

Phase Transition Study on Graphite at Room Temperature

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ABSTRACT : High pressure X-ray diffraction study was carried out on a polycrystalline graphite to investigate the phase transition(s) at room temperature. Energy dispersive X-ray diffraction method was employed using a Mao-Bell type diamond anvil cell with an Wiggler Synchrotron Radiation at the National Synchrotron Light Source. Sodium chloride powder was used as the internal pressure sensor for the high pressure determinations as well as the pressure medium for quasihydrostatic pressure environment. Graphite transforms into a hexagonal diamond phase and this phase persists when pressure is released down to 0.1 MPa. This result does not agree with the previously reported observations and this discrepancy would be due to the kinetics in phase transition as well as the uniaxially oriented pressure field in the diamond anvil cell.

Key words : energy dispersive x-ray diffraction, diamond anvil cell, wiggler synchrotron radiation, phase transition, hexagonal diamond phase

INTRODUCTION

Graphite has been a target of experimental as well as of theoretical studies considerably since it is one of the most highly anisotropic materials. In the crystal structure of graphite, the carbon atoms lie in honeycomb sheets, with extremely strong covalent bonds between the atoms in each sheet and the interlayer bonds are, however, relatively weak along the c-axis. The stacking sequence along the c-axis is the hexagonal symmetry. Because of this peculiar property in the crystal structure, the compressibility of graphite is significantly anisotropic (Zhao and Spain, 1989).

It was reported that the electrical resistivity increase of the single crystal graphite between 10 and 20 GPa at room temperature, but upon unloading to ambient pressure the resistivity returned to its initial value and the recovered specimen proved to be graphite (Aust and Drickamer, 1963). Compressed along the c-axis,

resistivity decreases slowly with increasing pressure to ~12 GPa. However, when graphite was heated above 1000°C under high pressure, a new phase appeared and this phase had an irreversible hexagonal diamond structure (Bundy and Kasper, 1967). This kind of pressure-induced phase transition of graphite was observed in the diamond anvil cell (DAC) 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).

In the diamond anvil apparatus, the thickness of the sample becomes less than 100 μm above 10 GPa and consequently, graphite provides very weak X-ray diffraction (XRD) patterns. Moreover, graphite has a layered structure and it is almost impossible to make a fine-grained powder by grinding. Even when a sin-

gle crystal of graphite is crushed into polycrystalline particles, they shatter into the flakelike shapes. Whenever such particles are compressed uniaxially, they develop a strong preferred orientation (Yagi *et al.*, 1992). All these kinds of obstacles have made it difficult to obtain high quality XRD patterns on graphite under high pressure. Consequently, in our previous study, it was recommended that X-ray source much higher in intensity than that of the Stanford Synchrotron Radiation Laboratory is needed for better resolution of the peaks of graphite (Kim and Na, 1994). The purpose of this study, therefore, is to report the experimental results by the energy dispersive X-ray diffraction (EDXRD) technique with the Synchrotron Radiation (SR) which an Wiggler device was inserted, using the Mao-Bell type DAC at the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory, USA.

EXPERIMENTS

In the EDXRD principle, $E \times d$ is constant, where E is the photon energy and d is the interplaner spacing (Giessen and Gordon, 1967). The present experimental set-up of $E \times d$ was 88.359, which is equivalent to the 2θ of 8.05°. The value of $E \times d$ has been increased very much compared with those of both 1994 and 1996 experiments at the SSRL (Kim and Na, 1994; Na and Kim, 1996). In this set-up at the NSLS, XRD peaks at the higher photon energy (i.e., smaller d -spacing) can be observed compared to the previous two runs.

Graphite powder sample for this experiment is the same as used previously (Na and Kim, 1996), which is the commercial product of the Nacalai Tesque Inc., Japan. Polycrystalline particles are in the flake-like shape under microscope. Pressure of the compressed sample was monitored by the internal pressure sensor of NaCl. A very small amount (i.e., less than ~3% to graphite in volume) of fine powder of NaCl was put on the top of the sample. NaCl also acts as a pressure medium for quasi-hy-

drostatic pressure environment in the sample chamber and prevents the sample from the preferred orientation as well.

Experimental set-up and its details are almost same as the previous work (Kim and Na, 1994). Differences from the previous experiment are as follows: Beam intensity has been hiked higher in several orders than the previous one by the insertion of the Wiggler device. Gasket material used is the fully hardened and heat treated stainless steel (T 301) and the hole dimension is 100 μm in diameter and 0.254 mm in thickness, respectively. Incident beam has been collimated to 50 μm in order to get the XRD pattern of the highest pressurized part in the sample chamber between anvils. The diamond culet of both upper and lower anvils is in the bevel-type (i.e., 200/400 μm , 7° of bevelled angle) each in diameter. Quality of diamond is of the gem level and the weight of each diamond reaches 0.3 carat (i.e., 60 mg).

In order to obtain a high detecting efficiency in the photon energy range of 20 to 80 KeV, an intrinsic Germanium solid state detector (ORTEC 573) was used. This detector operates at low temperature (i.e., 77 K) with a bias voltage of 0.3 KV power supply. (Oiffracted beam was also collimated to 50 μm is diameter to prevent it from over-saturation.)

Data were acquired through the multi-channel analyzer (MCA) system of 4096 channels. Photon energy calibration with an MCA system was completed just after apparatus set-up before loading pressures on the sample. This calibration was repeated after experiment for checking any disturbance(s) of the alignment during experimental processes by comparison with that of the initial set-up.

RESULTS AND DISCUSSIONS

The accumulated XRD data in MCA system were analyzed manually by picking-up the photon energy on each peak. The d -spacing on each peak was calculated using the relation of

$E \times d$ of 88.359. In this calculation, factors which reduced the accuracy of d -spacing could be the follows: coexisting of two phases, acquisition duration variations, crossing of the XRD peaks depending on the different compressibilities of graphite and NaCl. XRD data

of relative intensities with d -spacings in the loading process and unloading process are given in Tables 1 and 2, respectively. A sequence of XRD spectra on both loading and unloading processes is shown in Fig. 1. Quality of spectrum is variable each other depending on

Table 1. XRD data* of graphite on loading process

0.1 MPa			7.8 GPa			27.0 GPa			40.0 GPa		
I/I_0^{**}	d^{***}	phases	I/I_0^{**}	d^{***}	phases	I/I_0^{**}	d^{***}	phases	I/I_0^{**}	d^{***}	phases
100	3.353	G(002)	30	3.054	G(002)	10	2.866	B1(111)	10	2.979	B2(100)
15	3.255	B1(111)	40	3000	B1(111)	8	2.755	G(002)	8	2.232	G(002)
50	2.819	B1(200)	100	2.488	B1(200)	80	2.481	B1(200)	100	2.108	B2(110)
25	2.243	gasket	50	2.118	G(100)	80	2.161	B2(110)	5	2.039	G(100)
15	2.125	G(100)	60	2.002	G(101)	15	2.048	G(100)	10	1.980	G(101)
40	2.068	gasket	40	1.866	B1(220)	10	1.986	G(101)	90	1.859	h-D(101)
45	2.033	G(101)	20	1.525	B1(222)	100	1.884	h-D(101)			
25	1.995	B1(220)	10	1.317	G(004)	20	1.757	B1(220)			
40	1.962	gasket				15	1.446	B1(222)			
5	1.803	G(102)				15	1.239	G(004)			
15	1.678	G(004)									
15	1.630	B1(222)									
10	1.228	B1(420)									
10	1.214	G(110)									

*In phases, G stands for graphite, B1 for NaCl structured NaCl, B2 for CsCl structured NaCl, h-D for hexagonal diamond phase.

**Relative intensities. The intensities of the XRD peaks were determined by visual comparison.

***Interplaner d -spacings in Å

Table 2. XRD data* of graphite on unloading process

10.8 GPa			7.7 GPa			0.1 MPa		
I/I_0^{**}	d^{***}	phases	I/I_0^{**}	d^{***}	phases	I/I_0^{**}	d^{***}	phases
5	2.994	G(002)/B1(111)	10	3.149	G(002)/B1(111)	40	3.353	G(002)
50	2.599	B1(200)	80	2.633	B1(200)	15	3.255	B1(111)
60	2.155	h-D(100)/G(100)	70	2.174	h-D(100)/G(100)	90	2.821	B1(200)
100	1.905	h-D(101)	80	2.021	h-D(002)/G(101)	40	2.192	G(100)/h-D(100)
			100	1.927	h-D(101)	100	2.032	G(101)/h-D(002)
						5	1.998	B1(220)
						50	1.940	h-D(101)
						10	1.631	G(004)/B1(222)
						7	1.523	G(103)
						8	1.493	h-D(102)
						15	1.436	B1(400)
						10	1.275	h-D(110)
						10	1.264	B1(420)

*In phases, G stands for graphite, B1 for NaCl structured NaCl, h-D for hexagonal diamond phase.

**Relative intensities. The intensities of the XRD peaks were determined by visual comparison.

***Interplaner d -spacings in Å

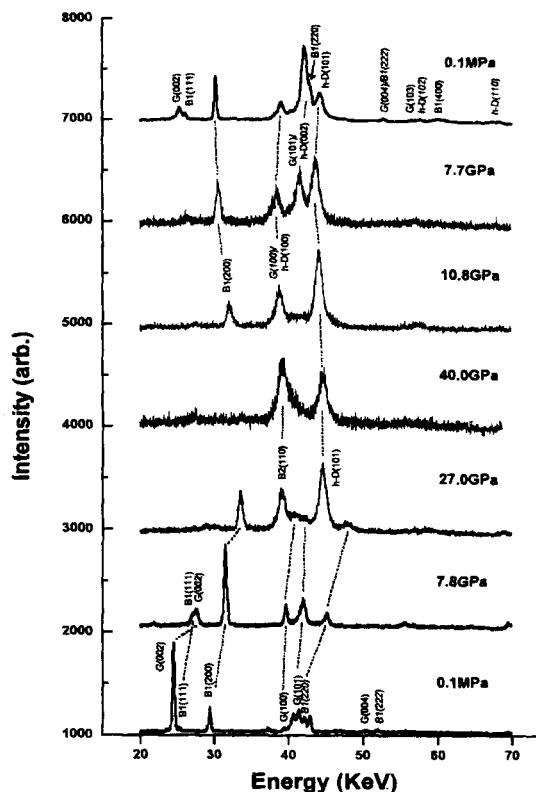


Fig. 1. A series of XRD peaks of graphite and NaCl with pressure. G is for graphite, B1 for NaCl-structured sodium chloride phase, B2 for CsCl-structured sodium chloride phase and h-D for hexagonal diamond phase. Intensity is in arbitrary unit.

the acquisition time in live-time mode that ranges from 10 to 30 minutes.

A spectrum of the graphite with NaCl at ambient conditions (i.e., room temperature and 1 atmospheric pressure) is shown in Fig. 2. There are three gasket lines appear at 2.243 Å, 2.068 Å and 1.962 Å, respectively. After this run, sample was moved slightly in order to get rid of gasket lines. This adjustment dose not effect the $E \times d$ value because the incident beam is perpendicular to the sample chamber face. Lattice parameters of graphite were calculated from six XRD peaks to be: $a_0 = 2.436(7)$ Å and $c_0 = 6.727(42)$ Å (c.f., $a_0 = 2.463$ Å and $c_0 = 6.714$ Å, ASTM 41-1487, $a_0 = 2.539$ Å and $c_0 = 6.702$ Å, Kim and Na, 1994). The present value was determined by the limited number of XRD peaks

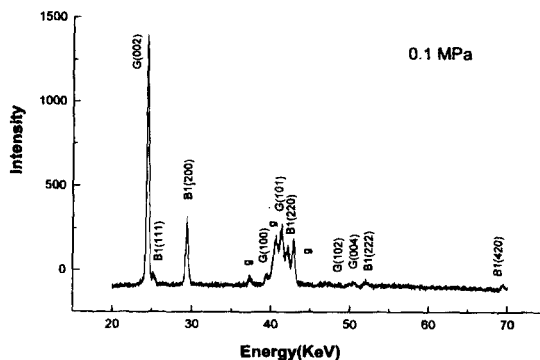


Fig. 2. XRD pattern of the starting phase at 0.1 MPa. There are three gasket peaks shown, G is for graphite and B1 for NaCl-structured sodium chloride phase.

in the diamond anvils. Thus, disagreement in lattice parameters with ASTM could be due to the data collection method differences. Lattice parameters of Kim and Na (1994) were determined on the powder specimen which was scratched from the heat-treated graphite pot.

At the pressure of 7.8 GPa in Table 1, XRD patterns shift to the lower d -spacing side. Both (002) and (004) peaks of graphite shift significantly compared with other XRD peaks. This is attributed to the fact that carbon atoms within the layers of graphite are connected by sp^2 -type covalent bonds, while the bond between layers has the nature of the van der Waals force. Consequently, compressibility along the c -axis is much greater than that along a -axis and thus G (002) peak appears at higher energy than NaCl (111) (Fig. 1).

At 27.0 GPa, B2 phase of NaCl (i.e., CsCl structure of NaCl) appears with B1 phase (i.e., NaCl structure) together. From the B1(200) and B1(220), the present pressure was determined to be approximately 27.0 GPa. It is well known that the phase transition pressure to a hexagonal diamond phase of graphite lies between 11 GPa and 18 GPa from various experimental studies (eg, Yagi *et al.*, 1992; Zhao and Spain, 1989; Hanfland *et al.*, 1989). The (101) of hexagonal diamond (h-D) phase appears at the d -spacing of 1.884 Å. It is very clear that this peak is definitely new from the

fact that G(100) and G(101) shrinks slowly and B1(220) moves to at the d -spacing of 1.757 Å.

At 40 GPa, the highest pressure in this run, B1 phase of NaCl disappears. From the d -value of (110) peak from B2 phase of NaCl, pressure was estimated to be approximately 40 GPa (Bassett *et al.*, 1968; Heinz and Jeanloz, 1984). At this pressure, weak (100) peak of B2 phase appears together with several graphite phases (Table 1). Because the thickness of sample is very thin at this highest pressure (e.g., the thickness of the sample becomes less than 100 µm above 10 GPa), the good quality XRD patterns were not obtained.

Upon rapid unloading to 10.8 GPa, B1 phase of NaCl reappears and B2 phase disappears. Therefore, all peaks should belong to NaCl and two polymorphs of graphite (Table 2 and Fig. 1). The XRD peak at 2.155 Å should belong to graphite and/or hexagonal diamond phase. However, as pressure was released to 7.7 GPa, an additional peak appears at the d -spacing of 2.021 Å (Table 2). Compared with the previous run at 10.8 GPa, this peak is definitely new and can be assigned to be a mixture of h-D(002) and G(101). A peak at 2.174 Å represents a mixture of h-D(100) and G(100) at this pressure.

At the completely unloaded state to 0.1 MPa (Table 2 and Fig. 3), h-D(101) is distinctive and this peak does not belong to any phases such as graphite, NaCl or even gasket. Furthermore, h-D(101) at 1.940 Å and h-D(110) at 1.264 Å appear at this ambient condition. These three peaks do not overlap with any peak of other phase(s). Two additional peaks of h-D(100) and h-D(002) overlap with G(100) and G(101) peaks, respectively. It is thus clear that high pressure hexagonal diamond phase is preserved at the unloaded ambient conditions. Based on the data in Table 2, lattice parameters of graphite were calculated to be $a_c=2.489(20)$ Å and $c_o=6.515(46)$ Å which are slightly different from those of the starting phase. This difference would be due to the overlapping of graphite with hexagonal diamond phase as well as the

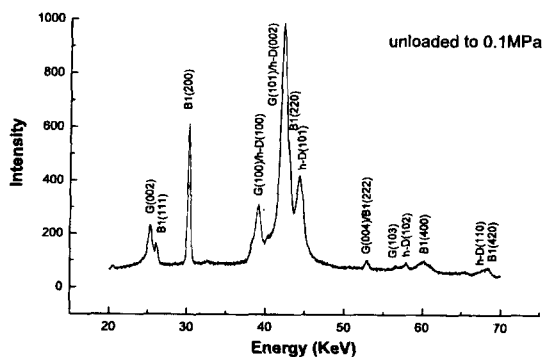


Fig. 3. XRD pattern when unloaded to 0.1 MPa after compression. G is for graphite, B1 for NaCl-structured sodium chloride phase and h-D for hexagonal diamond phase of graphite.

sample orientation change before and after loading.

The variations of the d -spacing of the graphite and hexagonal diamond phase with pressure are summarized in Fig. 4. Five diffraction peaks of the high pressure phase can be indexed by a hexagonal unit cell and two of them overlap with the peaks of graphite. Lattice parameters of hexagonal diamond phase calculated from five XRD peaks are $a_o=2.548(3)$ Å and $c_o=4.060(10)$ Å and compared with the previously reported values in Table 3 (i.e., $a_o=2.513(6)$ Å and $c_o=4.171(5)$ Å, Yagi *et al.*, 1992;

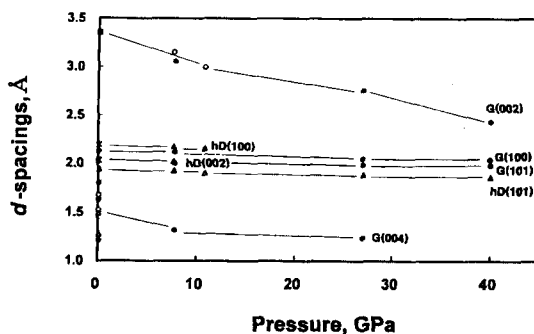


Fig. 4. Variation of the d -spacings of graphite and hexagonal diamond phase with pressure. Circles and triangle are for graphite and hexagonal diamond phase, respectively. Mixture of graphite and hexagonal diamond phase is designated as the cross mark at 0.1 MPa. Solid square for G(002) at 0.1 MPa is for graphite of the starting phase and the unloaded phase at the same position. Solid mark is for loading process and open mark for unloading process.

Table 3. Lattice parameters and *d*-spacings* of the hexagonal diamond phase at 0.1 MPa

(hkl)	obs.** (Bundy & Kasper, 1967)	obs.** (Yagi <i>et al.</i> , 1992)	calc.	obs. (This study)	calc.
(100)	2.19	2.180	2.176	2.192	2.207
(002)	2.06	2.086	2.086	2.032	2.030
(101)	1.92		1.929	1.940	1.943
(102)	1.50		1.506	1.493	1.484
(110)	1.26	1.256	1.257	1.275	1.274
(103)	1.17		1.172		1.153
(112)	1.075	1.074	1.076		1.079
(201)	1.055		1.053		1.064
	a=2.52 Å	a=2.513(6) Å		a=2.548(3) Å	
	c=4.12 Å	c=4.171(5) Å		c=4.060(10) Å	

*Unit in Å

**Quenched sample from high pressure-high temperature treatment

***Extrapolated to 0.1 MPa linearly

$a_0=2.52$ Å and $c_0=4.12$ Å, Bundy and Kasper, 1967). The error range of *c* parameter in the present study is within 0.2%. In this table, four *d*-spacings of the XRD peaks observed by Yagi *et al.*, (1992) were extrapolated linearly to 0.1 MPa and lattice parameters were calculated based on these data. Furthermore, they did not observe the (101) and (102) peaks, which are more or less in strong intensities. In our data, XRD peaks at the higher energy region than 70 KeV (i.e., (103), (112) and (201) peaks of hexagonal diamond phase) were impossible to acquire in the present set-up of $E \times d$. Compared with parameter ratio of *c/a* in Table 3, all values (i.e., $c/a=1.635$, Bundy and Kasper, 1967; $c/a=1.660$, Yagi *et al.*, 1992; $c/a=1.593$, this study) are apart from the ideal value of 1.63 in the hexagonal close-packing structure. The *c/a* of this study, thus, indicates the contraction along *c*-axis, which is probably due to the repulsion between the carbon atoms along *a*-axis.

The proposed relationship between graphite and hexagonal diamond structure was that *c*-axis orientation is not changed before and after phase transition (Yagi *et al.*, 1992). The hexagonal diamond structure has tetrahedral covalent bonds just as does the cubic diamond structure. Difference from cubic diamond structure is that the hexagonal diamond structure is

in wurtzite-type structure in stacking sequence of ABAB... From this relation, it is anticipated that the bulk modulus of hexagonal diamond phase of graphite is lower than that of the cubic diamond phase of graphite (i.e., K_0 of cubic diamond=442 GPa, Xu and Huang, 1994). The present experimental result, however, is not enough to confirm all these relationships.

Present experimental results are quite different from those of the previous workers (Utsumi and Yagi, 1991; Yagi *et al.*, 1992), who reported a reversible change to graphite when unloaded to ambient pressure at room temperature. Because the present experiment was performed very quickly, the pressure induced phase transition might be time-dependent. Thus, the final run at 0.1 MPa was acquired for 6 hours to minimize this kinetic effect. Nevertheless, several peaks of hexagonal diamond phase persisted. Bundy *et al.*, (1996) concluded that the observed behavior of a given specimen of graphite during compression depends on its initial degree of crystallinity, the direction and homogeneity of the pressure field, the rapidity of compression and the type of measurement performed. Therefore, the present result would be attributed to the uniaxial stress effect in the DAC and the rapidity of loading and unloading

processes. In order to clarify the quenchability of hexagonal diamond phase in this graphite, the special type anvil apparatus (i.e., large volume press) containing large amount of sample at the real hydrostatic environment is needed.

SUMMARY

1) EDXRD experimental methods were employed with a Wiggler SR at the NSLS. Mao-Bell type DAC has been used for the compression of graphite up to approximately 40.0 GPa at room temperature.

2) Phase transition of graphite to a hexagonal diamond phase was observed.

3) High-pressure hexagonal diamond phase of graphite persisted even when pressure was released to 0.1 MPa. The present result is in contrast with the previously reported ones. This discrepancy would be due to the kinetics in phase transition as well as the uniaxially oriented inhomogeneities of the applied pressure field in the DAC.

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REFERENCES

- Aust R.B. and Drickamer H.G., 1963, Carbon-a new crystalline phase. *Science* 140, 817-819.
- Bassett W.A., Takahashi T. Mao H.K. and Weaver J.S., 1968, Pressure-Induced Phase Transformation in NaCl. *J. Applied Physics*, 39(1), 319-325.
- Bundy F.P. and Kasper J.S., 1967, Hexagonal diamond-a new form of carbon. *J. Chem. Phys.*, 46, 3437-3446.
- Bundy F.P., Bassett W.A., Weathers M.S., Hemley R.J., Mao H.K. and Goncharov A.F., 1996, The pressure-temperature phase and transformation diagram for carbon; Updated through 1994. *Carbon*, 34(2), 141-153.
- Hanfland M., Beister H. and Syassen K., 1989, Graphite under pressure: Equation of state and first-order Raman modes. *Phys. Rev. B*39(17), 12598-12603.
- Heinz D.L. and Jeanloz R., 1984, Compression of the B2 high-pressure phase of NaCl. *Phys. Rev. B*30(10), 6045-6050.
- Giessen B.C. and Gordon G.E., 1967, X-ray diffraction: New high-speed technique based on X-ray spectroscopy. *Science*, 159, 973-975.
- Kim Y.H. and Na K.C., 1994, High pressure X-ray diffraction study on a graphite using Synchrotron Radiation. *Jour. Petrol. Soc., Korea*, 3(1), 34-40.
- Na K.C. and Kim Y.H., 1996, Experimental study on the phase change of a graphite using piston cylinder, DAC and Synchrotron Radiation. *J. Petrol.Soc., Korea*, 5(2), 129-134.
- Utsumi W. and Yagi T., 1991, Formation of hexagonal diamond by room temperature compression of graphite. *Proc. Japan Academy*, 67, B(9), 159-164.
- Yagi T., Utsumi W., Yamakata M., Kikegawa T. and Shimomura O., 1992, High pressure *in-situ* x-ray diffraction study on the phase transformation from graphite to hexagonal diamond at room temperature. *Phys. Rev. B*46(10), 6031-6039.
- Xu J.-A. and Huang E., 1994, Graphite-diamond transition in gem anvil cells. *Rev. Sci. Instrum.* 65(1), 204-207.
- Zhao Y.X. and Spain I.L., 1989, X-ray diffraction data for graphite to 20 GPa. *Phys. Rev. B*40(2), 993-997.

(책임편집 : 박계현)

고압하에서 방사광을 이용한 흑연에 대한 연구

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요 약 : 흑연에 대한 육방정계 다이아몬드 구조로 상변이에 대한 고압실험이 상온상태에서 이루어 졌다. 에너지분산 X-선 회절법을 마오-벨 형 다이아몬드 앤빌기기와 위글러 방사광과 함께 이용하였다. 소금분말 은 시료의 고압상태 압력값의 결정과, 시료방의 압력전달 상태를 정압상태에 가깝게 하기 위하여 이용되었다. 압력을 증가 시킴에 따라 흑연이 육방정계 다이아몬드 결정구조로 상변이 하는 것이 관찰되었으며, 압력을 1기압상태로 환원하여도 이 고압상은 존재하고 있다. 이 결과는 지금까지 발표된 현상과 일치하지 않으며, 이러한 차이는 다이아몬드 앤빌기기에 의한 압력의 일축성과 상변이시 시간에 따른 동력성의 영향에 의한 것으로 판단되어 진다.

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