental results as well as technical problems during the present high pressure experiments at the Stanford Synchrotron Radiation Laboratory (SSRL).

EXPERIMENTS

Sample Preparations

Graphite for this study was prepared from a graphite pot as well as from a graphite rod of a pencil core. Graphite itself is very ductile, and it is impossible to grind into fine powder with a mortar. Powder was collected by scratching the surface of bulk body. Then, powder graphite was pounded in the metal anvil into finer grains.

Diffraction peaks from two different starting graphites turn out to be identical (Fig. 1). Sample preparation from graphite rod was easier than from graphite pot in this study. Thus, graphite rod powder has been used for further high pressure experiments.

Experimental Methods

Principles of the energy dispersive X-ray diffraction method

The condition for the diffraction of X-rays by a crystal lattice can be expressed in the Bragg's form:

$$\lambda = 2 d_{hkl} \cdot \sin\theta \quad (1)$$

where d_{hkl} is the interplanar spacing of the reflecting planes with the Miller indices (hkl) , θ is the glancing angle of incidence on the plane of (hkl) , and λ is the wavelength of the radiation used.

For evaluation of the d-spacings from the diffraction pattern, Bragg's law can be written in terms of photon energy E :

$$E = h \cdot c / \lambda \quad (2)$$

where h is Planck constant, and c is the speed of light.

From (1) and (2), we obtain

$$h \cdot c / E_{hkl} = 2 d_{hkl} \cdot \sin\theta \quad (3)$$

Relation in (3) can be written

$$E_{hkl} \cdot d_{hkl} = h \cdot c / (2 \sin\theta) = 6.199 / \sin\theta \quad (4)$$

Equation (4) is the function of the variable, diffraction angle θ . When θ is fixed, (4) becomes

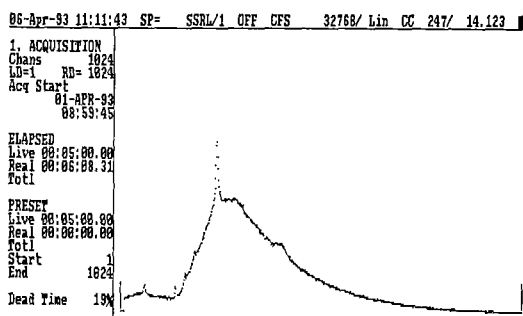


Fig. 1. A spectrum of a polycrystalline graphite at 1 bar. Live time is 5 minutes. Main peak is for graphite (002) plane.

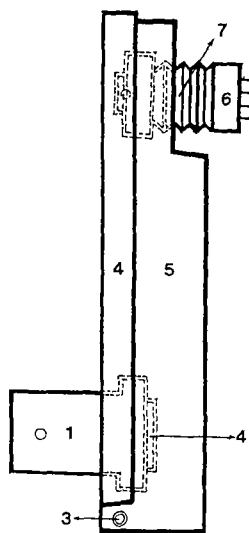


Fig. 2. A schematic sketch of the Mao-Bell type DAC. 1. cylinder, 2. piston, 3. fulcrum, 4. lever, 5. main cell body, 6. drive screw, 7. Belleville washers.

constant value (Giessen and Gordon, 1967);

$$E \cdot d = \text{constant} \quad (5)$$

Peak search was done by the integration of the peak area occupied by the diffracted photon energy. From (5) of the EDXRD principle, volume changes were calculated using following relations: $(E_a/E_h)^3 = (d_h/d_a)^3 = V_h/V_a$ at different diffraction conditions, where 'a' and 'h' for ambient and high pressure conditions, respectively.

Mao-Bell type diamond anvil cell

A schematic diagram of this DAC is in Fig. 2.

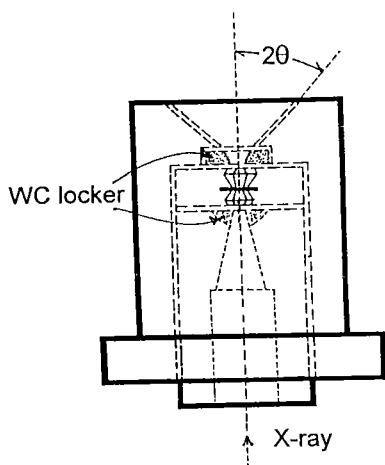


Fig. 3. Cross sectional view of piston-cylinder part of Mao-Bell type DAC. X-ray hits the sample in gasket between diamonds. Lockers for support the diamonds are tungsten carbide (WC) made.

For piston-cylinder part, a cross sectional view is provided in Fig. 3. The size of the diamond culet in both upper and lower anvils is 500 μm each in diameter. The diamond of the anvil cell is of gem quality, and the weight of each diamond reaches 0.3 carat (i.e., 60 mg). Sample was compacted into the circular hole of gasket between upper and lower diamond anvils. Small amount of fine powder of NaCl (i.e., less than $\sim 3\%$ in volume to graphite) was put on the sample. Gasket material used is Inconel 718 alloy metal plate, and hole dimension is 250 μm in diameter and 0.127 mm in thickness, respectively.

The highest pressure with this type DAC has been reported to be 5.6 megabar (i.e., 5,600 kbar) using bevelled diamonds for anvil on ruby powder sample (Xu *et al.*, 1989).

Synchrotron radiation

Whenever a charged particle is accelerated or decelerated, it gives off electromagnetic (EM) radiation. When electrons are traveling at relativistic speed nearly as fast as light, the radiation increases dramatically in intensity, directionality and frequency. Synchrotron and storage rings are sources of such EM radiation because they are machines that force relativistic

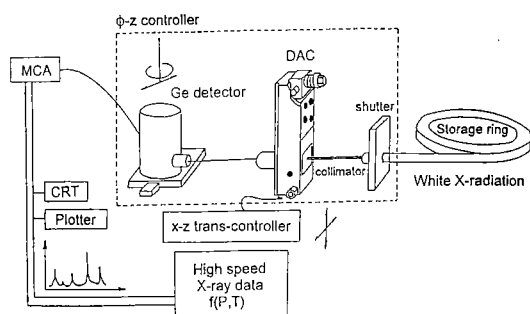


Fig. 4. A general view of the experimental set-up at the SSRL. A broken line is for the hutch box for protection from radiation hazards. The Φ -Z controller is for rotation and up-down movements of the Ge-detector, respectively. The X-Z trans-controller is for movements of DAC in the transverse and up-down directions to the X-ray. These controllers are used for collimation of the apparatus to the white X-radiation. MCA is for multi-channel analyzer, and CRT for cathode ray terminal. Size of DAC in figure is exaggerated enormously compared to the original.

electrons into circular paths by means of powerful bending magnets.

SR has the characteristics as follows: high spectral brilliance, broad spectral range, wavelength tunability, high degree of polarization as well as collimation, and pulsed time structure. Using these characteristics, SR has been applied to many fields of sciences. Geophysics is one of these branches and has been used for the related specific problems such as kinematics, phase transitions, compressibilities and etc. for the Earth materials.

Experimental set-up at SSRL

A schematic experimental set-up at the SSRL has been shown in Fig. 4. Fig. 5 is the detailed view of the DAC and detecting apparatus set-up with MCA. In this study, SR has been collimated to 100 μm in diameter to irradiate to the highest pressurized portion in the sample chamber.

In order to obtain a high efficiency in detecting the photon energy ranging between 10 and 50 KeV, an intrinsic Germanium solid state detector (ORTEC 573) was used. Its resolution is 141 eV at 5.9 KeV and degrades to 490 eV at 122 KeV. This detector operates at a low temperature (i.e.,

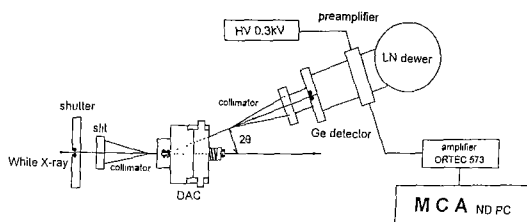


Fig. 5. An over view of the DAC and detection apparatus with MCA system.

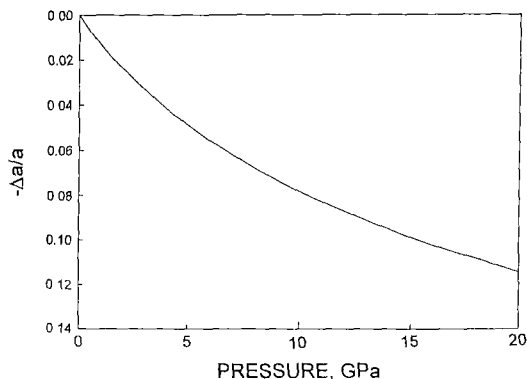


Fig. 6. Equation of state of NaCl at 25°C. This curve is used for high pressure determinations. The calculated $\Delta a/a$ of NaCl extends to curve, then pressure value was read.

77 K) with a bias voltage of 0.3 kV power supply. Detector was positioned ~60 cm away from DAC to prevent it from oversaturation by SR. Data were acquired through the MCA system of 1024 channels.

Pressure calibration

Knowledge of accurate pressure of the compressed sample is essential for the volume determinations at the specific high pressure. Because of the technical difficulties of the laser induced ruby fluorescence pressure sensor, an internal pressure calibrant has been used for high pressure experiments (e.g., Kim, 1989). A good internal pressure calibrant should have the following properties: chemical inertness, good X-ray scattering capability, simple structure, large compressibility, commercial availability, reproducible purity, reliable equation of state data and no phase transformation at the given P-T

conditions (Manghnani *et al.*, 1984). One of the drawbacks when using the internal pressure calibrant is the overlappings of the diffraction peaks between the sample itself and pressure sensor material. Therefore, preliminary check on their overlappings is necessary prior to the compression.

For graphite, sodium chloride (NaCl) was selected because of its least overlapping of its X-ray peaks with those of specimen compared with other candidates such as MgO, Pt, Au, Al, Ag and so on. The equation of state of NaCl is shown in Fig. 6. Lattice parameter shrink (i.e., $\Delta a/a$) was calculated from the photon energy shifts with pressure and this was used to determine the pressure value at the curve of NaCl in Fig. 6.

Energy calibration

Photon energy calibration with a MCA (multi-channel analyzer) system should be done just after experimental set-up before loading pressures on sample. This calibration also should be done after an experiment for checking any disturbance(s) of the alignment during experimental processes by comparison with those of the beginning set-up.

Using the various X-ray sources of Cu, Rb, Mo, Ag, Ba and Tb, energy calibration with respect to the channel has been completed. The relation has been calculated using the least square method and determined as follows:

$$E(\text{KeV}) = 0.786 + 0.054 \text{ CH}, \text{ where } E \text{ is photon energy and CH is channel number.}$$

EXPERIMENTAL RESULTS

(1) There are two spectra shown in Fig. 7 from the graphite only at ambient conditions. Because of poor resolution of spectra from samples at live-time of 5 minutes, it was extended up to 60 minutes of live-time mode. However, it does not show any difference in XRD patterns between two live-time modes. Therefore, the 5 minutes mode was set for the further work.

The upper spectrum in Fig. 7 is from the mixture of graphite and NaCl. Three of NaCl XRD peaks, (111), (200) and (220), appear with graphite

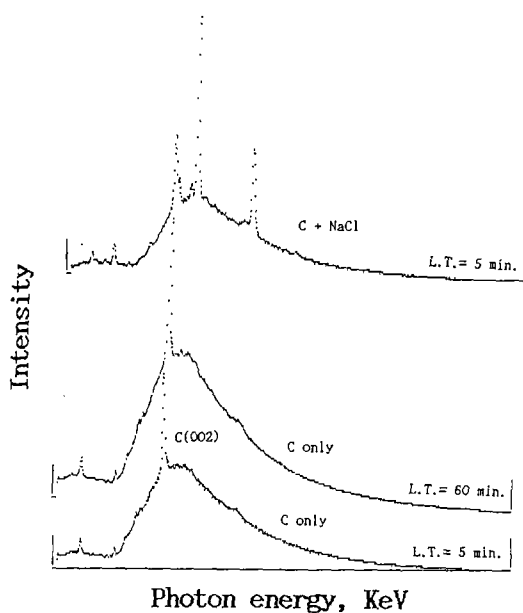


Fig. 7. Spectra of graphite only (C-only) at different live-time modes (L.T.=5 min. and L.T.=60 min.). Upper spectrum is from a mixture of graphite with NaCl (C+NaCl) for 5 minutes of live time.

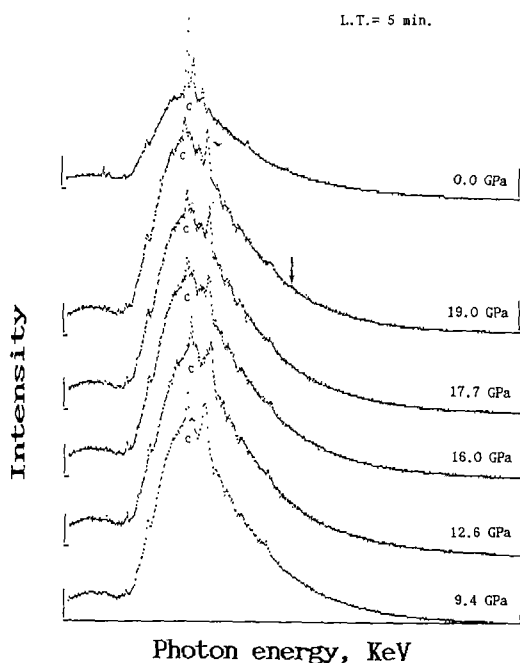


Fig. 8. A series of spectrum at high pressures at live-time of 5 minutes. High pressure values are expressed in GPa. Note the arrow marked at 19.0 GPa spectrum for possible hexagonal phase.

Table 1. Peak search data of graphite with NaCl at 0 GPa

Energy KeV	d-Spacings Å	Phases ^a	Lattice parameters ^b
13.798	3.374	C (002)	
14.285	3.259	NaCl (111)	5.644
16.502	2.821	NaCl (200)	5.642
22.287	2.089	C (101)	
23.315	1.997	NaCl (220)	5.647
28.560	1.630	C (004)	

^aC stands for graphite. ^bLattice parameter of NaCl based on 3 XRD peaks: 5.644(2) Å, Lattice parameter of graphite from 3 XRD peaks: $a_0=2.539$ Å, $c_0=6.702$ Å.

Table 2. The d-spacing variations of graphite 002 peak with pressure

Pressure GPa	Energy KeV	d-Spacings Å	d/d ₀
0	13.798	3.374	
9.4	15.691	2.967	0.879
12.6	16.231	2.868	0.850
16.0	16.502	2.821	0.836
17.7	16.610	2.803	0.831
19.0	16.826	2.767	0.820

peaks together. Although a small amount of NaCl fine powder was put on top of sample chamber, NaCl peaks appear more apparently due to the lightness of graphite. The NaCl (200) peak has been used for pressure monitoring both on loading and on unloading processes. Peak search data of graphite with NaCl is given at Table 1. Graphite (002) peak is apparent, and graphite (101) and (004) peaks are searched manually by their lower intensities. Lattice parameter of NaCl was determined to be 5.644(2) Å, which is in good agreement with ASTM data of 5.6402 Å. Three peaks of graphite were used for lattice parameter determination without confidence (i.e., $a_0=2.539$ Å; $c_0=6.702$ Å). These values are not in good agreement with the published ones (i.e., $a_0=2.463$ Å; $c_0=6.714$ Å in ASTM). Therefore, graphite (002) peak becomes unique tracer for its behavior under high pressures.

(2) The d-spacing variations of graphite (002) peak with high pressures are listed in Table 2. Fig. 8 shows the peak position shift with increasing

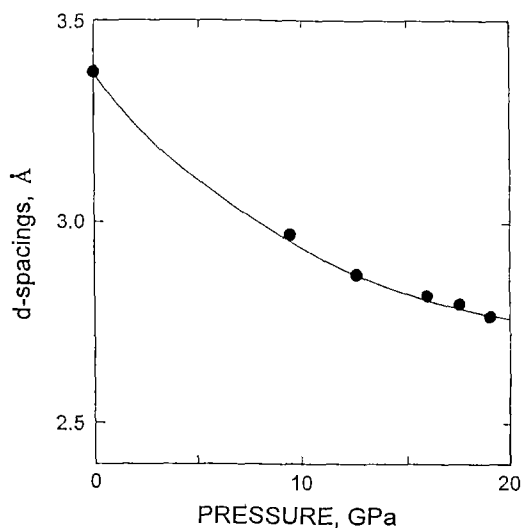


Fig. 9. The d-spacing variations of graphite 002 with pressures. Curve shows high compression at lower pressure region, however tardy shrinks of d-spacings at higher pressure region.

pressures up to 19.0 GPa, then unloading to 0 GPa (i.e., 1 bar). Compressions of graphite (002) interplanar spacings are plotted against pressures in Fig. 9. This procedure is not enough to determine the bulk properties of graphite. Therefore, compressibility of graphite can be deduced from the peak position changes with NaCl peaks in Fig. 8. It was found that the rate of shifts of graphite (002) and NaCl (111) peaks appears to be similar. From these observations, compressibility of graphite is estimated almost same as that of NaCl.

(3) It was previously reported that a new XRD peak of (100) from hexagonal diamond structure starts to form at the pressures higher than 18 GPa (Yagi *et al.*, 1992). However, it is difficult to pick up a new peak as a hexagonal diamond phase at the present XRD peaks of 19.0 GPa in Fig. 8. If (100) peak of hexagonal diamond phase appears at 19 GPa or higher pressures, the position of that peak would be marked at 19.0 GPa spectrum as shown in Fig. 8.

One important observation in the present study is that there appears a new peak of 17.529 KeV (i.e., $d=2.656 \text{ \AA}$) at 16.0 GPa in Fig. 8. This peak keeps existing at 17.7 GPa and 19.0 GPa with

17.475 KeV (i.e., $d=2.664 \text{ \AA}$). However, this new peak disappears when unloaded down to 0 GPa. It is difficult to identify this new peak at this moment, and some further works will be needed to have this observation clarified.

(4) Based on the preliminary analyses on the present experimental data, it could be recommended for further detailed studies on graphite as follows:

(a) A well crystalline powder graphite rather than those samples used at this experiment, should be employed for both compressibility and phase transition studies.

(b) More intense X-ray source than that of SSRL is needed for better resolution of the peaks from a light element of graphite (i.e., carbon). For example, X-ray source at Beam Line X-17C of the Brookhaven National Laboratory (BNL) in New York, U.S.A. is the Wiggler instead of bending magnet. This light of BNL is recommended for more detailed studies on graphite.

(c) More definite XRD peaks are expected if any anvil apparatus holds more sample than that in DAC. XRD experiments using Large Volume Apparatus such as the high pressure generating anvil established at the Photon Factory, in Tsukuba, Japan, would be more appropriate for the investigation of graphite at high pressure.

SUMMARY

(1) EDXRD experimental methods were introduced with SR. Mao-Bell type DAC has been employed for the graphite up to 19.4 GPa under room temperature conditions at the SSRL.

(2) Compressibility of graphite is estimated almost same as that of NaCl from their constant movements of peak position with increasing pressure. Observation of phase transition to hexagonal diamond was beyond the present experimental capability because of the poor resolution of the XRD peaks on graphite.

(3) X-ray source higher in intensity than that of the SSRL is needed to obtain better resolution of the peaks from a light chemical element of graphite. Moreover, clearer XRD peaks are

expected when the special type anvil apparatus (i.e., Large Volume Anvil Cell) holds more polycrystalline sample than that in DAC.

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(책임편집 : 안중호)

고압하에서 방사광을 이용한 흑연에 대한 연구

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요 약 : 흑연에 대한 압축성과 육방정계 다이아몬드 구조로 상변이에 대한 고압실험이 상온상태에서 이루어졌다. 에너지 분산 X-선 회절법을 마오-벨(Mao-Bell)형 다이아몬드 앤빌기와 방사광과 함께 이용하였다. 소금분말을 흑연시료의 고압상태 압력값의 지시물질로 사용하였다. 흑연의 X-선 회절분석도가 좋지 않아, 흑연의 압축성은 흑연 (002) 회절 피크를 이용하여 소금의 압축성과 유사함을 추정할 수 있었다. 육방정계 다이아몬드 결정구조로 상변이 현상은 본 실험에서 관찰하지 못하였다. 흑연의 결정 특성상, 보다 강력한 X-선 공급원인 위클리 방사광이나 다이아몬드 앤빌기기 보다 흑연 시료를 보다 많이 압축할 수 있는 대용량 고압기의 사용이 흑연에 대한 압력에 의한 상변이 및 압축성 연구에 필요하다.

핵심어 : 에너지 분산 X-선 회절, 다이아몬드 앤빌 기기, 방사광, 상변이, 육방정계 다이아몬드 상(相)