Development of the high pressure technology with sintered diamond anvils and the study of graphite to hexagonal diamond transition

焼結ダイヤモンドアンビルを用いた高圧技術の開発及び黒鉛－六方晶ダイヤモンド変換の研究

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Abstract.

In the static high pressure experiments, the multi-anvil type apparatus and the diamond anvil apparatus are widely used. The multi-anvil apparatus can generate uniform pressure in a fairly large volume, but its maximum pressure is quite low compared with that generated by diamond anvil apparatus. In order to raise the attainable pressure in the multi-anvil apparatus, we developed new high pressure technique using large size sintered diamond anvils. Pressure generation up to 18 GPa in the cubic anvil apparatus, up to 30 GPa in a Drickamer anvil type apparatus, and more than 23 GPa in a 6-8 two stage system were attained. Although some problems still remain, such as the occurrence of cracks in the anvils and blow out on release of pressure, this sintered diamond material is eminently suitable for use in the multi-anvil apparatus.

Recently, the behavior of graphite under high pressure and room temperature condition has been one of the great interest. In the present study, by the optical observation using a diamond anvil apparatus, we clarified that when very thin single crystal graphite was compressed under quasi-hydrostatic condition, it transformed to a light transparent phase at 18 GPa. In order to determine the structure of this high pressure phase, *in situ* X- ray observation was carried out using the sintered diamond anvil apparatus. New diffraction peaks clearly observed under high pressure could be indexed as a hexagonal unit cell, and it became clear that hexagonal diamond (Lonsdaleite) was formed by the room temperature compression of graphite. The diffraction profiles from two different directions support the orientation relationship of the martensitic transformation

from graphite to hexagonal diamond. This hexagonal diamond has a large bulk modulus comparable to the cubic diamond and the transition pressure is very sensitive to the nature of the starting material as well as the nature of the pressure applied to the sample.

Die Entwicklung der Hochdrucktechnik mit Sinter-Diamant-Ambossen und die Studie über die Umwandlung von Graphit zu Hexagonal-Diamant

In statischen Hochdruckexperimenten werden in der Regel Multi-Amboss-Apparaturen und Diamant-Amboss-Apparaturen verwendet. Eine Multi-Amboss-Apparatur kann gleichmässigen Druck in einem relativ grossen Volumen erzeugen, der maximale Druck ist jedoch im Vergleich zu dem mit einer Diamant-Amboss-Apparatur erzeugten Druck relativ nieder. Um den Druck in der Multi-Amboss-Apparatur zu erhöhen, entwickelten wir eine neue Hochdrucktechnik, bei der grosse Sinter-Diamant-Ambosse verwendet werden. Dabei konnten in kubischen Amboss-Apparaturen bis zu 18 GPa, in Drickamer-Amboss-Apparaturen bis zu 30 GPa und in 6-8 Zweistufensystemen mehr als 23 GPa Druck erreicht werden. Obwohl noch einige Probleme ungelöst bleiben, wie z.b. das Auftreten von Brüchen in den Ambossen und Explosionen bei Druckverminderung, sind Sinter-Diamanten sehr gut für die Verwendung in Multi-Amboss-Apparaturen geeignet.

In letzter Zeit stand das Verhalten von Graphit unter hohem Druck und bei Zimmertemperatur im Mittelpunkt des Interesses. In dieser Studie verwendeten wir eine Diamant-Amboss- Apparatur zur optischen Beobachtung und stellten fest, dass ein sehr dünner Einkristall-Graphit, der unter quasi-hydrostatischen Bedingungen gepresst wurde, bei einem Druck von 18 GPa in eine transparente Phase eintrat. Um die Struktur dieser Hochdruckphase zu bestimmen, wurde eine in situ Röntgenstrahlenbeobachtung unter Verwendung einer Sinter-Diamant-Amboss-Apparatur durchgeführt. Neue Diffraktionsspitzen, die unter Hochdruckbedingung eindeutig beobachtet wurden, konnten als hexagonale Gitter gedeutet werden. Damit wurde klar, dass bei Kompression von Graphit bei Zimmertemperatur Hexagonal-Diamant (Lonsdaleit) entsteht. Diffraktionsprofile aus zwei verschiedenen Richtungen bestätigten den Charakter einer martensitiscken Transformation von Graphit zu Hexagonal-Diamant. Der Hexagonal-Diamant hat einen grossen Volumen Elastizitätsmodul, der mit dem eines kubischen Diamanten vergleichbar ist. Der Umwandlungsdruck ist sehr sensibel in bezug auf das Ausgangsmaterial und auf die Probe ausgeübten Druck.

CHAPTER 1.

Development of the High Pressure Technology with Sintered Diamond Anvils

1-1. Introduction.

The static high pressure technology is widely used in the field of physics, chemistry, mineralogy, geophysics, material science, and so on. The progress of the high pressure technology such as an expansion of attainable pressure region or an enlargement of the sample volume have made a breakthrough of the scientific frontier in each field. In the recent high pressure experiments under the condition over 5 GPa region, the multi-anvil type apparatus and the diamond anvil cell are widely used. The diamond anvil cell, which uses two single crystal diamonds as opposed anvils, can generate more than 1 Mbar region, although its sample volume is quite small (μg order). X-ray and visible light can pass through the anvils, thus this diamond anvil cell is widely used for the various physical measurements. However, because of the limitation of the anvil size, the enlargement of the sample volume in this apparatus is very difficult.

On the other hand, the multi-anvil apparatus has the advantage that it can generate uniform pressure in a fairly large volume compared with the diamond anvil cell. Thus a small furnace can be embedded in the pressure medium and the sample can be heated uniformly. This apparatus is suitable for use not only in the physical measurements but also in the synthesis of various materials using high pressure and high temperature conditions. However, the maximum pressure generated by the present multi-anvil apparatus in common use is less than about 25 GPa, mainly because of the limitation of the hardness of the WC alloy which is used as an anvil material.

It has been thought that the use of a much harder material than WC alloy such as sintered diamond might raise the upper limit of the pressure in the multi-anvil apparatus. Sintered diamond compacts, which is made from small powder diamond particles and binding metals, have high compressive strength, and in future, large size compacts comparable to the WC anvils currently used will be available. Hence, by applying the sintered diamond to the multi-anvil system, much higher pressure is hope to be generated without the reduction of the sample volume.

First attempt to use a sintered diamond as an anvil material was made by Bundy et al. [1975]. They applied small size synthetic sintered diamond to the Drickamer type anvil apparatus, and reported that more than 50 GPa could be generated although the top area of the anvil was very small (0.6mmϕ). (In this experiment, generated pressure was estimated by the measurement of electrical resistance jump in Fe-V alloy caused by the phase transition, and recent experiment made it clear that this pressure value was overestimated [Endo et al., 1987]). This sintered diamond project was developed by Japanese group in Osaka University [Endo and Ito,1982, Endo et al.,1985], and using small opposed anvils embedded in a large cubic pressure medium (6-2 type apparatus), pressure generation up to 60 GPa was confirmed by *in situ* X-ray observation of the lattice constant of gold and NaCl [Utsumi et al.,1986]. Moreover, they used sintered diamond in the 6-8 two stage multi-anvil apparatus, and more than 30 GPa was generated [Endo et al., 1987]. A similar experiment was also carried out by Ohtani et al. [1989], and

40 GPa was reached. Although these experiments were carried out at room temperature condition and the sample chambers were quite small compared with the current WC multi-anvil apparatus, the basic capability of sintered diamond for high pressure generation was confirmed by these results. Therefore, the next step is to generate higher pressure by applying larger size sintered diamond anvils to the multi-anvil apparatus. Our purpose in the present paper is to enlarge the sample volume from the very small one attained by the sintered diamond anvil in the previous studies to that attained by the WC anvil apparatus currently used. Moreover, we also aim to develop the technique for the generation of simultaneous high pressure and high temperature using sintered diamond anvil.

The high quality sintered diamond compacts suitable for the high pressure generation could not be obtained easily for a long time. Thus those who wanted to use sintered diamond anvil must have made sintered diamond compacts by themselves. However, due to the recent developments in high pressure technology, nowadays, fairly large size sintered diamond compacts can be obtained from several companies. We tried to carry out high pressure experiments by applying this sintered diamond compact to the DIA apparatus (one of the cubic anvil type apparatus), the Drickamer type apparatus, and the 6-8 two stage apparatus. In the following section, we will first describe the property of the sintered diamond compacts and the machining process to the anvil shape, and subsequently, the detail of the pressure generation using sintered diamond anvils in each high pressure apparatus will be described. Moreover, in the section of DIA apparatus, a new DIA apparatus named MAX90 which was constructed for the *in situ* X-ray observation using synchrotron radiation under high pressure and high temperature condition is also described.

1-2. Anvil material

The compacts of polycrystalline diamond, which is known as carbonado, have been found from natural resources [Trueb et al. 1969]. This material is thought to have been produced under the condition in which diamond is not stable thermodynamically. On the other hand, synthesis of this carbonado type material in the industrial process is ordinary made by the sintering of powder diamond under high pressure and high temperature condition with the help of some binding material [Hall, 1970, Katzman and Libby, 1971]. As a binding material, several kinds of metal, such as Co, Ni, Si, are used. In the case of sintering using Co binder, diamond powder (particle size is from 1 to 100 micron) are packed in the hole of a WC-Co ring. At high temperature and high pressure in the diamond stable region (1500 °C, 6GPa), molten cobalt extrudes from the ring, penetrates into the gap between diamond particles, and eventually cements them closely by the liquid phase sintering process. Formation of direct diamond-diamond bonding is formed by this sintering process, but not every commercially supplied compact have the perfect direct bondings.

Because this diamond sintering needs a lot of knowhow and very high technology, the size of the sintered diamond compact was very limited and its quality was not sufficient for the anvil use for a long time. However, due to the development of high pressure technology, recently, several companies supply various kinds of sintered diamond compacts for the use of machining tools. We obtained these sintered diamond compacts and checked their quality, price, and suitability for anvil shape. The material we have chosen in the present study is SYNDIE 15151 from De Beers company. The reason we have chosen this among the compacts supplied from several companies is as follows; (1) This is the largest one which is commercially available at present. (2) This sintered diamond compact is surrounded by a steel ring, and it can be removed easily. The sintered diamond compacts supplied from other companies are supported by tungsten carbide ring. The latter ones were easily cracked at edges near the boundary of diamond and tungsten carbide in a cutting process. This crack was probably caused by the thermal stress arisen from the difference of thermal expansion coefficient between diamond and tungsten carbide. The supplied SYNDIE 15151, which is originally sold as a wire making tool, is 15 mm in height and 15 mmϕ in diameter. This compact is made from fairly large size diamond particles (70 micron) with cobalt metal as a binding material (Cobalt content is about 15 weight %).

Fig.1-1 and Fig.1-2 show the sintered diamond anvils for the DIA apparatus and 6-8 two stage apparatus, respectively. To fashion the anvils into the proper shapes, an electro-discharge method and grinding by a diamond wheel were used. The anvil for the DIA apparatus is 15 mm in diameter, 15 mm in height and the top area of the anvil is 4 mm * 4 mm or 3 mm * 3 mm. In the 6-8 apparatus, a cube shaped anvil with a edge length of 9.5 mm was used, and the truncation edge length of the anvil was 2.0 mm. The accuracy of the square size of anvil top is less than 0.05 mm, and the perpendicularity of each plane is within 0.01 deg. The size of these sintered diamond anvils are quite large compared with

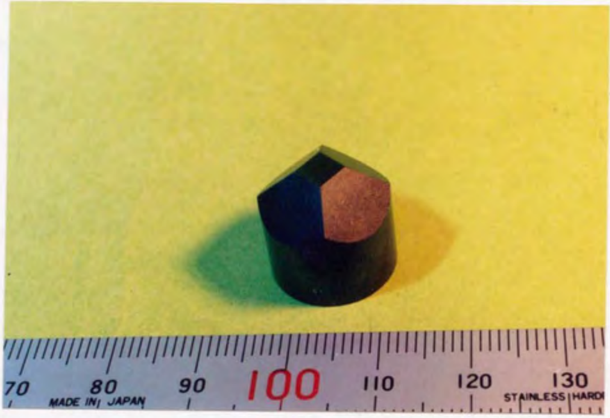

Fig.1-1
Sintered diamond anvil for the DIA apparatus.

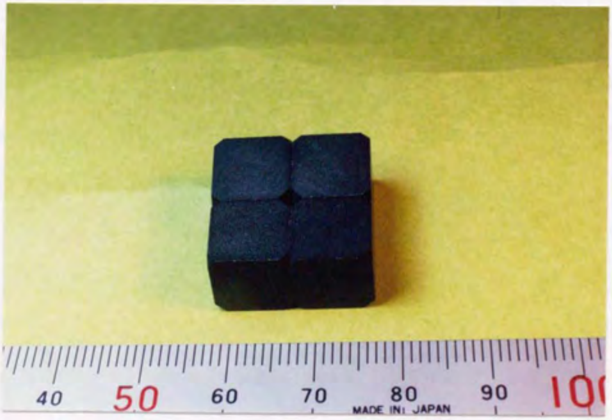

Fig.1-2
Sintered diamond anvils for 6-8 two stage apparatus.

those used in the previous studies, thus a much larger sample volume can be compressed.

1-3. Pressure generation with the DIA type apparatus.

Among the several multi-anvil type apparatus, the DIA apparatus, which is one of the cubic anvil type systems, is the most suitable for *in situ* X-ray observation [Inoue and Asada, 1973]. MAX80, which was installed in the National Laboratory for High Energy Physics (KEK), Tsukuba, for the purpose of X-ray diffraction study using synchrotron radiation, has this DIA type high pressure vessel [Shimomura et al., 1985]. Combining the DIA type high pressure apparatus with powerful synchrotron X-ray source, there have been performed various kind of experiments in many fields and a lot of interesting results have been presented by this MAX80 system [Kikegawa et al., 1989]. In order to make a further development of high pressure and high temperature experiments with synchrotron radiation, we designed and installed a new DIA apparatus named MAX90.

A) MAX90: A new DIA apparatus with sintered diamond anvils for synchrotron radiation use.

MAX80, a high temperature and high pressure apparatus dedicated to synchrotron radiation use at the Photon Factory (PF) in

KEK, was installed in 1980. At first, MAX80 was operated at the bending magnet beam line, but later it moved to the high field wiggler beam line of BL14 where X-ray energy up to 100 keV can be used. In 1986, it was replaced to the beam line AR-NE5 of the Accumulation Ring (AR). For the synchrotron radiation experiments, AR is operated with 6.5 GeV and high energy X-ray up to 130 keV can be used. There have been performed various kind of experiments in many fields and a lot of interesting results have been presented.

Similar type apparatus have been installed in the other synchrotron radiation facilities, such as National Synchrotron Light Source at Brook Haven (U.S.A.), or Hamburg Synchrotron Laboratory (HASY LAB, Germany). Thus, we intended to make a further development of high pressure and high temperature experiments with SR by using sintered diamond anvils instead of WC anvils.

A newly constructed system, named MAX90, consists of a cubic type high pressure vessel, a 350 ton press, a 4-axes stage, a goniometer, a base and data collection and machine control system. Fig.1-3 and 1-4 are total view and conceptual design of MAX90, respectively.

High pressure vessel is a cubic anvil type (DIA10 by Kobe Steel Co.), which is the same as in MAX80. This DIA10 vessel is fairly large for the ordinary use of the WC anvils with truncation size of 3 to 6 mm. However, for higher pressure generation with sintered diamond anvils, high rigidity of the vessel is needed. Thus we adopted DIA10 type vessel. This is full compatible to MAX80, where two stage type system is also operated.

A thrust of 100 ton is needed to generate 10 GPa with 4 mm anvil

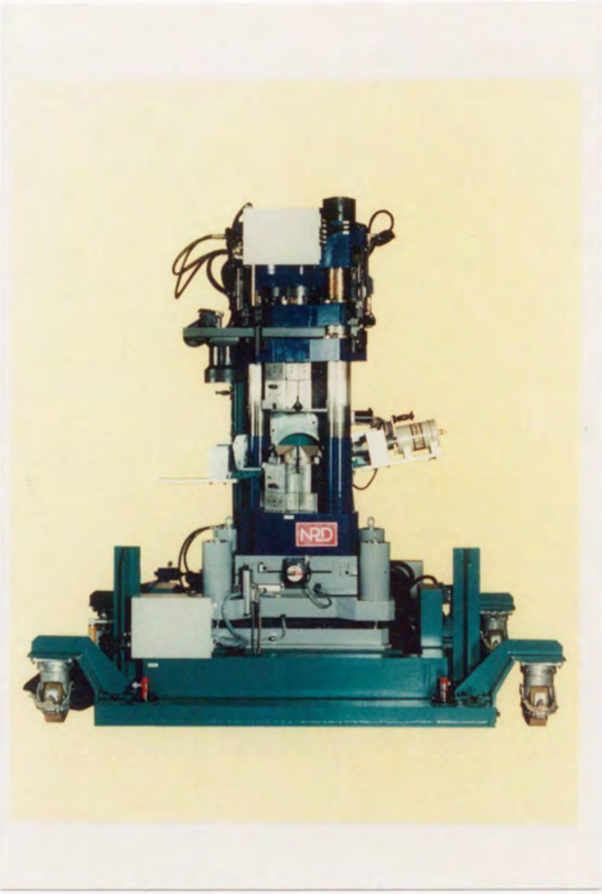

Fig.1-3
Total view of the MAX90 system.

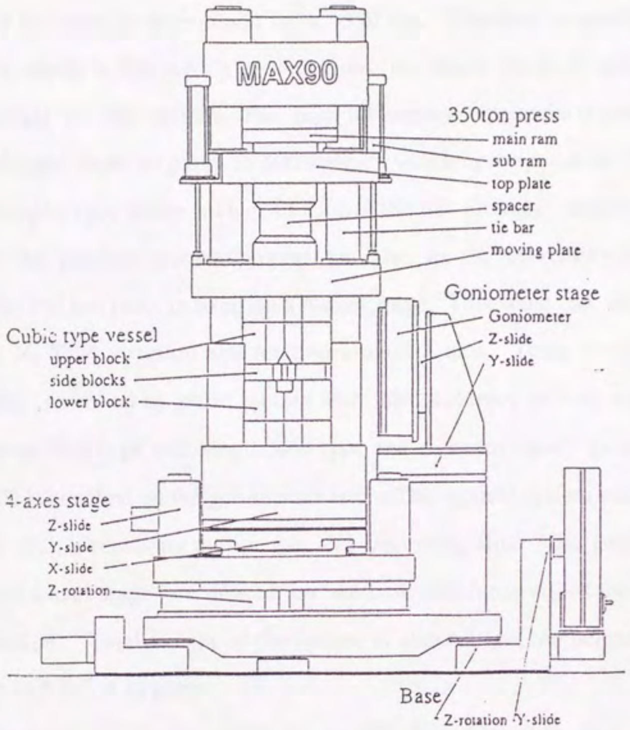

Fig.1-4
Conceptional design of MAX90. It consists of cubic anvil type high pressure vessel, 350 ton press, 4-axes stage, goniometer with two axes stage and base.

according to the experience of MAX80. A rough extrapolation of this relation to 20 GPa reaches the tonnage of 200 to 300 ton. Thus the thrust of the press is determined to be 350 ton. This size is smaller than MAX80, which is 500 ton. The reduction in thrust helps to reduce the total weight of the system. The high oil pressure operation is controlled by a plunger type oil pump to 500 kg/cm^2 which corresponds to 350 ton. This plunger type pump enables to control the oil pressure smoothly not only in the pressure increase process but also in the decreasing process.

The 350 ton press is fixed on a 4-axes stage. This stage can adjust the press in X, Y, Z direction and rotation around Z axis. These motions are externally controlled by pulse motors with the accuracy of 0.01 mm. The goniometer is a large size single axis type and a handy pure germanium type SSD is attached on the goniometer arm. The optical system consists of incident slits, a receiving collimator and receiving slits. The goniometer stand and 4-axes stage are placed on the base which can adjust the height and rotation. Total weight of the system is about 8 ton, the height is 3 m and 2.5 m * 2.5 m in plane.

Temperature is controlled by an AC power supply with power control mode. A thermocouple is used to measure the sample temperature, but sometimes we encounter thermocouple troubles such as the breaking off or its instability by the chemical reaction with other material in the cell. (In such cases, the sample temperature should be estimated by an established power vs. temperature relation.) Thus, the power control method is safer than the temperature feed back control by thermocouple.

MAX90 system is operated at BL13 or BL14 on the floor of Photon Factory. At BL13, which is a 27 poles Multi-pole wiggler line, the maximum intensity is located at 25 keV and usable energy range is 10 to

60 keV. At BL14, the maximum intensity is at 35 keV and usable range is 15 to 100keV. The difference in beam profile at two beam lines indicates that it is suitable to adopt the different diffraction methods at each beam line. An energy dispersive method using high energy white X-ray is favorable at BL14. On the other hand, an angle dispersive method is preferable at BL13 because of high flux density in the energy range of 15 to 40 keV. In this paper, all experiments were carried out by energy dispersive method. Angle dispersive method in this system is now in progress [Kikegawa et al., private communication].

B) High pressure generation.

The present experiments were carried out using MAX80, MAX90, and the DIA type apparatus installed in the Institute for Solid State Physics, Univ. of Tokyo.

A design of the cubic anvil with sintered diamond for MAX90 is shown in Fig.1-5. The left is the original design made of tungsten carbide, which has been used for MAX80. The top part of tungsten carbide is replaced with sintered diamond. Outside dimension is the same for the compatibility. So far, we have tested the sintered anvils with the top area of 3*3 mm^2 and 4*4 mm^2. Fig.1-6 is a typical cell assembly for high pressure generation using sintered diamond anvils with a truncation of 3 mm. In this apparatus , the selection of a suitable material for the pressure transmitting medium is a very important factor. We repeated the pressure generation tests using three different types of pressure medium; a mixture of amorphous boron and epoxy resin (4:1 by weight), a mixture of

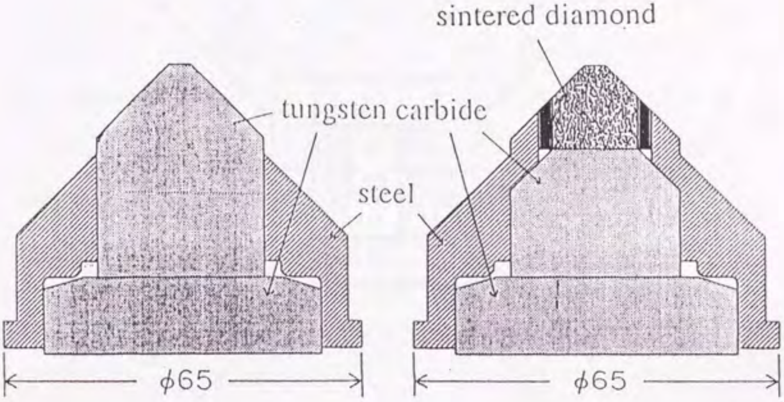

Fig.1-5
Comparison of designs of cubic anvil with tungsten carbide (left) and with sintered diamond (right).

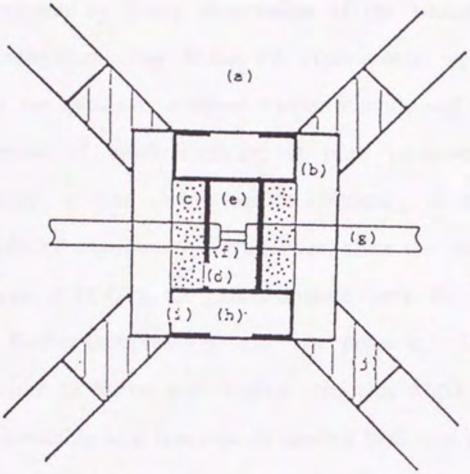

Fig.1-6
Typical cell assembly for the DIA apparatus. (a) sintered diamond anvil with truncation of 3 mm (b) pressure medium (c) sleeve made of a mixture of boron and water glass (d) graphite furnace (e) sample chamber (f) thermocouple (g) alumina tube (h) end plug (i) gold electrode

boron, mica and epoxy resin, and semi-sintered MgO. The initial size of the cube in each case was 5 mm in edge length. In all the experiments, pyrophyllite pre-formed gaskets were used.

Fig.1-7 shows the pressure generation versus the applied load. Pressure was determined by X-ray observation of the lattice constant of NaCl placed in the sample chamber. Before the experiments, we anticipated that mica added to the pressure medium was sufficiently soft that it could prevent the occurrence of anvil cracking at high pressure. In the experiments, however, it was so soft that the efficiency of the pressure generation was reduced significantly. Moreover, since the flow of the gasket was very large, at 14 GPa, the gasket became very thin (less than 0.05 mm). Thus, further compression was not possible. On the other hand, when a mixture of boron and epoxy resin or MgO were used, pressure increased smoothly as a function of applied load, and pressures up to 18 GPa were generated. This pressure value is much higher than 12.5 GPa, so far generated by MAX80 using WC anvils with a truncation of 3 mm [Akimoto et al.,1987].

Further compression was applied in an attempt to reach higher pressure, but a sharp noise caused by the occurrence of an anvil crack was heard during the compression, and we had to stop increasing pressure. The crack started nearly at the center of the anvil and it ran all the way to the bottom. This situation is quite different from that of WC anvils. In case of cracked WC anvils, plastic deformation of the anvil around the top area is always observed, and sometimes the crack confined to the top area. On the other hand, for sintered diamond anvils, no plastic deformation is observed even in cracked anvils. Fig.1-8 is an optical microscopic image of the crack observed in the surface of a sintered diamond anvil. The

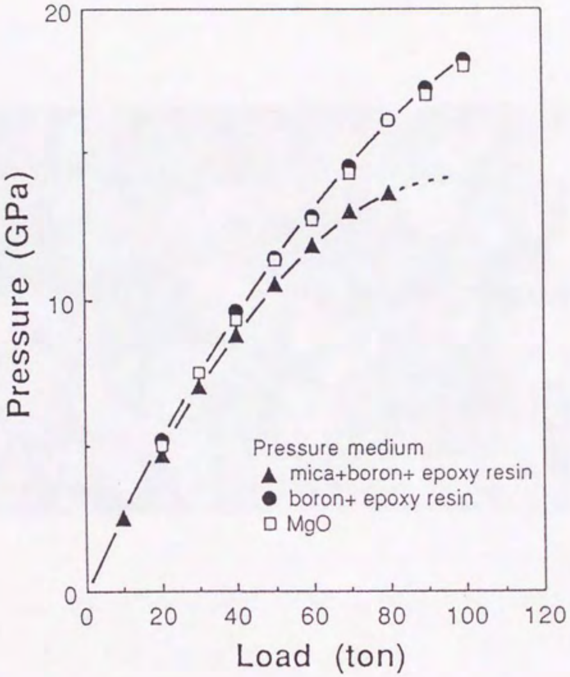

Fig.1-7
Pressure generation curve against the applied load in the DIA apparatus.

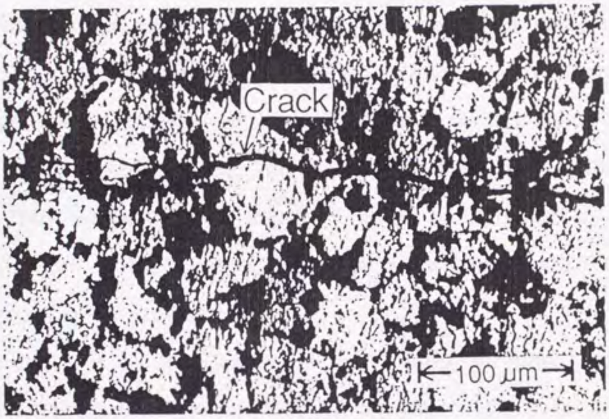

Fig.1-8
Optical microscopic image of a crack in a sintered diamond anvil

white part is a diamond particle, and the average grain size is about 70 microns. The black part is the cobalt metal binder. The crack does not run in the grain boundaries but runs directly through the diamond particles. This fact strongly indicates that the crack was not caused by incomplete sintering of the material. All cracks occur suddenly without any deformation of the anvil top. Thus one may expect that pressurization could continue even after an anvil cracks. Unfortunately, when an attempt was made to generate higher pressures using cracked anvils, additional cracks was developed, and the complete breakdown of the anvil resulted. Thus we could not use the cracked anvil repeatedly. The generated pressure in the present apparatus is therefore limited by the first occurrence of an anvil crack.

Generally, it is considered that the knoop hardness and the compressive strength of the sintered diamond are much higher than those of WC. However, its transverse rupture strength is comparable or sometimes weaker than that of WC. One of the reasons for the occurrence of cracks is this weak transverse rupture strength. Sintered diamond with fine particle diamond is considered to have higher transverse rupture strength. Thus, by using this fine particle sintered diamond, it is hoped that much higher pressure can be generated. Very recently, this type of sintered diamond has been commercially available. We made a preliminary test by using Bridgeman anvil with sintered diamond made from large particle size diamond and small particle one. It became clear that the anvil made of particle size of 25 micron can generate the pressure above 23 GPa, while the one made of large particle diamond can generate only less than 18 GPa [Taniguchi, in private communication]. We are now preparing experiments using this sintered diamond in

MAX90.

Another problem is the occurrence of blow outs during the release of pressure. When a mixture of boron and epoxy resin was used as a pressure medium, because of its large internal friction, the internal pressure did not decrease smoothly during the release of applied load. This caused blow outs during the release of pressure. When the generated pressure became higher, the energy of the blow out also became larger, and sometimes it resulted in the destruction of all the anvils. A lot of efforts have been made to find a suitable material for the pressure medium and pre-formed gaskets. However, a perfect material which can prevent blow outs and also generate extremely high pressure without anvil cracking has not been found yet.

C) High temperature generation.

For high temperature generation, before the experiment, we had been afraid that because of the high electrical resistance of the sintered diamond anvils, we could not use the anvil directly as an electrode for supplying electrical current to the inner furnace. However, it became clear that the resistance of the anvil was much smaller than we had expected. The electrical resistance of each anvil under the experimental conditions is about 15 mohm, while the inner graphite furnace is 80 mohm. When electric current is supplied through the anvils, the anvil itself has a Joule heating. However, because of the large thermal conductivity, the increase of the temperature of the anvil is not so high. Fig.1-9 shows the temperature of the center of the inner furnace and the surface of the

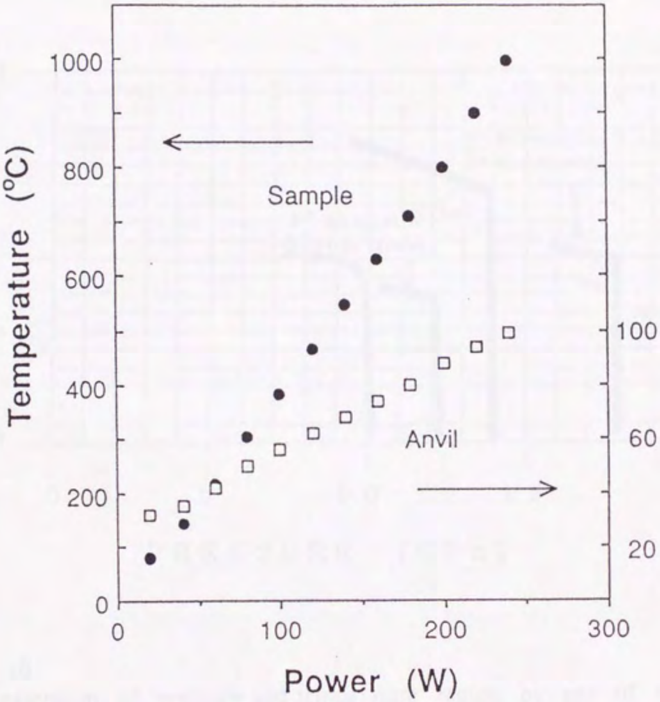

Fig.1-9
Temperature of the central position of the furnace and the top face of the anvil against the supplied power.

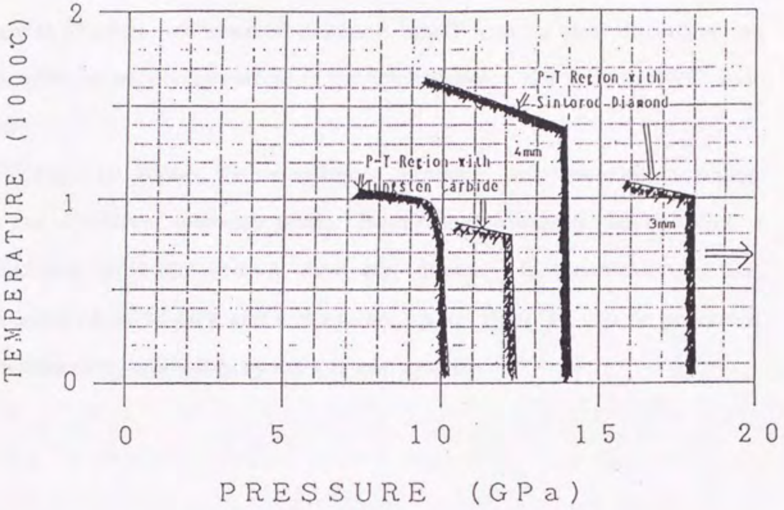

Fig.1-10
The extension of pressure and temperature region by use of sintered diamond anvil compared with that by WC anvil.

anvil top against the supplied power (pressure medium: boron and epoxy resin). When the temperature of the sample area was more than 1000 °C, the surface of the anvil top was about 100 °C. Therefore, it became clear that when the inner furnace is a fairly high electrical resistance material such as graphite, the sintered diamond anvil can be used directly as an electrode for supplying current to the inner furnace just as in the WC anvil case.

Fig.1-10 shows the extension of pressure and temperature region by use of sintered diamond anvils. Both results using the anvils with a truncation of 4 mm and 3 mm are drawn. In conclusion, so far, pressures up to 18 GPa and temperature up to 1000 °C can be generated simultaneously and stably by the present system.

1-4. Pressure generation in Drickamer anvil apparatus.

The Drickamer anvil apparatus is one of the opposed anvil type high pressure apparatus. Due to application of the massive support and lateral support, this Drickamer anvil apparatus can generate quite high pressure in spite of its simple design. Several attempts to utilize sintered diamond in this apparatus have been made, but all previous studies were carried out using very small anvils with top diameters of less than 1 mm. In order to increase the sample volume in this apparatus, we designed an apparatus using large size sintered diamond anvils.

A) Experimental.

Fig.1-11 shows the cross section of the cell used in the present experiment. The anvils are prepared from the same cylindrical shaped sintered diamond compacts (De Beers, SYNDIE 15151) as is used in the DIA apparatus. Eight facets are made on one end of this cylinder so that an octagonal shaped top face is formed. The diameter of the anvil top is 3 mm and the angles between this top face and the facets surrounding the top face are 30 degrees. We have tested several different angles and found that this is the optimum angle to get large sample volume without loosing the pressure generation efficiency too much.

The pressure medium is a mixture of amorphous boron and epoxy resin (2:1 by weight). In the ordinal Drickamer anvil apparatus, the angle relation between the anvils and pressure medium is very sensitive to the pressure generation, and the reproducibility of the generated pressure value strongly depends on the accuracy of these angles. Therefore, in the present experiments, we divided the pressure medium into three parts an shown in Fig.1-11. Two end parts are made by compacting boron-epoxy mixture using anvils as a pattern. Central disk is made of the same material by compacting it in a piston cylinder type jig. In this way, very accurate pressure medium which has a same angle could be made. The initial size of the sample chamber is 1 mmϕ * 1 mm high. This chamber deforms when it is squeezed between two anvils and the recovered chamber has changed into approximately 1.2 mmϕ * 0.6 mm high after it has compressed to 30 GPa.

In the present experiment, generated pressure value was determined by the X-ray observation of the lattice constants of gold. The

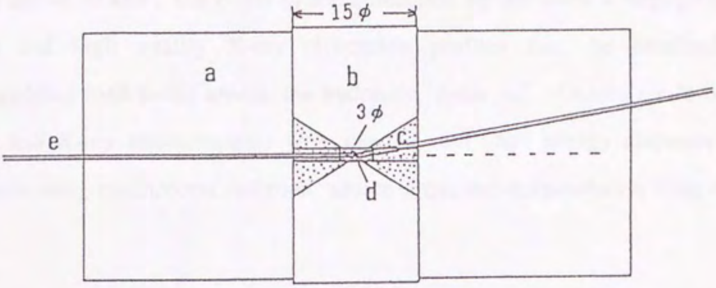

Fig.1-11
The cross section of the Drickamer-type high pressure apparatus using sintered diamond anvils. (a)Cylinder (b)Sintered diamond anvil (c)Pressure medium made of a mixture of amorphous boron and epoxy resin (d)Sample (e)X-ray beam

incident X-ray beam get into the sample chamber through a hole in the outer cylinder, and are collected by a solid state detector. Part of the diffracted X-ray should pass through the anvils, however, in the energy range above 30 keV, the effect of the absorption by the anvil is negligibly small and high quality X-ray diffraction profiles can be obtained. For applying load to the anvils, the hydraulic press of MAX80 could be used, and X-ray measurements were carried out by energy dispersive methods using synchrotron radiation source from the Accumulation Ring in KEK.

B) Results.

Fig.1-12 is a typical pressure generation curve at room temperature determined by the observation of lattice constants of gold, which was mixed with NaCl and placed in the sample chamber. (Pressure was calculated by the equation of state of gold determined by Jamieson et al. [1982] .) The anvils survived to a pressure approaching 30 GPa, with no reduction in the efficiency of pressure generation. We repeated the experiments up to 30 GPa more than 20 times, and no plastic deformation of the anvils was observed. For the comparison, the results using WC anvils are also plotted in Fig.1-12. In contrast with the sintered diamond anvils case, WC anvils deformed considerably above 10 GPa, and fractured at around 16 GPa, which resulted loss in efficiency.

By using this apparatus, we successfully made an X-ray diffraction study of the phase transformation of graphite under high pressure. The details will be described in Chapter two.

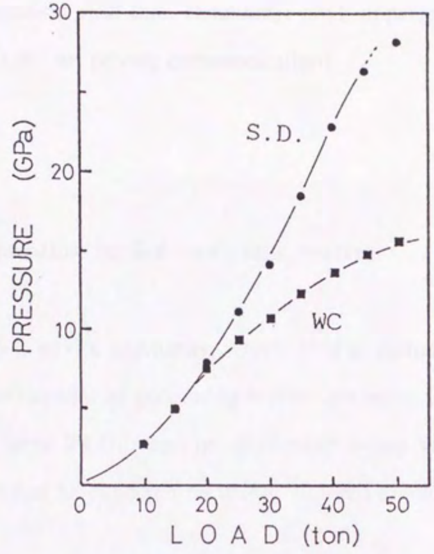

Fig.1-12
Pressure generation by sintered diamond and WC anvils as a function of applied load in the Drickamer anvil apparatus.

Because the anvils used in the present experiment have larger top face than in the previous experiments, sample heating by the inner furnace can be made more easily. The development of experimental techniques for high temperature generation with this Drickamer anvil apparatus is now in progress [Funamori et al. in private communication].

1-5. Pressure generation in 6-8 two stage system.

The two stage 6-8 anvils apparatus, which is also called the MA8 apparatus, have proven capable of generating higher pressure than the DIA apparatus. Pressures up to 25 GPa can be generated using WC anvil and much higher pressures can be expected by using sintered diamond anvils in this system.

A) CAPRICORN: A new DIA apparatus for 6-8 system.

As mentioned in the DIA section, sintered diamond anvils are easy to crack and destroy unless they are treated very carefully. To avoid the occurrence of crack during the compression, the parallelism and synchronized movement of the first stage anvil are very important. The DIA type apparatus is suitable for this purpose because it can drive first stage anvils very accurately. The thrust of the DIA type press already installed in I.S.S.P. is only 250 ton, which is not enough for the use of two stage system. Therefore, we designed and installed a new DIA type press

Fig.1-13
Total view of the CAPRICORN system.

for the special use of 6-8 two stage system with sintered diamond anvils.

The new system, named CAPRICORN, consists of a cubic type high pressure vessel and 500 ton press (Fig.1-13). The top area of the first stage WC anvils is 18 mm * 18 mm. Because of the limitation of the hardness of first stage anvils, the maximum load applied to the pressure cell is about 450 ton. Thus the thrust of the press was determined to be 500 ton. A plunger type oil pump is used to control the oil pressure.

B) Experimental.

In the present experiment, an octahedral pressure medium made of semi-sintered MgO (edge length is 6.0 mm) and pyrophyllite pre-formed gasket were used for the pressure generation. A set of eight cube shaped sintered diamond anvils (edge length 9.5 mm and truncation size 2.0 mm) and a pressure cell were compressed by six first stage cubic anvils (Fig.1-14). Generated pressure was calibrated by detecting the semi-conductor to metal transition of ZnS (15.6 GPa), GaAs (18.7 GPa), and GaP (23 GPa) by the measurement of their electric resistance.

C) Results and discussion.

Fig.1-15 shows the generated pressure in the present experiment as a function of the applied load. For the comparison, the results with the WC anvils (Toshiba G1F) under the same experimental conditions are also plotted. For WC anvils, because of plastic deformation of the

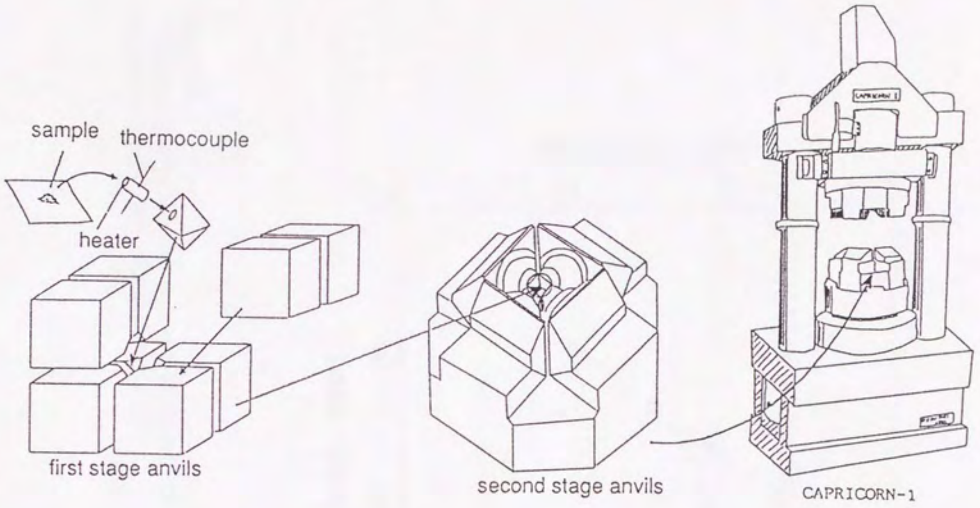

Fig.1-14
High pressure generation in 6-8 two stage system with CAPRICORN.

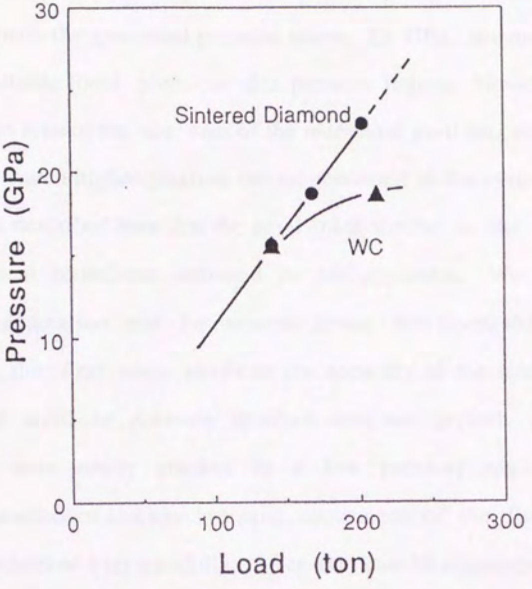

Fig.1-15
Pressure generation by sintered diamond and WC anvils as a function of applied load in 6-8 two stage apparatus.

anvil top, the efficiency of pressure generation decreased considerably above 16 GPa. On the other hand, for sintered diamond anvils, pressure increased smoothly against the applied load up to 23 GPa. Unfortunately, we could not estimate the generated pressure above 23 GPa, because there is presently no reliable fixed point in this pressure region. However, no plastic deformation around the top area of the recovered anvil was observed, thus , we believe much higher pressure can be generated in this system.

It should be described here that the anvil crack similar to the one in the DIA experiment sometimes occurred in this apparatus. We carried out the pressure generation test for several times, and found that when the alignment of the first stage anvils or the accuracy of the size of the sintered diamond anvil or pressure medium were not perfect, sintered diamond anvils were easily cracked in a low pressure region. In particular, the parallelism and synchronized movement of the first stage anvils need to be checked very carefully. After the careful alignment of the first stage anvil with the accuracy of 0.01 mm, the occurrence of the anvil crack was reduced. Therefore, it is important to use an apparatus such as the DIA which can drive first stage anvils very carefully.

Another advantage of the sintered diamond is its transparency for X-ray beam. When this 6-8 system is combined with the MAX80 apparatus, and *in situ* X-ray observation is carried out, the diffraction beam from the sample should pass through the second stage anvil. This length is about 14 mm, thus , if the WC is used as a second stage anvil, X-ray cannot pass through at all. In contrast, although the sintered diamond in the present study contains Co metal as a binding material, it is fairly transparent for the high energy X-ray beam. According to our preliminary test, more than 20% X-ray beam (energy was 60 keV) passed through the sintered diamond material whose thickness was 15 mm. This result means that when very high energy X-ray such as from Wiggler source is used, *in situ* X-ray observation can be easily made by the 6-8 apparatus with sintered diamond anvils.

1-6. Conclusion.

High pressure generation using sintered diamond as an anvil material has been carried out. The largest size sintered diamond which is commercially available at present was applied to the DIA apparatus, Drickamer anvil, and 6-8 two stage apparatus. In all these experiments, much higher pressure than in the case using WC anvils could be generated, and it became obvious that sintered diamond is extremely useful for anvil material. Under high pressure condition, anvil cracks occurred without the plastic deformation of the top area of the anvil, and this marked the limit of the generated pressure in each case. This sintered diamond anvil could be used as an electrode for supplying electric current to the inner heater, thus the high temperature experiments could be made almost in the same way as in the WC anvil case.

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CHAPTER 2.

The study of graphite to hexagonal diamond transition

2-1. Introduction.

Although extensive studies have been carried out on the conversion of graphite into diamond by static pressure using catalyst or solvent method, little is known about the direct transformation from graphite to diamond under high pressure. Aust and Drickamer [1963] and Bundy and Kasper [1967] observed a rapid increase of the electrical resistivity of well crystallized graphite when it was compressed above 15 GPa. At room temperature, this change was reversible on release of pressure. However, when the sample was heated above 1000 °C under pressure, Bundy and Kasper observed irreversible increase of the electrical resistivity even after the complete release of pressure. In the recovered sample, they observed some new diffraction lines which could be indexed as a hexagonal diamond structure. A mineral which gives similar powder X-ray diffraction pattern was found in meteorite and was named Lonsdaleite [Hanneman et al., 1967, Frondel and Marvin, 1967].

Fig.2-1 shows the crystal structures of cubic diamond and hexagonal diamond. Hexagonal diamond is related to ordinary cubic diamond as wurtzite is related to zinc blend. The carbon- carbon distances are essentially the same, but the layers of wrinkled hexagons are stacked in a different way. In cubic diamond (Fd3m), all the puckered hexagons are of the chair type, in whatever direction they occur. On the other hand, in hexagonal diamond ($P6_3/mmc$), it is only the hexagons whose

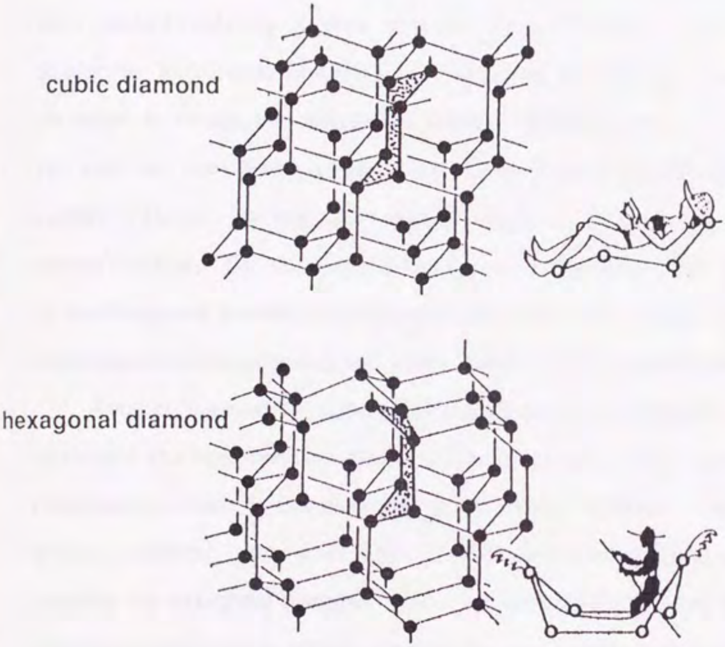


Fig.2-1
Crystal structures of cubic diamond and hexagonal diamond. In cubic diamond, all the puckered hexagons are of the chair type. In the hexagonal diamond, only the hexagons whose mean plane is (002) are of the chair type, and those whose mean plane is one of (100) are of the boat type.

mean plane is (001) that are of the chair type. Those whose mean plane is one of (100) are of the boat type.

Although very long time has passed since the first finding of the hexagonal diamond, many uncertainty still remain. Its existence has been studied only by a poor powder X-ray diffraction pattern or by an electron microscope observations. Moreover, pressure and temperature condition to obtain this hexagonal diamond phase has not been confirmed yet, and no one could so far synthesize well crystallized single phase sample. Hence, its accurate crystal structure and physical property remain unclear. By the shock compression of graphite, the formation of the hexagonal diamond was reported, but in this case also, only very poor crystalline was obtained, and many other carbon phase coexisted.

Another uncertainty is the relation between the hexagonal diamond phase and the high pressure phase obtained by the room temperature compression which is unquenchable to ambient condition. Bundy and Kasper inferred that even by room temperature compression of graphite, the hexagonal diamond phase was already formed and when this phase was heated above critical temperature, this crystal could be quenched. However, this was just a speculation.

Recently, due to the development of the diamond anvil apparatus, many studies on the behavior of graphite under high pressure and room temperature have been carried out using optical method. Hanfland et al. [1989] observed a sudden drop of an optical reflectivity and a broadening of the high frequency E_{2g} Raman line above 9 GPa, which indicated the onset of the transformation. This transformation was fully achieved at about 17 GPa. Goncharov et al. [1990] made Raman and reflectivity study and observed a sharp decrease in the reflectivity and a simultaneous broadening of the intralayer Raman spectra between 15 and 35 GPa. Takano et al.[1991] reported the existence of several discontinuous volume changes at 18 and 25 GPa. Moreover, Zhao and Spain [1989] carried out powder X-ray diffraction experiments and reported that some new diffraction peaks appeared above 11 GPa, but they could not identify the structure. These experimental results indicate the possibility of a pressure induced transformation in graphite at room temperature.

For this high pressure phase obtained by room temperature compression of graphite, various speculations such as formation of sp^3 bonded structure [Bundy and Kasper, 1967, Hanfland et al., 1989], a formation of amorphous phase [Goncharov et al.,1990], or a formation of an intermediate phase between graphite and hexagonal diamond [Takano et al., 1991] were made. However, the nature of this high pressure phase or the relation with hexagonal diamond is not clear yet. In addition, the pressure of this transformation that reported in previous studies are very scattered.

The purpose of the present study is to clarify these points, namely, the determination of the transition pressure and the structure of the high pressure phase obtained by room temperature compression of graphite are the main subjects of this chapter. In the following section, optical observations of this phase transformation by a diamond anvil cell is described. Very drastic change of the sample was observed in this experiment. In the third section, the study of the X-ray observation under high pressure and room temperature condition to determine the structure of the high pressure phase is described. The combination of newly developed high pressure apparatus using sintered diamond anvils which is described in the first chapter and the very intense X-ray from synchrotron radiation made it possible to get high quality in situ X-ray diffraction data on this high pressure phase. In order to obtain the information about the quenchability of the hexagonal diamond, *in situ* X-ray observation under high pressure and high temperature condition should be carried out. In the last section, the results of this experiment will be described.

2-2. Visual observation of the phase transformation.

Although several studies on the phase transformation of graphite under high pressure using diamond anvil cell were made, the results were quite scattered. In most of these experiments, powder sample were used, and they were compressed under the non- hydrostatic condition. In order to see the transition clearly, we carried out an experiment using very thin single crystal sample.

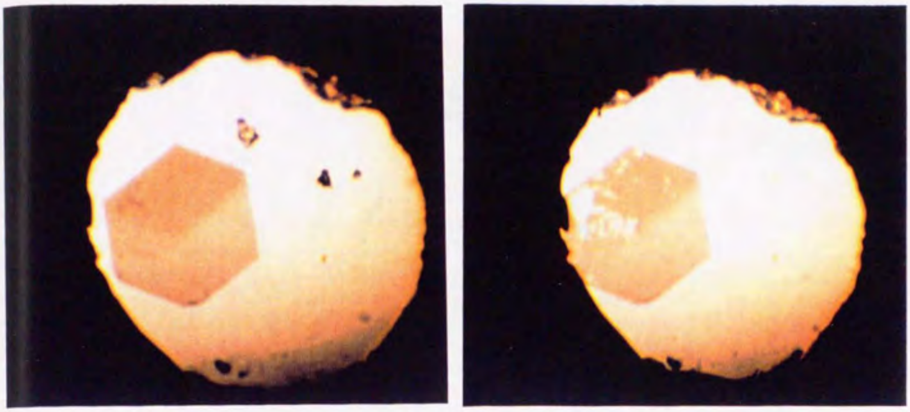
A) Experimental.

A single crystal kish graphite (TOSHIBA ceramics Co.), which was formed by the supersaturation of carbon in molten iron, was used as a starting material. This sample was easily cleaved using a razor edge, and we prepared a very thin hexagonal shaped single crystal (1 μm thickness and 150 μm edge length). The experiments were carried out with a modified Mao-Bell type diamond anvil cell [Yagi et al., 1987] and the pressure was determined by the ruby fluorescence method. Mixture of methanol and ethanol (4:1) was mainly used as a pressure medium. In order to see the temperature effect on this transformation, a yttrium- aluminum-garnet (YAG) laser was used.

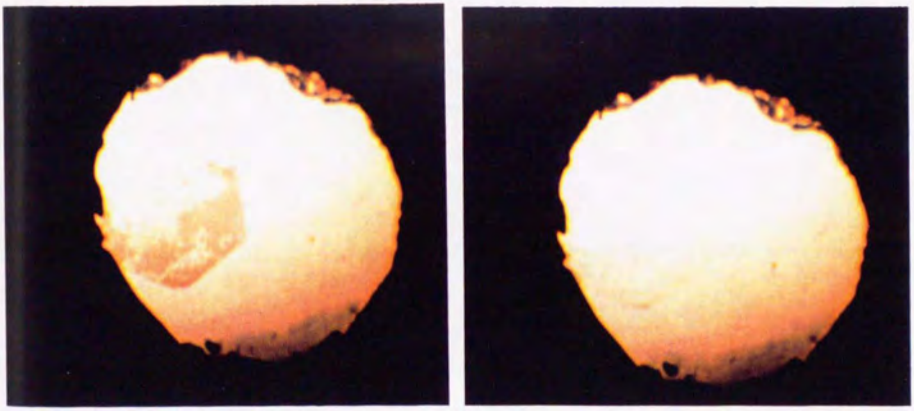
B) Results and discussion.

Fig. 2-2-a is a photograph of the sample before the compression. Because the sample was very thin, it was not completely opaque even at atmospheric pressure. When the pressure was increased at room temperature, no noticeable change was observed by a visual observation in the pressure range below 18 GPa. However, at 18 GPa, several light transparent spots suddenly appeared in the sample (Fig. 2-1-b), and they spread to the whole sample area while the pressure was kept constant. Figures 2-1-c and d were taken 30 min and 2 hours after the transformation had started, respectively. As is clear from these figures, in each spot, the color change was not gradual but was discontinuous and drastic. On release of the pressure, the transparent phase reversed suddenly to the original dark color phase at 2.5 GPa, thus the high pressure phase could not be quenched at ambient condition.

Absorption spectra of the sample were measured at various conditions and no noticeable structure was found in the spectra of visible light. Pressure variation of the optical density at 580 nm is plotted in Fig.2-3 for both pressure increasing and decreasing process. It is clear that this transition is reversible with large hysteresis. Optical density of the recovered sample is slightly higher than that of the starting material, probably because of the polycrystalline nature of the recovered



(a) 0.1 MPa (b) 18 GPa



(c) 30 min later (d) 2 hours later

Fig.2-2
In situ observation of a single crystal graphite during the phase transformation at 18 GPa and room temperature. Sample thickness is about 1μm.

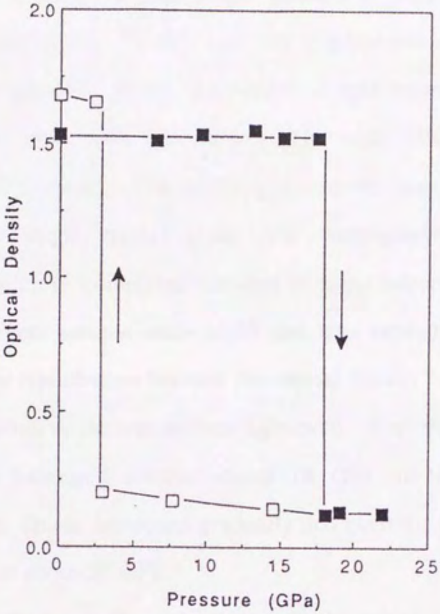


Fig.2-3
Pressure variation of the optical density of graphite at 580 nm for both increasing and decreasing pressure.

material.

We have repeated the same experiments with graphite of different thicknesses. In every case, we observed the discontinuous color bleaching at 18 GPa. Fig.2-4 is a photograph of the 5 μm thickness sample during the phase transformation. In this case, the graphite part is completely opaque and the high pressure phase is observed as light brown area. The straight lines which cross with 120 degree angles each other are also strongly observed. It is possible that each high pressure area surrounded by these lines is a single crystal grain and consequently, the whole sample after the transition is completed consists of many twin crystalline.

When much thicker sample such as 10 μm was used, however, the transformation became less obvious because the optical density of the sample became too large to observe the transmitted light even after the transition. As the pressure was increased further above 18 GPa, the transmissivity of this high pressure phase increased gradually and even the thick sample became transparent at about 50 GPa.

Our present results are in fair agreement with the report by Hanfland et al. [1989] except that in some cases they observed the initiation of the transition at pressures lower than 10 GPa. We thought this disagreement might be caused by the local stress concentrations around the sample because they used KCl as a pressure medium. Thus, we repeated our observation using KCl as pressure medium but the result was unchanged. We could not find any change until the pressure was increased to 18 GPa. Their other evidence of the onset of the transformation near 9 GPa was the broadening of the E_{2g} Raman mode. However, this pressure is close to the freezing pressure of the methanol- ethanol mixture used in their Raman mode measurement. Thus, there is a possibility that this

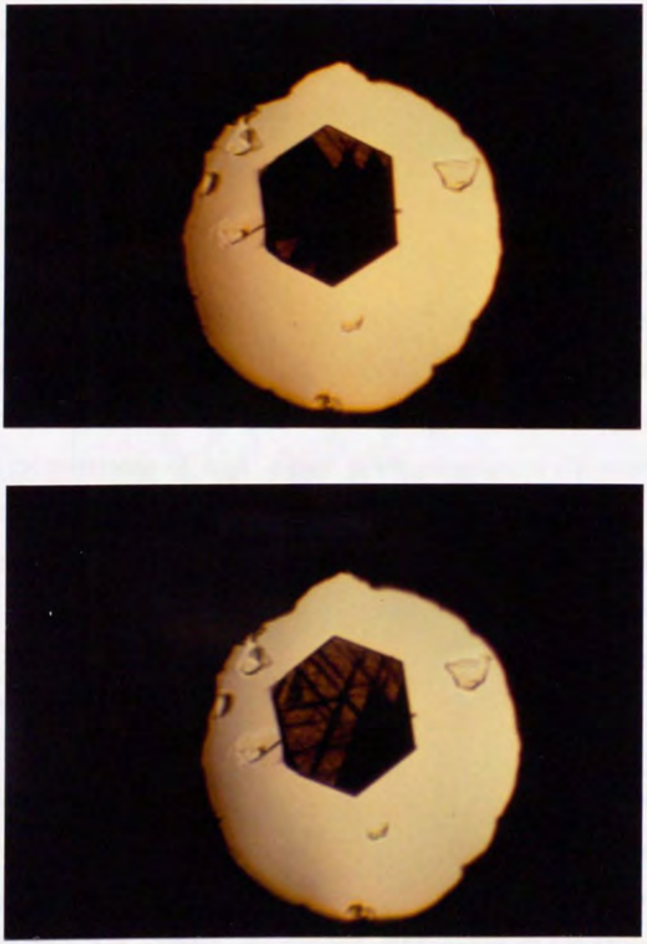


Fig.2-4
Phase transformation of graphite with a thickness of 5 μm under high pressure.

broadening was caused by the sudden change of the stress in the sample.

On the other hand, Goncharov et al. [1990] reported that noticeable change in color started at pressure of above 35 GPa. This result is probably because they used so thick sample that they missed the beginning of the bleaching at 18 GPa. Onset of the anomalies in the other measurements (reflectivity and the Raman signal) are in harmony with our present results.

Some of the X-ray observations [Zhao and Spain ,1989, Shu et al., 1990] indicate the onset of the transition at lower pressures than 18 GPa. These experiments were carried out by compressing powdered sample under nonhydrostatic condition. A large uniaxial component of pressure and the orientation of each crystal to the compression axis might be responsible for these discrepancies.

We can conclude that when a single crystal of graphite is compressed in a quasi-hydrostatic environment, a phase transformation occurs at 18 GPa at room temperature which accompanies the sudden increase of the light transmissivity.

Our next question was the behavior of this high pressure phase under high temperature condition. We heated the high pressure phase at 20 GPa using a YAG laser. Because of the very large temperature gradient of the laser heating, it is difficult to measure the temperature accurately. From the incandescent light, however, it is expected that a large portion of the sample was heated up to more than 1000°C. Fig. 2-5-a shows the sample before the heating. The thin edges are colorless while the thick central portion is still dark brown. After the laser heating, the sample became much more transparent than before (Fig.2-5-b). This transparent

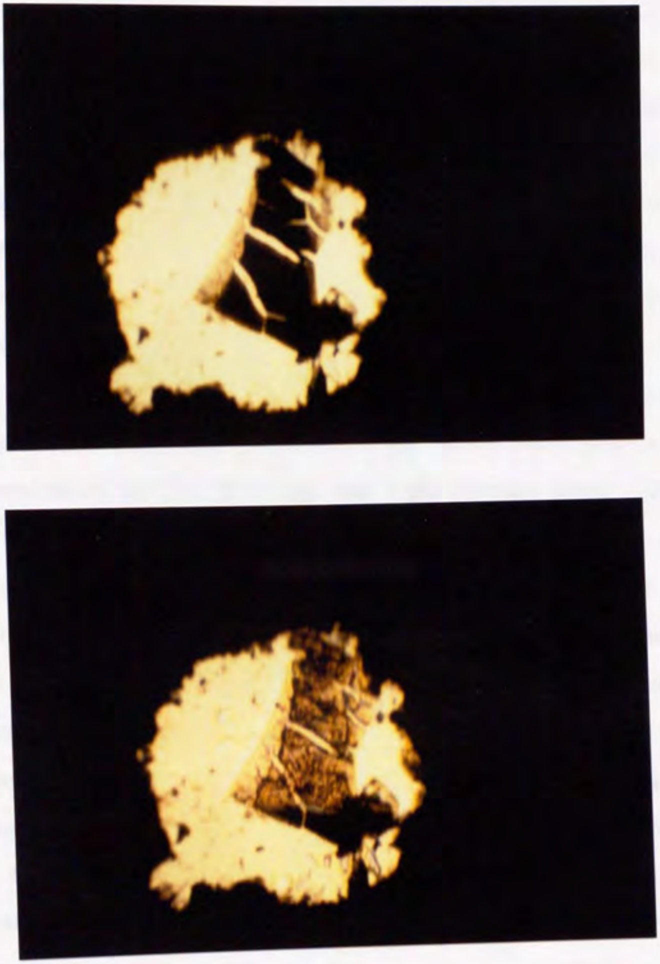


Fig.2-5
Effect of heating on the high-pressure, room-temperature phase.
(A) Before the heating (20GPa). Although the whole sample has already transformed to the high-pressure phase, the sample is too thick to allow us to observe the transmissivity of light except the thin edges.
(B) After heating by a YAG laser. The transmissivity of light increased drastically.

phase was retained even when applied pressure was released completely.

The fact that this phase is quenchable and the resemblance of the P-T condition of the present experiments with those reported by Bundy and Kasper suggest that hexagonal diamond phase is included in this quenched sample. Considering the temperature generation by YAG laser, however, this quench product might include many cubic diamond. Unfortunately, because of the difficulty of the X-ray diffraction of this very small amounts of the sample, this remains uncertain.

It is very interesting that the high pressure phase formed at room temperature became almost as transparent as the heated phase when it was compressed above 50 GPa. However, this high pressure phase without heating was unquenchable at ambient condition even if it had very high transmissivity in high pressure range. From this fact, one may expects that the high pressure phase achieved at room temperature has a different structure from the hexagonal diamond, but in the next section it will become clear by the X-ray observation under high pressure that this phase has also the hexagonal diamond structure. The gradual change in transmissivity by further compression at room temperature is probably caused by the advance of the transformation from graphite to hexagonal diamond phase.

2-3. High pressure *in situ* X-ray diffraction study at room temperature.

A) Difficulties of the experiment.

In order to determine the structure of the light transparent high pressure phase induced by room temperature compression of graphite, *in situ* observation under high pressure should be made because this phase is unquenchable to ambient condition. However, there are many difficulties on this experiment.

Raman scattering is one of the powerful method to estimate the structure, and several studies have been already carried out. In this case, however, most important line corresponds to sp^3 bond cannot be observed because it is hidden by the strong background due to the diamond anvil itself. Although previous studies reported the decrease or broadening of intralayer Raman spectral line, they could not conclude accurate nature of the high pressure phase.

The optical observation using cross nicol is also very difficult for this transformation. The diamond anvil has a cubic structure, but under very high pressure condition it deforms considerably and information on the polarization of light from the sample is strongly modified.

Single crystal X-ray diffraction study is a direct way to determine the structure. However, so far it is very difficult to generate high pressure enough to induce the phase transformation of graphite by the diamond anvil cell for the single crystal X- ray study.

Therefore, the only possible method is a powder X-ray diffraction study under high pressure, but in this case also there are some serious difficulties. In the diamond anvil apparatus, the thickness of the sample is usually less than 100 micron above 10 GPa and the light element material such as graphite gives very poor diffraction pattern. Moreover, graphite has a layered structure and it is difficult to make fine powder. Even when single crystal is crushed into fine particles, they have flake-like shape and when such sample is compressed uniaxially, a strong preferred orientation is formed. Hence, the intensity of the diffraction lines strongly depends on the direction of the observation and the accurate intensity measurement for the identification of the structure is very difficult.

All these situations made it difficult to obtain high quality X-ray diffraction data on graphite under pressure. Several attempts to determine the crystal structure of the high pressure phase by X-ray diffraction were made using diamond anvil cell [Zhao and Spain, 1989, Shu et al., 1990], but because of these difficulties, the structure is remained unsolved.

The purpose of the present study is to overcome these difficulties and clarify the crystal structure of the high pressure phase formed by the room temperature compression of graphite. Combination of newly developed high pressure apparatus using sintered diamond and the very intense X-ray from synchrotron radiation made it possible to get high quality *in situ* X-ray diffraction data on this high pressure phase.

B) Experimental.

Three different types of high pressure apparatus, Drickamer- type anvil, cubic anvil, and diamond anvil, were used.

In the ordinary Drickamer-type apparatus, WC alloy is used as an anvil material. By this anvil, however, it is difficult to generate high pressure enough to induce phase transition of graphite at room temperature, mainly because of the limitation of the hardness of WC alloy. Therefore, in the present study, we used a new Drickamer-type high pressure apparatus with sintered diamond anvils which was described in chapter 1. The initial size of the sample chamber is 1 mmϕ * 1 mm high, which deforms into approximately 1.2 mmϕ * 0.6 mm high after the compression. This hole is filled with the sample and gold pressure marker, so the volume of the sample exposed to X-ray is more than ten times compared to the diamond anvil case.

The sample was compressed by the top and bottom anvils using a uni-axial press. Incident x-ray beam irradiated the sample from the direction perpendicular to the compression axis. In order to obtain the information on the preferred orientation of the sample, we observed the diffraction in two different directions (Fig.2-6). In the first method, a solid state detector was placed in the vertical plane which contained compression axis ("V" in Fig.2-6). In the horizontal method, it was placed in the horizontal plane perpendicular to the compression axis ("H" in Fig.2-6). In both methods, 2 theta angle was 10 degrees. In the vertical method, the diffraction by the crystal plane which is almost perpendicular to the compression axis is strongly observed. On the other hand, information on the plane almost parallel to the compression axis is obtained by the horizontal method.

The advantage of this apparatus over diamond anvil apparatus is as follows; 1) Because of the much larger size of the sample chamber, diffracted X-ray from the sample with low atomic number such as graphite is much stronger and high quality X-ray diffraction profile can be obtained. 2) X-ray gets into the sample chamber from the direction perpendicular to the compression axis of the opposed anvils and the diffracted X-ray can be observed in two different orientations

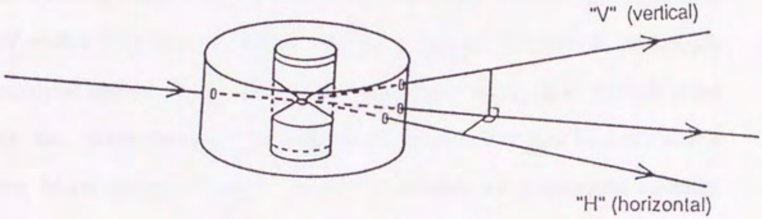


Fig.2-6
Two observational direction for the powder X-ray diffraction study using Drickamer anvil apparatus.

relative to the compression axis. Consequently, it is possible to get various information of the crystal structure of highly preferred oriented sample.

All the X-ray experiments were carried out using synchrotron radiation source at the National Institute for High Energy Physics (KEK), Tsukuba. X-ray source used for this apparatus was a white beam from the bending magnet of the Accumulation Ring which was operated at 6.5 GeV with a ring current of 15 to 30 mA. Energy dispersive technique was employed and an X-ray in the energy range from 20 to 80 keV were used for the measurement. Incident X-ray was collimated to a 0.1 mm x 0.3 mm beam using 10 mm thick slits made of a tungsten carbide. Powdered gold was embedded at the bottom of the sample chamber and by changing the position of the incident beam, X-ray diffraction patterns from the sample and the gold pressure standard were obtained separately. Pure germanium detector was adopted and a typical exposure time for the sample was 300 to 1000 seconds, while 200 second exposure was long enough to get high quality patterns for gold. Pressure was determined using equation of state of gold calculated by Jamieson et al. [1982].

Second type of high pressure apparatus is a cubic anvil which can compress the samples isotropically. Two systems, "MAX80" and "MAX90", were used. A cube shaped pressure transmitting medium is squeezed subtropical by six anvils with a truncation of 3 mm. In this case also, sintered diamond anvils were used to generate enough high pressure for the transformation.

Incident synchrotron radiation beam was collimated to 0.1 mm x 0.1 mm and a typical exposure time was 1000 second when energy dispersive technique was adopted. Collected data were accumulated in a 2048 channel memory of a multi-channel pulse height analyzer and then sent to a computer for analysis. Background of the spectrum was subtracted and then the peak position of the diffraction profiles were determined by the least squares fitting of a Gaussian curve to the diffraction peaks. Accuracy of the d- values determined by these systems in KEK are usually about 0.05 %. In the present study, however, various factors such as low signal to noise ratio, broad nature of the diffraction lines, coexistence of two phases, and overlapping of several diffraction lines, reduced the accuracy considerably. Because of all these factors, accuracy of the d-values reported in this paper is approximately 0.2 %.

The third high pressure apparatus is a diamond anvil apparatus with a lever and spring type [Yagi et al., 1987]. Monochromatized X-ray from the bending magnet of the Photon Factory was focused to the sample through a pin hole collimator with a diameter of 120 micron. X-ray was detected by Imaging Plate (IP) which has higher sensitivity and wide dynamic range of intensity compared with the conventional film method [Miyahara et al., 1986]. The distance between sample and Imaging Plate was 153 mm. Energy used for the experiment was 18 keV and a typical exposure time was 6 hours. Recorded data on the Imaging Plate was measured and digitized by a two dimensional optical reader and the intensity of the diffracted X-ray was calculated as a function of 2 theta by integrating the observed intensity along the polar coordinates. After this integration, obtained data can be treated just like a data obtained by an angle dispersive technique using conventional diffractometer. The detail of this total system combining the diamond anvil cell and the Imaging Plate was described by Shimomura et al. [1991].

Starting material of most of the present experiment is kish graphite, the same material used for the optical observation reported in the previous section. This well crystallized single crystal graphite was crushed into powder by grinding it in a mortar and then fine powder was selected by the gravity separation after dispersing it in acetone. Fine powder (typical size was a few micron across) thus collected was then compacted into a small cylindrical shape and then inserted in the sample chamber. Starting materials thus prepared had already strong preferred orientation because in spite of the small grain size, each particle has flake-like shape. In order to see the effect of the starting material on the transition pressure, a fine carbon powder for chemical analysis was also used in a different run. For a comparative study, we also carried out the same experiment with the Drickamer apparatus by using hexagonal BN, which has the same structure as graphite and known to transform to the wurtzite form, similar structure to the hexagonal diamond.

C) Results.

Diffraction profiles obtained in the "V"(vertical) direction using Drickamer-type anvil is summarized in Fig.2-7(a) and Fig.2- 7(b) for increasing and decreasing pressure process, respectively. Compacted starting material was placed in the sample chamber so that c-axis of the graphite was preferentially aligned parallel to the incident x-ray beam. Consequently, before the compression, (002) diffraction line of graphite was very weak while (100) and (110) diffractions were strong. As soon as the pressure is applied, because of deformation of the sample chamber

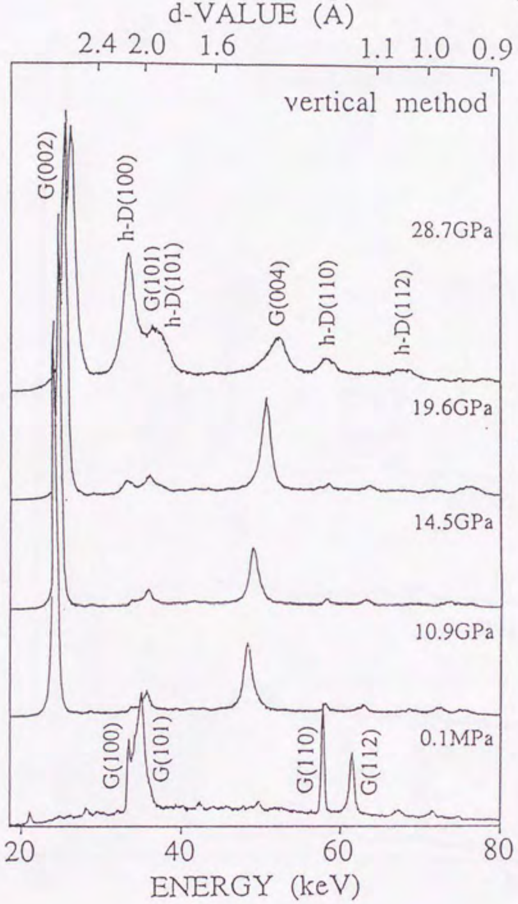


Fig.2-7(a)
The variation of the X-ray diffraction profiles of graphite in the pressure increasing process observed in the vertical direction using Drickamer anvil apparatus. (002) lines of graphite becomes strong as soon as the pressure is applied. New diffraction lines indexed by a hexagonal unit cell appears at 14 GPa, and they become stronger as the pressure is increased.

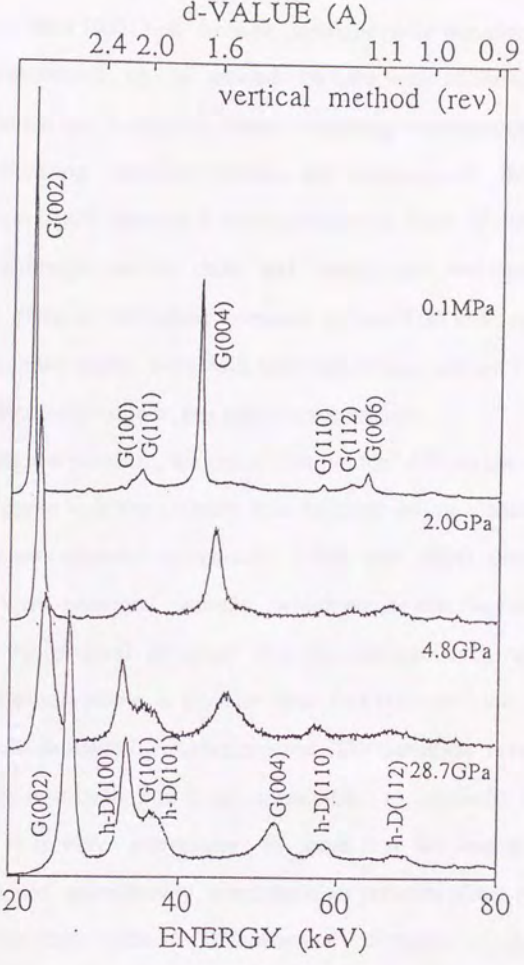


Fig.2-7(b)
The variation of the X-ray diffraction profiles of graphite in the pressure decreasing process observed in the vertical direction. The diffraction lines of high pressure phase remains until the pressure is released below about 3 GPa, but completely converted to graphite at ambient pressure.

and rotation of the crystals, c-axis are aligned preferentially to the compression axis. Thus (002) line became stronger with pressure. When the pressure was increased up to around 14 GPa, new diffraction peak began to appear which has a slightly larger d-spacing value than (100) of graphite. By increasing pressure further, the intensity of this peak increased, and we could observe 3 more diffraction lines of the high pressure phase, although one of them was broad and overlapped with (101) of graphite. Even at the highest pressure achieved in this experiment (28.7 GPa), the graphite peaks were still observed clearly and we could not get the pure diffraction profile of the high pressure phase.

By decreasing the pressure, we could observe the diffraction lines of the high pressure phase until the pressure was released below about 3 GPa. After the pressure was released completely, (002) and (004) diffractions of the graphite were observed strongly, which means that the orientation has changed into the original direction after the retrogressive transition.

From these observations, it became clear that the transition starts at around 14 GPa in the pressure increasing process. The transition is reversible but has very large hysteresis and it is impossible to quench the high pressure phase. It is very interesting to note that the line widths of graphite are broadened considerably when the high pressure phase coexists.

Results of the observation in "H"(horizontal) direction is shown in Fig.2-8. In this case, (100) and (101) diffraction lines of graphite were observed strongly during compression, in contrast to the (002) line in the vertical direction. This is quite reasonable since the c-axis of graphite was preferentially aligned parallel to the compression axis. At about 14 GPa, new lines of the high pressure phase appeared. The position of the most intense line of high pressure phase was between the (100) and (101) peaks

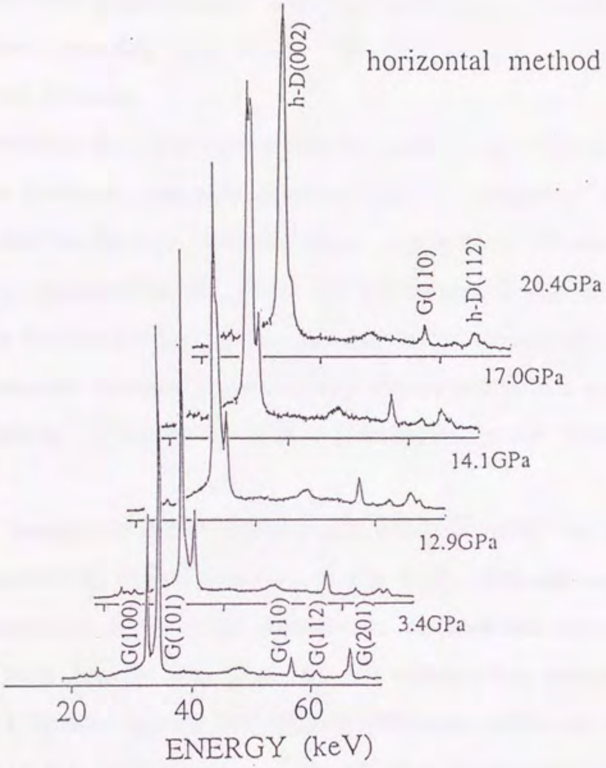


Fig.2-8
The variation of the X-ray diffraction profiles of graphite under high pressure observed in the horizontal direction. Phase transformation occurs at around 14 GPa and most intense peak of the high pressure phase is observed at the position between the (100) and (101) lines of graphite, which remarkable contrast with the vertical observation.

of graphite, which was quite different from that observed in the vertical direction. The new lines became stronger with pressure but the diffractions from graphite did not disappear completely. The behavior in the pressure decreasing process was also the same as that observed in the vertical direction.

Combining the informations obtained both in the vertical and the horizontal directions, we could observe 6 and 5 diffraction lines for graphite and for the high pressure phase, respectively. Change of the d-values of these diffraction lines are summarized in Fig. 2-9. Five diffraction lines for the high pressure phase can be successfully indexed by a hexagonal structure. Since the line indexed as h(101) is overlapped with graphite, its d-value has large uncertainty and is not included in Fig.2-9.

An example of the diffraction profile obtained using the diamond anvil apparatus at 20 GPa is shown in Fig. 2-10. Although very well monochromatized X-ray from synchrotron radiation and very sensitive Imaging Plate detector were used and the exposure time was quite long (6 hours), the S/N ratio of the obtained diffraction profile was very low because of the small thickness of the sample in the diamond anvil cell. Only a few strong lines can be observed and the detailed analysis was impossible. Besides, a small portion of the incident X-ray beam was hitting the gasket in this particular run and the diffraction from the gasket was also observed. In spite of the poor quality, the diffraction profile obtained by this method is similar to that obtained by the horizontal observation in Drickamer-cell. That is, (100) and (101) lines of graphite were observed strongly and the strongest line of the high pressure phase appeared between them. In the diamond anvil apparatus, incident X-ray gets into

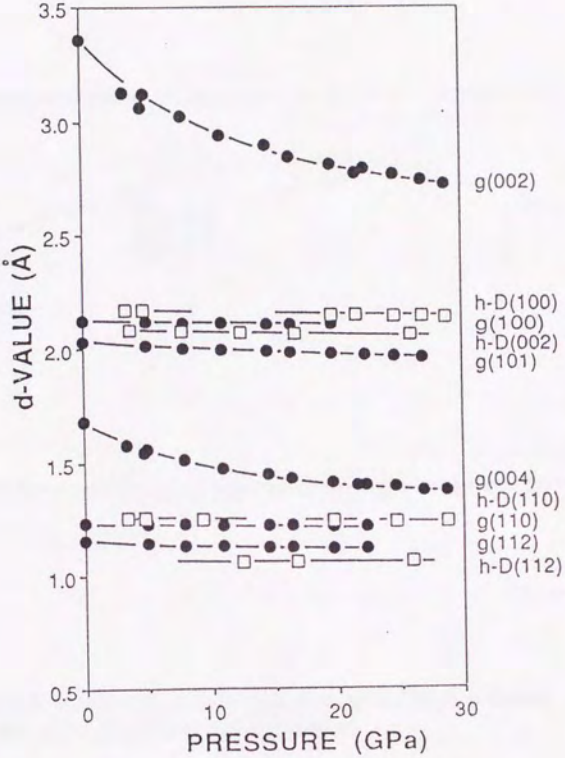


Fig.2-9
Variation of the d-spacing values of graphite and hexagonal diamond as a function of pressure obtained by Drickamer anvil apparatus. Solid circle and open square represent graphite and hexagonal diamond phase , respectively.

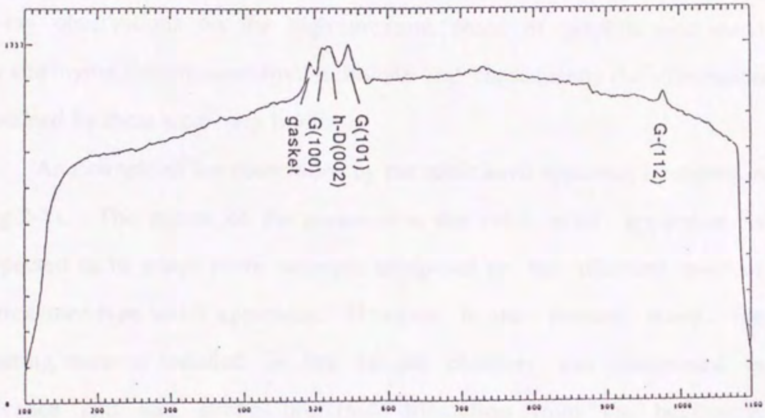


Fig.2-10
Typical X-ray diffraction profile of graphite under high pressure obtained by the diamond anvil cell and Imaging Plate.

the sample chamber parallel to the compression axis of the opposed anvils. Therefore, the crystal planes almost parallel to the compression axis contribute to the diffractions and it is quite reasonable that the diffraction lines observed by the diamond anvil is very similar to those observed in the horizontal direction in Drickamer-type anvil. Most of the previous X-ray observations on the high pressure phase of graphite were made by employing this diamond anvil technique and consequently the information obtained by them were very limited.

An example of the observation by the cubic anvil apparatus is shown in Fig.2-11. The nature of the pressure in the cubic anvil apparatus is expected to be much more isotropic compared to the diamond anvil or Drickamer-type anvil apparatus. However, in the present study, the starting material installed in the sample chamber was compacted in advance and had strong preferred orientation from the beginning. Consequently, the observed diffraction profile was very similar to that observed in the vertical direction of the Drickamer-type anvil. In this case, however, the onset of the transition was delayed until the pressure was raised to 18 GPa, even though the starting material was identical. This means that the transition pressure is sensitive to the nature of the pressure.

Transition pressure in the pressure increasing process varied a lot depending not only on the nature of the applied pressure, but also on the nature of the starting material. In order to see this effect, a fine carbon powder for chemical analysis (Tokai Carbon Co.) which has high purity but is poorly crystallized, was compressed by the Drickamer-type anvil and the cubic anvil apparatus. In both case, transition pressure was delayed considerably. In the experiment using Drickamer anvil, the

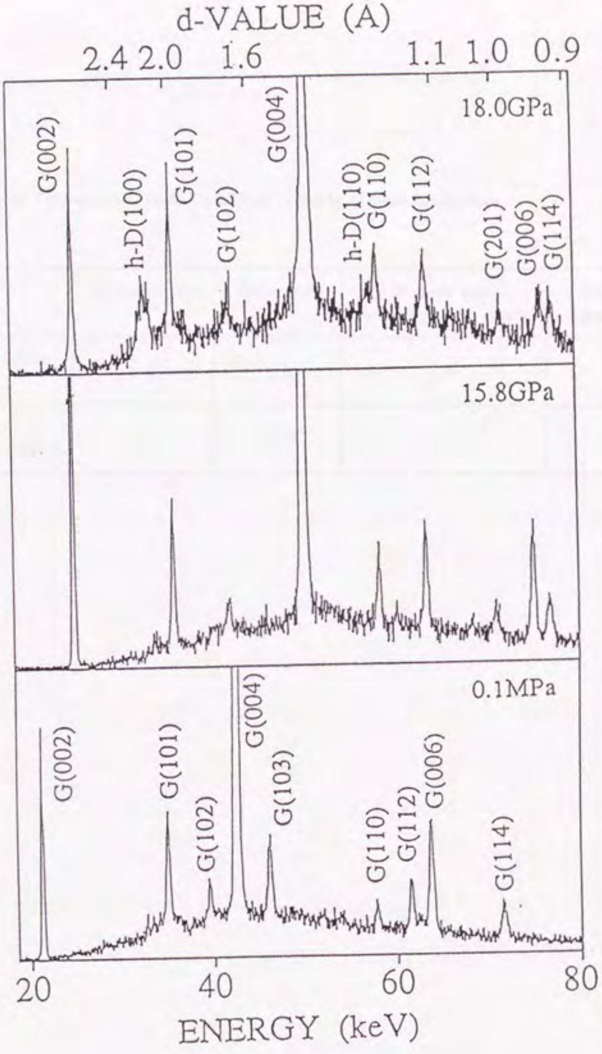


Fig.2-11
The variation of the X-ray diffraction profiles of graphite under high pressure obtained by the cubic anvil apparatus. The transition does not occur until the pressure is raised to 18 GPa.

Table 2-1

Graphite - Hexagonal Diamond Transition Pressure at Room Temperature

	Drickamer anvil	Cubic anvil	Diamond anvil (single crystal sample)	Diamond anvil (powder sample)
kish graphite	14	18	18	15
graphite for chemical analysis	23	>18	--	--

(GPa)

diffraction peaks of the high pressure phase appeared at about 23 GPa. In the cubic anvil experiment, no peaks of the high pressure phase was observed at all even when the sample was compressed up to 18 GPa, which was the maximum pressure generated by this apparatus. The variation of the transition pressure in all the experiments are summarized in Table 2-1.

D) Discussion.

Compression of graphite phase.

Fig.2-12 shows the variation of the lattice parameters a/a0 and c/c0 of graphite phase obtained by the cubic anvil apparatus. As described before, in this apparatus, graphite did not transform to the high pressure phase until 18 GPa. Because of its large size of the sample chamber, high quality X-ray diffraction pattern was obtained and the precise compression curve of the lattice parameters were determined from the six diffraction lines. For the comparison, the previously reported data was also plotted in the same Figure. The compression along the c axis reported by Hanfland et al. [1989] (open triangles in Fig.2-12) is in fairly good agreement with our present data, though their results were derived from only two diffraction lines ((002) and (101)) obtained by the diamond anvil cell. They also reported that above 14 GPa, these diffraction lines of graphite disappeared and high pressure phase was formed though its structure could not be identified because of the poor quality of the diffraction pattern. This transition pressure 14 GPa is the same as that obtained in the present experiment using Drickamer- type anvil. On the

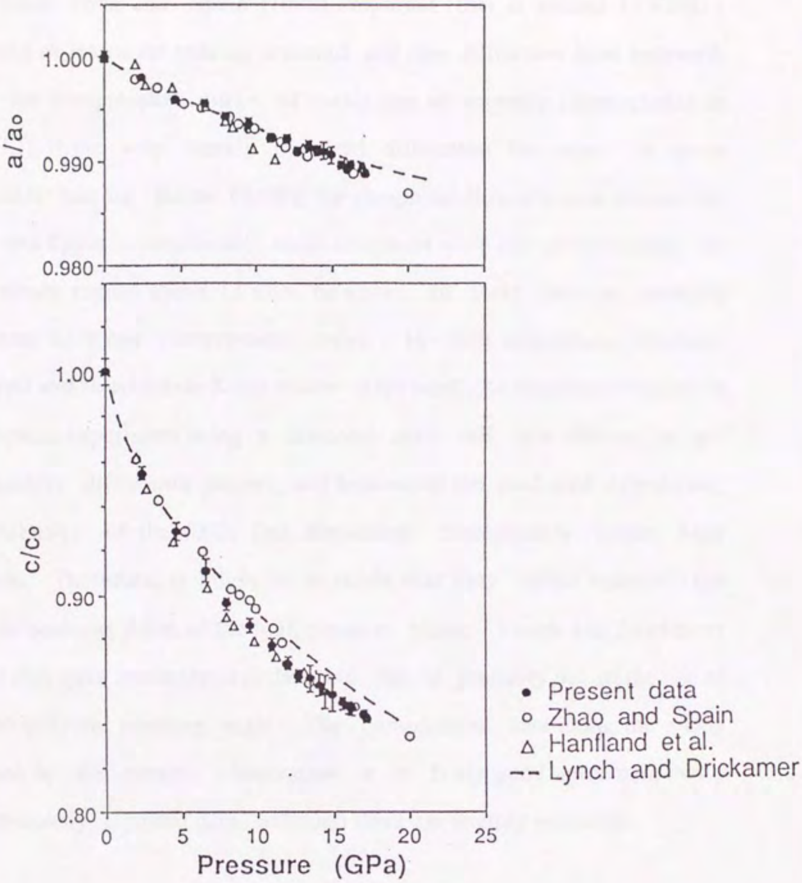


Fig.2-12
Relative lattice parameters a/a0 and c/c0 of graphite as a function of pressure. The solid circles correspond to the present results obtained by the cubic anvil apparatus. For the comparison, previous data are also plotted.

other hand, Zhao and Spain [1989] reported that at around 11 GPa, a softening of interlayer spacing occurred and new diffraction lines appeared. Thus the compression curve of c-axis has an anomaly (open circles in Fig.2-12), if the very weakly observed diffraction line near 3 Å gives the c-axis spacing. Below 10 GPa, the compressibility of c-axis derived by Zhao and Spain is considerably small compared with our present data. In the pressure region above 11 GPa, however, all their data is perfectly consistent with our compression curve. In their experiment, diamond anvil cell and fixed-anode X-ray source were used. As mentioned before, in the graphite experiment using a diamond anvil cell, it is difficult to get high quality diffraction pattern, and because of the preferred orientation, the intensity of the (002) line diminishes considerably under high pressure. Therefore, it might be possible that they miss- indexed the graphite peaks as those of the high pressure phase. Lynch and Drickamer [1966] also gave incompressive data, but this is probably due to the use of old and different pressure scale. The compression data along the a-axis obtained by the present observation is in fairly good agreement with the previously reported data, although there are slightly scattered.

Structure of the high pressure phase.

All the new diffraction lines of the high pressure phase obtained by the present study are successfully indexed by a hexagonal unit cell. Observed and calculated d-values and the unit cell parameters at 25 GPa and 5 GPa are summarized in Table 2-2, together with the data on hexagonal diamond reported by Bundy and Kasper. The present high pressure phase is unquenchable and it is impossible to make direct comparison with the quenched hexagonal diamond, which was observed at

Table 2-2 D-spacing parameter of the hexagonal diamond

	d (A)						
hkl	25 GPa		5 GPa		0.1 MPa		
	obs.	calc.[a]	obs.	calc.[a]	obs.[b]	calc.[a]	obs.(Bundy and Kasper)[c]
100	2.139	2.137	2.170	2.165	2.180	2.176	2.19
002	2.055	2.053	2.079	2.079	2.086	2.086	2.06
101	(1.9)[d]	1.895	(1.9)[d]	1.920	···	1.929	1.92
102	···	1.480	···	1.499	···	1.506	1.50
110	1.234	1.234	1.249	1.250	1.256	1.257	1.26
103	···	1.152	···	1.167	···	1.172	1.17
112	1.057	1.057	1.169	1.071	1.074	1.076	1.075
201	···	1.034	···	1.048	···	1.053	1.055
	a=2.467(3) c=4.105(5)		a=2.500(6) c=4.158(6)		a=2.513(6) c=4.171(5)		a=2.52 c=4.12

a) Calculated value based on the lattice constants derived from the observed diffraction peaks
b) Extrapolated value (see text)
c) Quenched sample from high pressure and high temperature condition
d) Overlapped with (101) peak of graphite

atmospheric pressure. Therefore, d-values at ambient condition obtained by the extrapolation of the present high pressure data between 25 and 5 GPa and the unit cell calculated from these extrapolated d- values are also listed in Table 2-2. The unit cell thus obtained is very close to that of hexagonal diamond (Lonsdaleite) reported by Bundy and Kasper, which suggests that the high pressure phase observed in the present study has the same structure as hexagonal diamond, although the present high pressure phase is unquenchable on release of pressure.

In order to get definite conclusion, it is necessary to compare the intensity of the diffraction lines. In the present experiment, however, highly preferred orientation was formed in the sample and it was very difficult to analyze the crystal structure by the comparison of the observed and calculated intensity. Actually, as is clear from Figures 2-7 and 2-8, observed intensity for the high pressure phase differs a lot depending on the direction of observation. Intensities in vertical and horizontal observations are reproducible, which means certain orientation relation exist between graphite and the high pressure phase. Fig.2-13 is a comparison of the diffraction profiles of graphite between the vertical and horizontal observation. Our observation can be summarized as follows; (1) When the (002) line of graphite was observed strongly, the (100) line of high pressure phase was observed strongly (vertical method). (2) On the other hand, when the (100) line of graphite was observed strongly, the (002) line of high pressure phase was observed strongly (horizontal method). Mechanism and orientation relation of the phase transformation from graphite to hexagonal diamond were previously proposed by Bundy and Kasper [1967] and Lonsdale [1971]. They proposed that graphite makes martensitic transformation to hexagonal

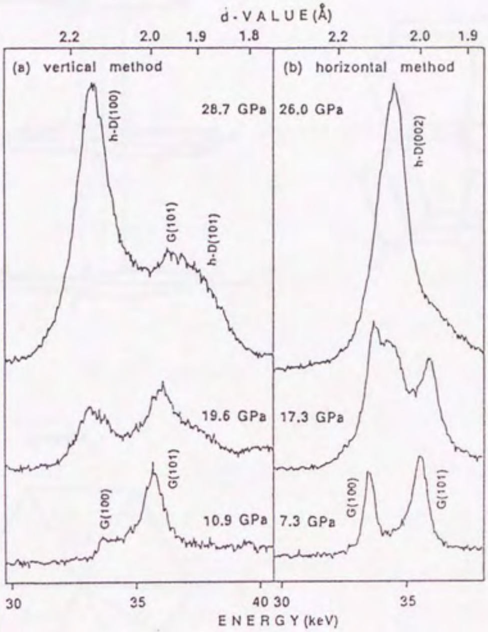


Fig.2-13
Comparison of the diffraction profiles of graphite between the vertical and horizontal observation. In the vertical method, (100) and (101) of the hexagonal diamond peaks are observed, while in the horizontal method, (002) peak is strong.

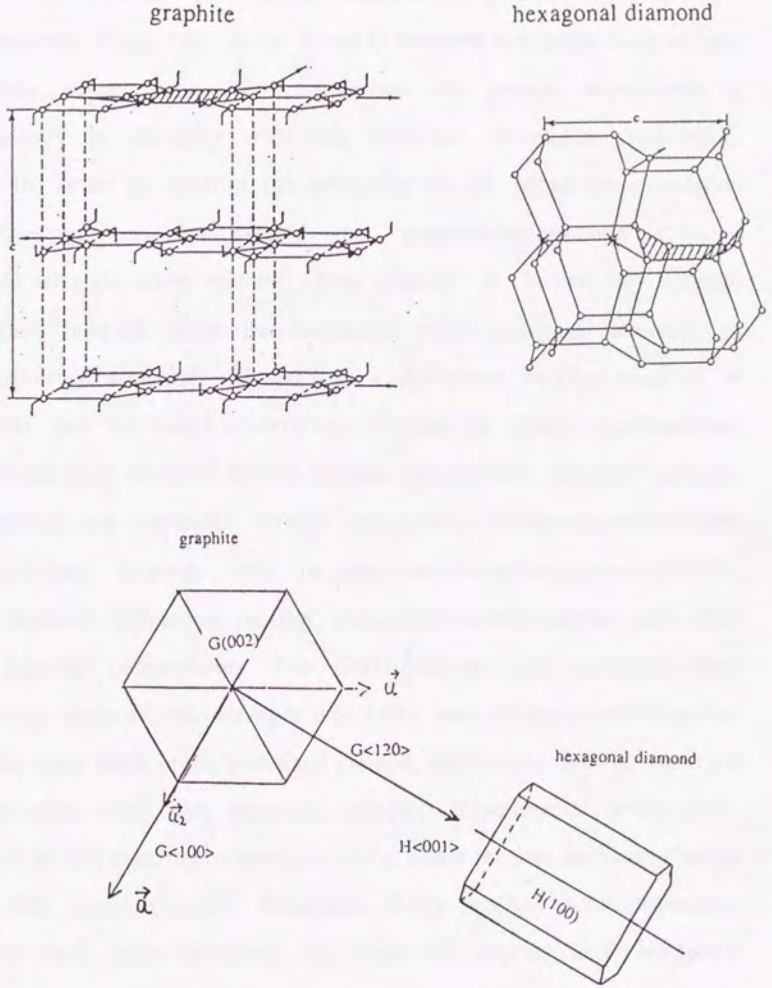


Fig.2-14
Orientation relationship of the phase transformation from graphite to hexagonal diamond.

diamond with the orientation relationship that H(100) parallel to the G(002), and H<001> and H<100> being parallel to G<120> and G<100>, respectively (Fig.2- 14). Here, H and G represent hexagonal diamond and graphite, respectively. It is clear that our present observation is completely in harmony with this proposed orientation relationship.

In order to confirm the reliability of the observed orientation relationship, we also studied the phase transformation in boron nitride using the same method. This material is known to undergo pressure induced phase transformation from hexagonal structure to wurtzite-type structure. Fig.2-15 is a diffraction profiles obtained in vertical and horizontal observation. Before the phase transformation, (002) and (100) peaks of the low pressure phase were observed strongly in vertical and horizontal method, respectively, which was similar to the graphite case. However, after the phase transformation at around 10 GPa, the observed diffraction profiles showed remarkable contrast with those of graphite compression. The (002) peak of high pressure phase (wurtzite structure) was stronger than (100) peak in the vertical method. On the other hand, in the horizontal method, (002) could not be observed at all while (100) was observed strongly. Experimental results shows that in the BN case, the orientation of the c-axis remains unchanged before and after transformation. Structures of low pressure and high pressure phases have close similarity to those of graphite and hexagonal diamond, respectively. However, because of the slight difference in the stacking sequence of basal plane in graphite-like structure, the orientation relationship between low and high pressure phases is different. For BN, the transformation occurs with hBN(002) parallel to wBN(002) (Fig.2-16). Here, h and w represent low pressure and high pressure

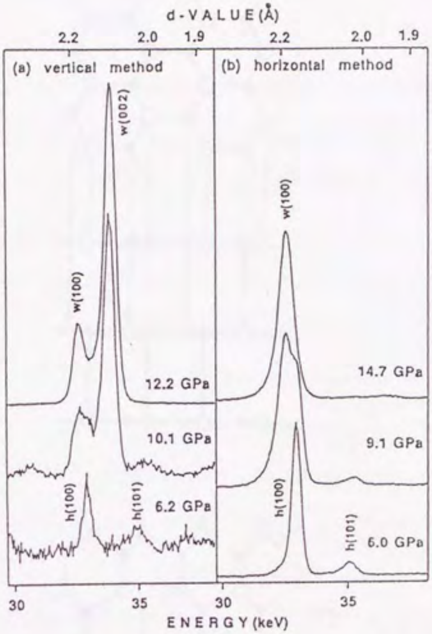


Fig.2-15
Comparison of the diffraction profiles of BN between the vertical and horizontal observation. Low pressure phase (denoted as h) transforms to wurtzite structured phase (denoted as w) under high pressure. In the vertical method, w(002) is observed strongly, while in the horizontal method, w(100) is strong. These profiles are contrast with those of graphite case.

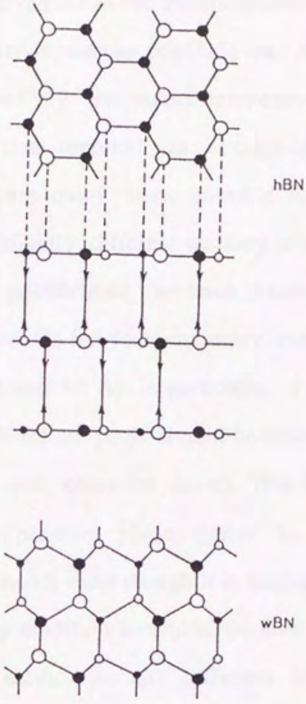


Fig.2-16
Orientation relationship of the phase transformation from hexagonal BN to wurtzite BN.

phases, respectively. The present experimental result on BN is in harmony with the orientation relationship described above and confirms the reliability of the observations of the transformation on graphite.

Based on these analysis, we can conclude that the crystal structure of the new phase formed by the room temperature compression of graphite is identical to that reported as hexagonal diamond. For the diamond polytypes, there are many other possible structures which have similar framework with slightly different stacking sequences [Spear et al., 1990]. To check these possibilities, we have examined the diffraction patterns carefully but we could not find any other meaningful lines in the d-value range between 3.5 and 1.0 Å. In particular, if the phase has a long periodic structure, new diffraction peak should be observed in a low energy region, but no such lines was observed at all. This means that, the basic framework of this high pressure phase cannot be different so much from the hexagonal diamond, even though it is impossible to exclude all the possibilities of slightly modified structure, because the peak resolution by the energy dispersive method is not sufficient enough to identify the slight difference of stacking sequences.

Present observation also supports the orientation relationship proposed by Bundy and Kasper. In their report, however, they could not get good enough diffractions to determine the unit cell precisely. They have assumed that the bond length in hexagonal diamond is identical to that in cubic diamond and consequently obtained the same density for both phases. In the present analysis, however, we could determine the unit cell without any assumption and found that the unit cell is slightly, but meaningfully, larger than that reported by them. The a-axis is almost the same but the c-axis is about 1 % larger. Fahy and Louie [1987] calculated the structural properties of hexagonal diamond using an *ab initio* pseudopotential local-orbital method, and obtained slightly larger c-axis also (4.14 Å, conferred to 4.12 Å in Bundy and Kasper). This expansion of c-axis is probably due to the repulsion between the carbon atoms which are aligned along the c-axis. Because of this slight expansion, c/a ratio obtained by the present observation has increased to 1.66, which is slight larger than 1.63, the ideal value of this hexagonal structure. This c/a ratio remains unchanged up to at least 30 GPa.

Relative volume of graphite, hexagonal diamond, and cubic diamond as a function of the pressure are compared in Fig.2-17. Graphite begins to transform to hexagonal diamond with a discontinuous volume change at around 14 GPa, but further compression is necessary to complete this transition at room temperature. The volume of the hexagonal diamond is about 1% larger than that of the cubic diamond because of its slight expansion of the c-axis from the ideal value. The bulk modulus of the hexagonal diamond calculated from the present data is 425±20 GPa, which is indistinguishable from that of cubic diamond within the experimental error.

Difference of the transition pressure.

As shown in Table 2-1, transition pressure varies a lot depending on many factors such as the nature of starting material and the way of compression. Existence of the orientation relation between low and high pressure phase suggests that the nature of this transition is not a diffusion type but a martensitic type. Graphite has a layered structure and carbon atoms inside the layer is connected by sp^2 type covalent bond while the bond between layers have a nature of Van der Walls force.

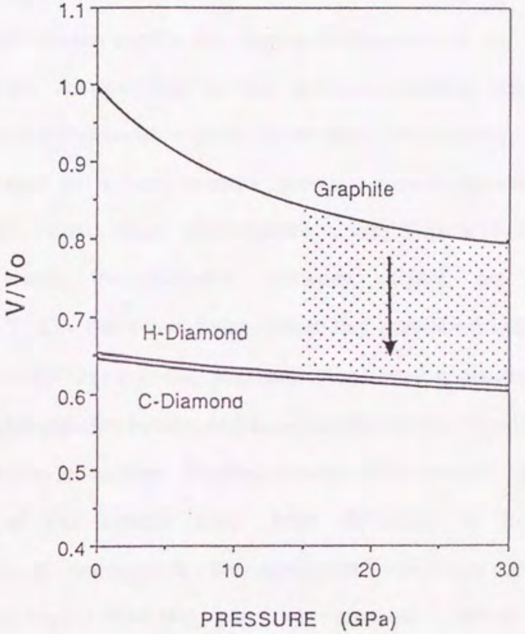


Fig.2-17
Relative volume change of graphite, hexagonal diamond, and cubic diamond as a function of pressure. Graphite begins to transform to hexagonal diamond at around 14 GPa by the room temperature compression, but further compression is necessary to complete this transformation.

Consequently, as shown in Fig.2-12, compressibility along c-axis is much larger than that along a-axis. At about 18 GPa, where the transformation starts in a quasi hydrostatic environment, the bond length between layer are approximately 2.8 Å. Since this transition has a martensitic nature, the condition of the adjusted layer is very important. When the distance between two layers became smaller than the above mentioned value, and two layers are properly positioned, then the transition is expected to occur.

These hypothesis can explain the observed differences of the transition pressure very well. As described in the previous section, when a very thin single crystal is compressed in quasi hydrostatic environment, transition starts and completed in a very narrow pressure interval between 18 and 19 GPa. In this case, since the sample is very thin, it is almost a perfect crystal and the distance between layers are reduced homogeneously. On the other hand, when the powdered sample is compressed directly in a solid pressure transmitting medium, very heterogeneous compression occurs and some portion of the sample can be compressed more then the average. Besides, because of the random orientation, some portion of the sample may have difficulty to find proper neighboring layer to accomplish the transition even when the nominal pressure is much higher than the transition pressure. Since the most important factor for the onset of the transition is the compression along c-axis, transition starts at lower nominal pressure when the sample is compressed uniaxially. This may be the reason why the transition pressure is low in Drickamer-type anvil.

The difference of the transition pressure in different starting material can be explained in a similar manner. Kish graphite is very well crystallized and the transition is easy to occur. On the other hand, high purity carbon for the chemical analysis is not so well crystallized and the transition is hard to occur.

So far, many high pressure studies have been done on graphite but the transition pressure reported are scattered. This is quite reasonable because high pressure apparatus and the nature of starting material used for each study had wide variety. Probably the reproducible results can be obtained only when high quality single crystal is compressed in a highly hydrostatic environment.

Conclusions.

High pressure in situ X-ray diffraction study on graphite were carried out up to 30 GPa at room temperature. Following results were obtained from these observations.

1) Phase transformation from graphite to a high pressure phase occurs at about 14 GPa when well crystallize single crystal (kish graphite) was squeezed using Drickamer-type high pressure apparatus.

2) Diffraction profiles obtained on this high pressure phase is well explained by the hexagonal diamond structure.

3) Transition pressure in increasing and decreasing pressure process has large hysteresis and the high pressure phase formed at room temperature was unquenchable on release of pressure.

4) Hexagonal diamond formed at room temperature has c/a ratio 1.66 which is slightly higher than that reported before.

5) Transition pressure is very sensitive to the nature of the starting material as well as to the nature of the pressure applied to the sample.

6) Transition has martensitic nature and the diffraction from two different orientation satisfies the orientation relationship proposed

before.

2-4. *In situ* X-ray diffraction study under high pressure and high temperature.

In the previous section, it became clear that the crystal structure of the high pressure phase formed by room temperature compression of graphite is indistinguishable from that of hexagonal diamond. However, the hexagonal diamond reported by Bundy and Kasper was a quenching product to atmospheric pressure while present high pressure phase is unquenchable and the reason of this difference remains unclear. In order to clarify the pressure and temperature condition in which hexagonal diamond can be synthesized and the quenchability of the hexagonal diamond, *in situ* X-ray observation under high pressure and high temperature was carried out.

A) Experimental.

A combination of synchrotron radiation and Drickamer type high pressure apparatus is a powerful tool for obtaining the information on preferred orientation of the sample. However, so far, stable high temperature generation is difficult by this apparatus. Thus, the DIA system with sintered diamond anvils (MAX80) was used for the high temperature experiment.

Fig.2-18 is a cell assembly for the present experiment. Starting material was a kish graphite, which is the same one used in the room

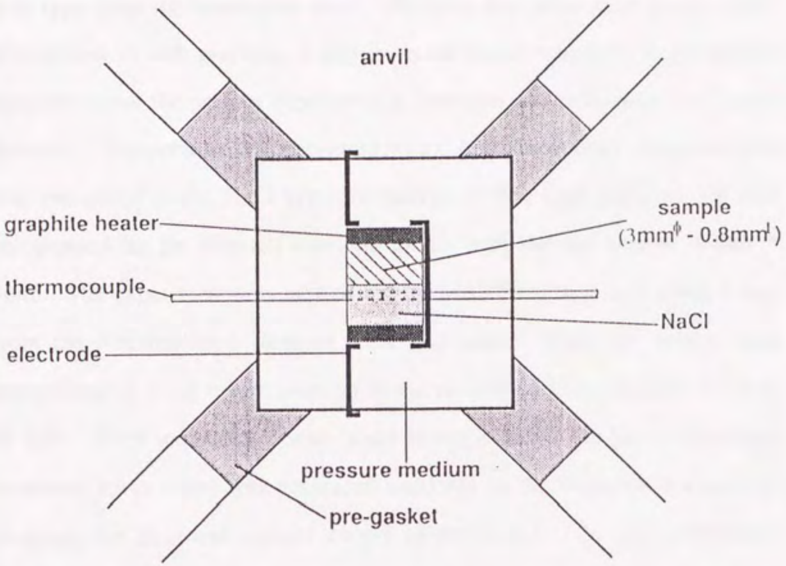


Fig.2-18
The cell assembly for the *in situ* observation of the graphite to hexagonal diamond transition under high pressure and high temperature.

temperature experiment. Since the fine powder sample was compacted into a cylindrical shape by a piston and cylinder type jig before the experiment, it had already strong preferred orientation. For the high temperature generation, disk type graphite heater was used. Because this graphite is not so well-crystallized as kish graphite, it was expected not to transform to hexagonal diamond under the present experimental condition and to be used as a heater material. Temperature was measured by a CA thermocouple whose junction was embedded in the NaCl pressure marker. The high pressure cell was compressed by the sintered diamond anvils with the top area of 3 mm * 3mm. The experiment was carried out by MAX80 system and white X-ray from the Accumulation Ring of KEK was used. First, the sample was compressed at room temperature up to the prescribed pressure such as 14 or 18 GPa. Then temperature was raised slowly. After the phase transition occurred, temperature was decreased suddenly to the room temperature by stopping the electrical current supply to the heater. In each condition, X-ray diffraction profile of the sample was detected by energy dispersive method.

B) Results and discussion

Diffraction profiles under high pressure and high temperature.

Fig.2-19 shows the variation of the X-ray diffraction profiles of the sample when temperature was increased from 25 °C to 890 °C at 18 GPa. As described in the previous section, by the compression with cubic anvil apparatus, graphite begins to transform to hexagonal diamond at 18 GPa by room temperature compression. Under this condition, however, the formation

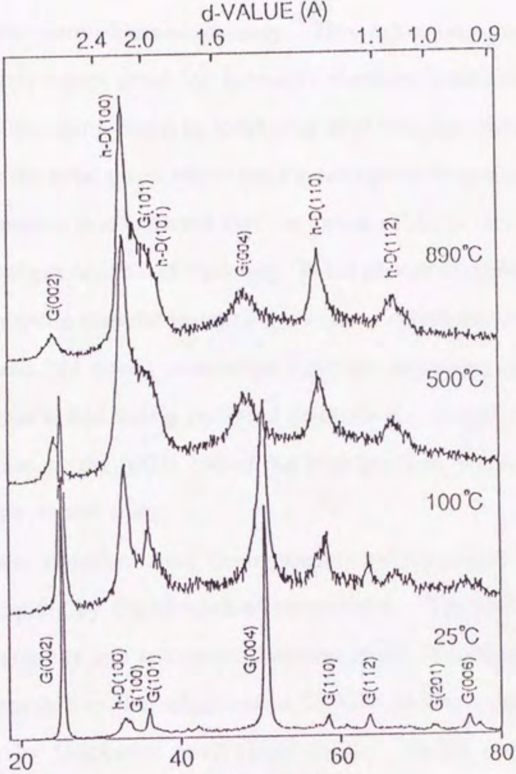


Fig.2-19
Variation of the X-ray diffraction profiles of graphite with increasing temperature at 18 GPa.

of the hexagonal diamond was very limited and only one peak corresponds to h-D(100) was observed very weakly. When temperature was increased , the intensity of the graphite peaks decreased and the diffraction peaks of the high pressure phase were observed strongly. This diffraction profile obtained under high temperature condition is exactly identical to that observed in the room temperature compression by Drickamer anvil cell, thus it was reconfirmed that these are the same phase which has the hexagonal diamond structure. In the DIA apparatus, it is expected that the nature of the pressure is isotropic and that the sample is oriented randomly. In the present experiment, however, because the starting material installed in the sample chamber was compacted beforehand and had strong orientation from the beginning, even after the phase transition it had strong preferred orientation. Hence, unfortunately, the information on the (002) line of the high pressure phase could not be obtained in the present study.

The phase transformation from graphite to hexagonal diamond was accelerated rapidly by the increase of temperature. The ratio of the peak intensity of graphite and hexagonal diamond under 18 GPa and 100 °C is almost comparable to that observed at 29 GPa in the room temperature compression by Drickamer anvil (Fig.2-7(a)). As the temperature was increased further, the diffraction peaks of the hexagonal diamond became stronger, but in the high pressure region above 500 °C, transforming rate from graphite to hexagonal diamond became small. Thus, even at the highest temperature achieved in this experiment (890 °C), the graphite peaks were still observed and we could not get the single hexagonal diamond phase.

On the other hand, it was clarified by the *in situ* X-ray observation that the disk shaped poor crystallized graphite which was used as a heater material did not transform to hexagonal diamond at all under the present experimental condition. As described in the previous section, this graphite to hexagonal diamond transformation is a martensitic transition and it strongly depends on the crystalline nature of the starting sample. Present experiment made it clear that even under high temperature condition more than 800 °C, phase transition from graphite to hexagonal diamond is difficult to occur when the starting graphite sample is not well crystallized. Since this heater did not transform to other phase, the electrical resistance of the heater was quite stable during the experiment.

Pressure-Temperature condition to produce hexagonal diamond.

The thermodynamical phase boundary of graphite and cubic diamond exists in a fairly low pressure region (about 2 GPa at room temperature) on the Pressure-Temperature diagram. However, in the practical experiment without catalyst or solvent, the direct conversion from graphite to diamond does not occur at this boundary, and much higher pressure or temperature is needed to induce the phase transition. Hence, for the practical meaning, the reaction boundary is defined as a boundary where the new phase begins to be produced. Fig.2-20 shows the reaction boundaries for carbon and BN obtained by the present study. For the BN experiment, well crystallized hexagonal structured BN (denoted as hBN), which was heated up to 2000 °C beforehand, was used as a starting material. *In situ* X-ray observation under high pressure and high temperature condition was carried out, and from the variation of the diffraction profiles, two reaction boundaries from hBN to wBN and from wBN to cBN were determined. (Here, wBN and cBN represent wurtzite structured BN and cubic structured BN, and these have analogous structure to hexagonal diamond and cubic diamond, respectively.) By the room temperature compression of hBN, it transforms to wBN at

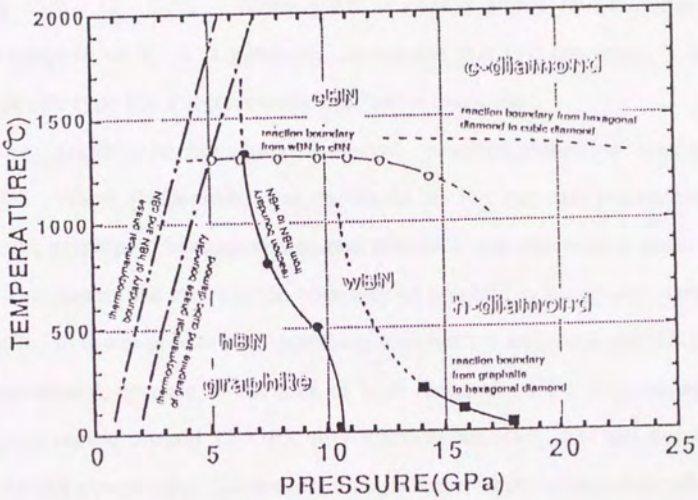


Fig.2-20
Reaction phase diagram of carbon and BN obtained by the present study.

10.5 GPa. On increasing temperature, transition pressure is shifted to lower pressure, and at 1000 °C, only 7 GPa is enough to produce wBN phase. However, below 6 GPa, this transition does not occur even if the temperature is extremely high. The reaction boundary from wBN to cBN exists at about 1300 °C in the pressure range of 5 to 12 GPa, and has a slightly negative slope above 12 GPa. When wBN is heated above this boundary, it transforms to cBN. It is generally considered that this transition is not a martensitic type but a reconstructive diffusive transition.

For graphite to hexagonal diamond transition, situation was quite similar. When temperature was increased at the constant pressure of 14 GPa, the graphite to hexagonal diamond transition was observed at about 200 °C. This means that the reaction boundary of graphite to hexagonal diamond is shifted to lower pressure on increasing temperature as well as the BN case. Unfortunately, because of the lack of high temperature experiments at the pressure region around 12 GPa, this reaction boundary has not yet been determined completely. However, it might be considered that there should be a critical pressure for the graphite to hexagonal diamond transition just as the hBN to wBN transition. In addition, the formation of the cubic diamond phase has been confirmed by the several high pressure and high temperature studies such as the heating experiment with diamond anvil and YAG laser (described in section 2-2) or the investigation of the recovered sample synthesized by 6-8 two stage system (Itani et al., private communication). Therefore, it is also expected that the reaction boundary of hexagonal diamond to cubic diamond exists at high temperature. As a consequence, the reaction phase diagram of carbon and BN have a great similarity.

Quenchability of the hexagonal diamond phase

Three different runs are made to see the nature of quenchable property of hexagonal diamond. The experimental conditions are as follows; (a) compression (at room temperature) up to 14 GPa, heating up to 860 °C, decompression to 0.1 MPa (at room temperature) (b) compression up to 18 GPa, heating up to 890 °C, decompression to 0.1 MPa (c) compression up to 18 GPa, heating up to 500 °C, decompression to 0.1 MPa. In all these runs, pressure was slightly (about 1 GPa) decreased by increasing temperature. The X-ray diffraction data at 0.1 MPa was collected in the situation that the sample was still in the high pressure cell and the applied press thrust was unloaded completely.

In Fig.2-21, the variation of the X-ray diffraction profiles in each run are summarized. In runs (a) and (b), hexagonal diamond phase was formed under the pressure and high temperature condition. Formation rate of the hexagonal diamond in run (b) was larger than in run (a), probably because of the difference of the pressure. When the pressure was decreased to 0.1 MPa, in both runs, the diffraction lines of the hexagonal diamond phase were still observed quite strongly, and thus hexagonal diamond could be quenched to 0.1 MPa, although the graphite peaks became stronger compared with those under high pressure and high temperature condition. (In run (b), blow out occurred on release of the pressure. Several extra peaks observed at 0.1 MPa are from NaCl and MgO due to this blow out.)

On the other hand, the hexagonal diamond phase synthesized by the heating up to 500 °C (run (c)) converted to graphite phase completely during the decompression below 2.9 GPa. Although the amounts of the hexagonal diamond phase under high pressure and high temperature condition estimated by the peak intensity was almost comparable to that in run (b), hexagonal

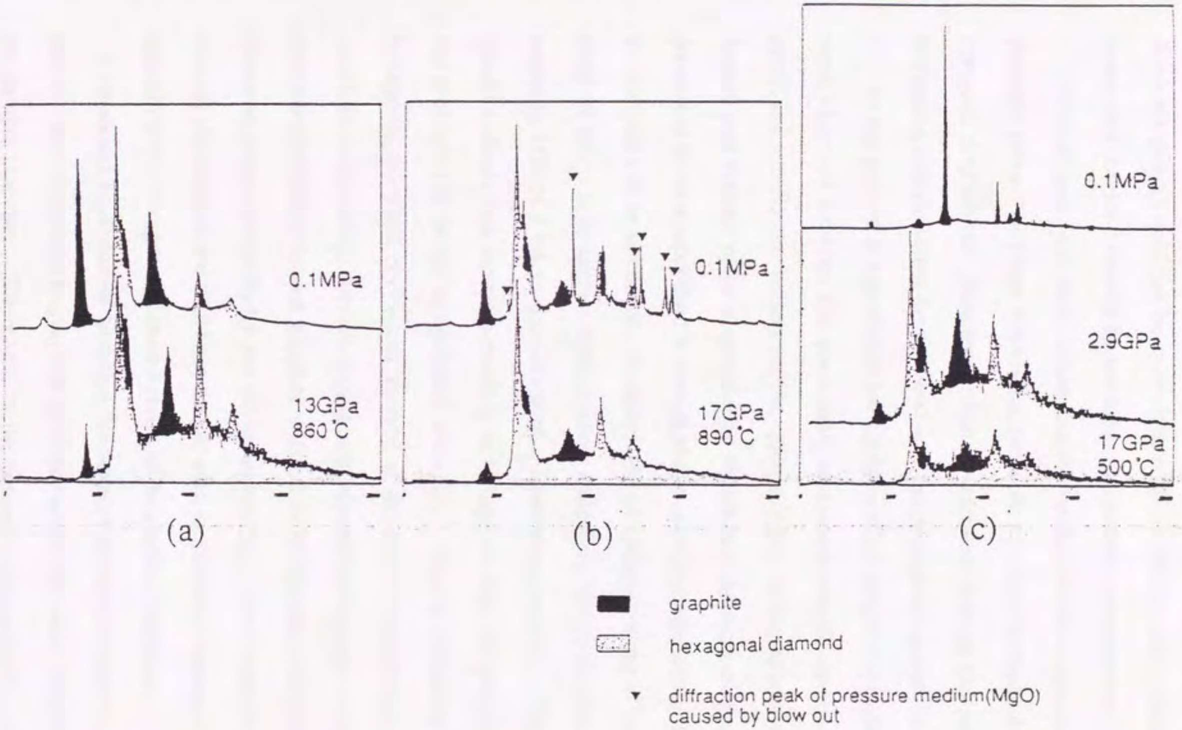


Fig.2-21
Variation of the X-ray diffraction profiles of the hexagonal diamond heated up in various pressure-temperature conditions.

diamond phase could not be quenched at all. This is quite similar to the hexagonal diamond formed by the room temperature compression.

It is obvious from these results that the heating of the sample under high pressure phase can lower the critical pressure at which hexagonal diamond converts to graphite. This means that an adequate heating can prevent the hexagonal diamond from the conversion to graphite on release of the pressure.

In the present X-ray diffraction profiles, no distinguishable differences were observed between the quenchable and unquenchable runs. Thus we could not clarify the reason on the quenchability of hexagonal diamond. Bundy and Kasper made a speculation that when the high pressure phase formed at room temperature is heated above critical temperature, this phase is "set" and can be quenched. However, the physical meaning of "set" is not clear at all. It is known that in some materials, the grain size and the impurity affects a lot to the nature of quenchable property. The present results indicate that the quenchability of hexagonal diamond depends not on the pressure but on the temperature strongly. Thus it is possible that the hexagonal diamond crystalline formed at the lower temperatures are too small or imperfect to survive during decompression at room temperature. Another possibility is that graphite existed as inclusions in the hexagonal diamond phase affects badly for the quenchability. Unfortunately, by the present observation, we could not decide what is the most impotant factor for quenching the hexagonal diamond phase to the ambient condition.

It should be described here that the hexagonal diamond phase in runs (a) and (b) were converted to graphite perfectly when they were recovered from the sample chamber. Therefore, in the present experiment, the hexagonal diamond phase could not be recovered to ambient condition. The least amount of the residual stress might exist in the high pressure cell even after the applied thrust was unloaded completely. It is possible that hexagonal diamond in the sample chamber reverted to graphite on release of this stress. Bundy and Kasper reported that in order to recover the hexagonal diamond phase to the ambient condition, the sample should be heated to temperature exceeding about 1000 °C, though their temperature measurement was not so accurate. The maximum temperature achieved in the present study was 890 °C because of the limitation of the apparatus. This may be the reason why the hexagonal diamond could not be recovered from the high pressure cell. In order to quench the hexagonal diamond phase to ambient condition, further heating up to higher temperature might have been needed.

Once the cubic diamond is formed under high pressure condition, it can be always quenched to 0.1 MPa. However, it is quite difficult to quench the hexagonal diamond phase. We consider that one of the reasons of the difficulty in recovering the hexagonal diamond is that c-axis is slightly expanded due to the repulsion between the carbon atoms which are aligned along the c-axis and as a result it is less stable than the cubic diamond at ambient condition.

Recently, Yoshida and Thadhani [1991] reported an interesting shock experimental data. They used well crystallized graphite and tried to synthesize diamond by shock compression under various pressure and temperature conditions. The phase transition occurred at the pressure range between 20 and 35 GPa, and the amounts of the cubic diamond in the recovered sample did not depend on the pressure but strongly depended on the maximum temperature. According to the Hugoniot and sound velocity measurements, whole sample transformed to diamond completely under high pressure. In the recovered sample, however, large amount of graphite and small amount of cubic diamond were contained, and hexagonal diamond was not observed at all. This result can be explained as follows; By the shock compression, martensitic transition from graphite to hexagonal diamond occurred under high pressure. Because temperature was also increased in the reaction, some of the hexagonal diamond could transform to cubic diamond but most of the sample remained hexagonal phase. On release of the pressure, this hexagonal phase reverted to graphite by martensitic transition. Someone might claim that it is possible that only cubic diamond was formed under high pressure and the graphite phase in the recovered sample was derived by the graphitization of this cubic diamond by the residual temperature after release of pressure. Yoshida et al. investigated the crystalline nature of recovered graphite sample and confirmed that it was completely different from the graphitization products from cubic diamond. Thus this claim should be rejected. The result of this shock compression study is in good agreement with our static high pressure experiment.

As described above, in the present study we confirmed that by the adequate heating of the sample under high pressure, critical pressure at which hexagonal diamond reverts to graphite can be lowered, and hexagonal diamond phase can be survived almost to the ambient condition. However, unfortunately, we have not yet succeeded in recovering the hexagonal diamond phase from high pressure chamber. Thus its physical properties still remains unclear. In order to clarify the relationship between the quenchability and the grain size of impurity in the crystalline, further studies using electron microscope observation will be required. Moreover, the synthesis of hexagonal diamond under further high pressure or high temperature condition by 6-8 two stage system with sintered diamond anvils should be tried.

Conclusion.

The following was clarified by the *in situ* X-ray diffraction study under high pressure and high temperature condition.

1) The graphite to hexagonal diamond transformation is accelerated by increasing temperature under high pressure.

2) The required pressure to induce the hexagonal diamond transition is lowered by the increase of temperature. Reaction phase diagram of carbon has a great similarity to that of BN.

3) By the heating of the hexagonal diamond phase under high pressure, conversion pressure from hexagonal diamond to graphite on release of the pressure can be lowered, and when the hexagonal diamond phase is heated to more than 850 °C under high pressure, it becomes quenchable almost to the ambient condition.

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Appendix: Formation of cubic diamond from C_{60} by room temperature compression.

Very recently, it was reported that when the football shaped C_{60}, which is a cage like carbon structure and is called fullerenes, was compressed uniaxially at room temperature, it transformed to cubic diamond at 20±5 GPa and could be quenched to ambient condition [Reguerio et al. 1992]. On the other hand, under hydrostatic conditions C_{60} is known to be stable up to 20 GPa [Duclos et al. 1991], though its compressibility is very large. This new discovery is in good agreement with our present results that hexagonal diamond is formed by room temperature compression of graphite. In this transformation also, transition starts at lower pressure when the sample is compressed uniaxially.

Under the ambient condition, each football- like molecule in C_{60} rotates randomly. With increasing pressure, the distance between the each molecule becomes small, and it is expected that when the molecules approaches each other to a critical distance, the rotation is stopped by the atomic force between the neighboring molecules. Probably, at this state the relation of the atomic positions with those of neighboring molecules can be satisfied for the martensitic transformation to cubic diamond. Thus, when further compression is made up to a critical pressure, it can transform to the diamond. Since it transforms not to hexagonal diamond but to cubic diamond, it can be quenched to ambient condition.

Taking into account of the experimental results on the carbon transition, it is considered that the polymorph of the carbon made up of mainly sp^2 bonds can transform to sp3 structured carbon such as cubic diamond at high pressure and room temperature if the starting sample is well crystallized and the carbon atoms in the crystalline are properly positioned for the martensitic transformation. Rhombohedral structured graphite is one of the polymorph of the carbon which can exist at ambient condition. This rhombohedral graphite has the structure that the position of the carbon atoms in the basal plane is completely the same as the ordinal graphite and the stacking sequence of the basal plane is ABCABC. Consequently, by the same atomic movement required in the transition from ordinal graphite to hexagonal diamond, the rhombohedral graphite is expected to convert to cubic diamond under high pressure. (Actually, the conversion of rhombohedral BN to cubic BN has been confirmed recently [Ueno et al., 1991].) Here, I predict that if well crystallized rhombohedral graphite is compressed up to about 25 GPa, it will transform to cubic diamond at room temperature, and can be quenched to ambient condition.

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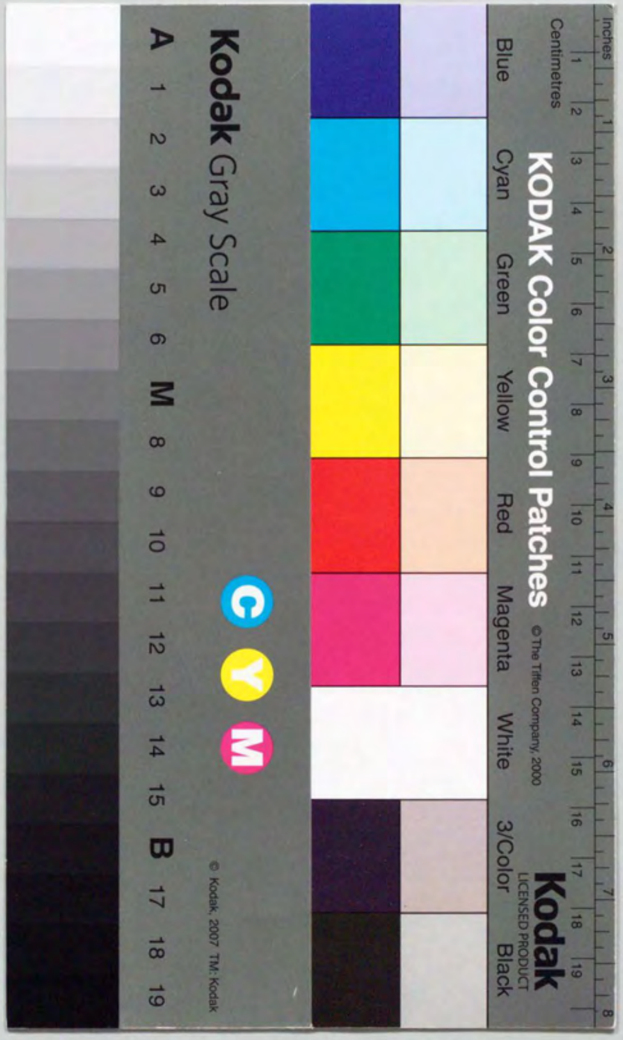
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