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X-ray diffraction and transmission-electron microscopy of natural polycrystalline graphite recovered from high pressure

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Natural polycrystalline graphite was compressed using a 6-8-type multianvil and a Drickamer cell, and the recovered samples were examined by x-ray diffraction and transmission-electron microscopy. Diamond was formed in the samples from 14 ~ 20 GPa and 800 ~ 1200 °C generated by the multianvil. These *P-T* conditions are included in the region where the formation of hexagonal diamond was reported by Bundy and Kasper. Hexagonal diamond was not apparent in any of the recovered samples. Instead, the formation of *n*-diamond, which is a new carbon phase recently identified in a shock-wave study, by static compression was confirmed in the samples from 40 GPa, 25 °C and 14 GPa, 1200 °C.

I. INTRODUCTION

Many *in situ* electrical, x-ray, and optical studies[1-10] have been carried out on graphite under high pressures at room temperature. All of them agree so far as some transition takes place in graphite in the pressure range from 12 to 22 GPa. As to the high-pressure phase, however, various results have been reported: an undetermined crystalline phase,[5] an amorphous phase[6] or hexagonal diamond.[9,10] Bundy and Kasper[2] synthesized hexagonal diamond by heating pyrotic graphite under static compression in the direction of the *c* axis.

These results may be ascribed to the starting samples of graphite and/or the types of high-pressure apparatus used in their experiments. Two disadvantages seemed to prevent a coincident conclusion. One is the low atomic scattering factor of carbon, which makes it difficult to obtain a clear x-ray diffraction pattern from the small amount of sample in a diamond-anvil cell. The other is related to the pressure values at which the transition is observed; a diamond-anvil cell or sintered diamond anvils must be used to generate such high pressures, then Raman-scattering signals and x-ray-diffraction lines of the samples are often not distinguishable from those of the diamond forming the anvils.

Previous studies at room temperature have indicated that none of the high-pressure phases were quenched to ambient pressure. In this study, we have performed x-ray-diffraction analyses and electron microscopy to observe the samples recovered from high-pressure compression at room temperature and to search for traces of the high-pressure phase. In addition, we examined the samples from various pressures and temperatures to clarify the relationship between this high-pressure phase and the hexagonal diamond phase, which can be quenched from high pressures and high temperatures.[2,10]

II. EXPERIMENTAL PROCEDURE

The graphite samples used in many previous studies were single crystals or polycrystals oriented in the direction of the *c* axis. They were compressed parallel to the *c* axis using a diamond-anvil cell or a Drickamer cell. In the present study we compressed polycrystalline samples using two kinds of apparatus. One was a Drickamer cell with sintered diamond anvils,[11] and the other was the 6-8-type double-staged multianvil[12] made of WC-Co alloy which can generate quasihydrostatic pressure by using a solid medium. The pressure was calibrated on the basis of the electrically detected α-ε transition in Fe-V alloys[13] for the former and of the lattice parameter of NaCl measured by x-ray diffraction for the latter.

The polycrystalline sample used in this study is a well crystallized natural graphite with lattice parameters of $a = 2.46$ Å and $c = 6.71$ Å. Using the same sample, Takano *et al.*[8] detected two transitions accompanied by a volume reduction at 18 and 22 GPa, respectively, at room temperature from the interruption of the generated pressure in the loading process of the diamond-anvil cell.

First, the electrical resistance was measured and the x-ray diffraction was studied under pressure at room temperature. Next, x-ray-diffraction analysis using a microdiffractometer (Rigaku) and transmission-electron microscopy (TEM) were performed upon the samples recovered from high pressures at ambient and high temperatures. TEM specimens were prepared by crushing the recovered samples in an agate mortar and skimming them on microgrids from an ethanol suspension.

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III. IN SITU RESULTS

A. Electrical resistance at room temperature

The electrical resistance of the natural polycrystalline graphite was measured at room temperature by the multianvil and the Drickamer cell up to 23 and 30 GPa, respectively. The result by the multianvil is shown in Fig. 1, in which the resistance is the value after an elapsed time of 30 min, since each pressure was achieved. Initially the resistance decreased with increasing pressure, then at around 17 GPa, it started to increase. The resistance at 23 GPa increases by a factor of 1.4 after a 12-h passage, which indicates that the transition related to the resistance increase is relatively slow. The pressure (17 GPa) at which the resistance begins to increase is higher than 12 ~ 13 GPa (the values by the revised pressure scale) by Aust and Drickamer[1] and Bundy and Kasper.[2] To clarify the origin of the difference, a similar experiment was performed using the Drickamer cell. In this experiment, the resistance increased at about 13 GPa, indicating that the point where the resistance begins to increase depends on the high-pressure apparatus.

B. X-ray diffraction at room temperature

X-ray-diffraction patterns were obtained under high pressure at room temperature by the multianvil apparatus equipped with an x-ray diffractometer.[14] An energy dispersive system combining a solid-state detector (pure Ge) and a white x-ray from a rotating-anode (W) type generator (Rigaku RU-300) was adopted. A finely crushed polycrystalline sample was packed in a boron-epoxy octahedral cell. Some of the patterns are shown in Fig. 2. The abscissa is the 2θ angle of the Cu $K\alpha$ radiation converted from the x-ray energy for the convenience of the computer program. At 18 GPa a new diffraction line corresponding to $d \simeq 2.04$ Å begins to appear between the two lines of graphite, $g(100)$ and $g(101)$, and its intensity becomes stronger with increasing pressure up to 26 GPa. Although this line seems to be a diffraction line, 002 of h-diamond,[15] only one line is insufficient to identify the structure of the high-pressure phase. The sample recovered to ambient pressure was a single phase of graphite according to the x-ray-diffraction profile.

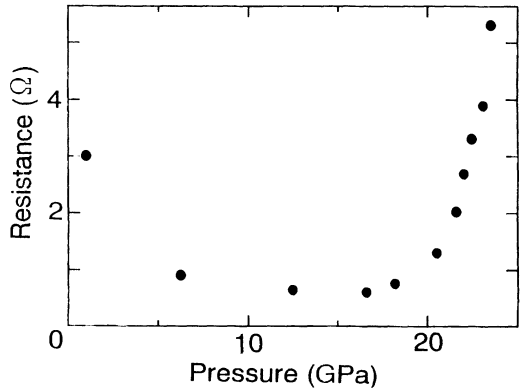

FIG. 1. Electrical resistance change of natural polycrystalline graphite as a function of pressure generated by the 6-8-type multianvil at room temperature.

IV. OBSERVATION OF SAMPLE RECOVERED FROM HIGH PRESSURE

A. Formation of c-diamond at high pressure and high temperature

To identify the unknown x-ray peak at ~2.04 Å appearing at 18 GPa at room temperature, we accelerated the transition by heating. A heater was included in the boron-epoxy octahedral cell for the 6-8-type multianvil. The samples recovered from various high-pressure and high-temperature conditions were examined by the x-ray microdiffractometry and the transmission-electron microscopy.

The x-ray diffraction patterns obtained for the samples heated at 20 GPa are shown together with that of the original graphite in Fig. 3. Although no apparent change is seen in the pattern of 600 °C, the appearance of the peaks belonging to c-diamond, $c(111)$, $c(220)$, and $c(311)$, is confirmed in the patterns of 800 and 1000 °C. At 14 GPa, these diffraction lines of c-diamond were also observed in the patterns from 800 and 1200 °C.

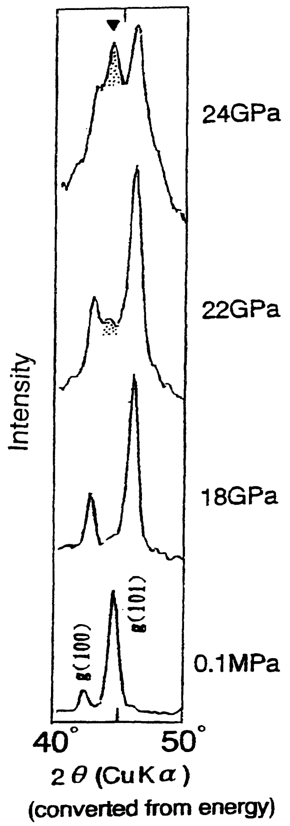

FIG. 2. *In situ* x-ray-diffraction patterns of graphite under high pressure at room temperature. g indicates graphite and ▼ a new peak.

In the patterns indicating the formation of *c*-diamond in Fig. 3, two peaks overlap with $c(111)$ of $d = 2.06$ Å at both sides. The peak at the low-angle side is identified as that of graphite, $g(100)$ of $d = 2.13$ Å. One of the main peaks of *h*-diamond, $h(100)$ of $d = 2.19$ Å,[15] cannot be seen in the 800 and 1000 °C patterns in Fig. 3. However, there remained the slight possibility that some *h*-diamond is formed under the above conditions. Thus, the recovered samples were observed by transmission-electron microscopy (TEM). A TEM image and an electron-diffraction pattern for the sample from 20 GPa and 800 °C are shown in Figs. 4(a) and 4(b), respectively.

The many small particles in Fig. 4(a) are *c*-diamond with average dimensions of 10 ~ 30 nm. The spotty Debye rings in Fig. 4(b) are a mixture of *c*-diamond and graphite. The *h*-diamond was not found by TEM observation in any of the pressurized and heated samples. Another peak at the high-angle side of $c(111)$ in Fig. 3 was identified as $g(101)$ of $d = 2.03$ Å. Although the unknown high-pressure phase appearing at room temperature should increase by heating, new peaks useful to determine its structure were not obtained from the recovered samples.

The *P*-*T* conditions where *c*-diamond was formed in the present experiment are represented by closed circles in Fig. 5, which is the diagram previously presented by Bundy.[16] Dashed area represents the *P*-*T* condition where *h*-diamond was formed by Bundy and Kasper,[2] who heated single crystalline or polycrystalline graphite compressed in the direction of the *c* axis. However, the present results indicated that, instead of *h*-diamond, *c*-diamond is formed in the same area by heating polycrystalline graphite under quasihydrostatic pressures. The previous two results indicating the formation of *c*-diamond in the neighborhood of the present *P*-*T* conditions are also plotted in Fig. 5; Wentorf[17] used the belt-type apparatus and Higashi[18] used the 6-8-type multianvil. The difference of the formation of *c*-diamond and *h*-diamond may be attributed to the method of compression. Special compression in the direction of the *c* axis seems to be effective for the graphite→*h*-diamond transition.[2,9,10] The temperature, 800 °C, at which *c*-diamond was formed in the present study, is probably the lowest reported for a direct graphite → *c*-diamond transition.

However, Yagi *et al.*[10] reported that x-ray-diffraction lines of *h*-diamond were observed at pressures above 17.5 GPa at room temperature in an experiment using kish graphite as the starting material and the multianvil installed at National Laboratory for High Energy Physics. They also describe that *h*-diamond formed by heating up to 500 °C returned to graphite at ambient conditions, but that heated to 800 °C or higher was quenched. The *c*-diamond was not formed by heating up to 1400 °C under

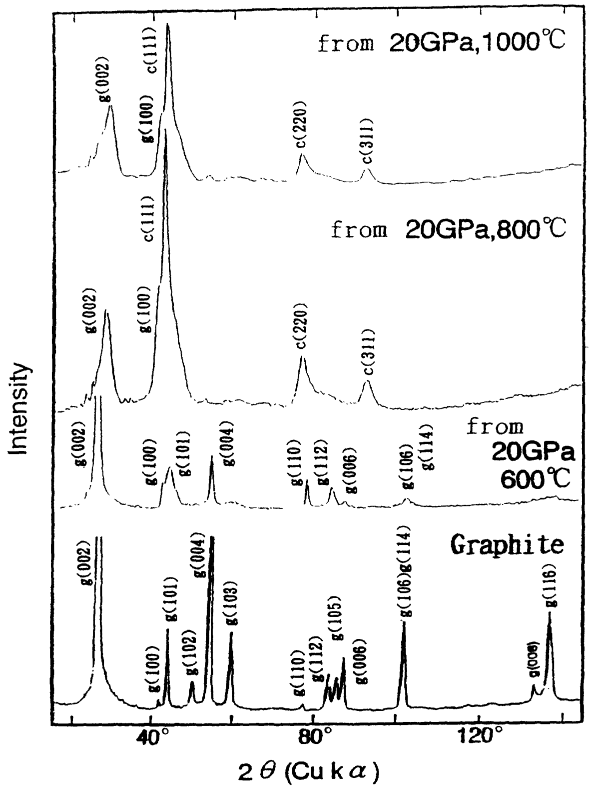

FIG. 3. X-ray-diffraction patterns of the original graphite and of those recovered from high temperatures at 20 GPa. The formation of *c*-diamond is confirmed in the samples from 800 and 1000 °C.

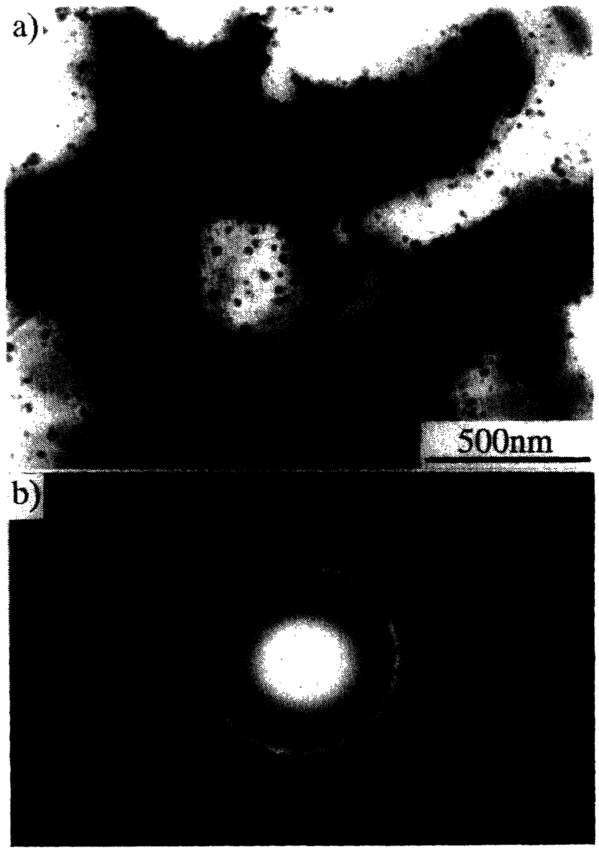

FIG. 4. A transmission-electron micrograph (a) and an electron-diffraction pattern (b), showing the formation of *c*-diamond in a sample recovered from 20 GPa and 800 °C.

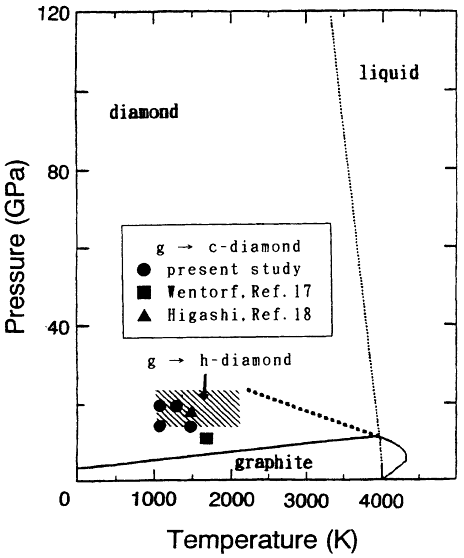

FIG. 5. The diagram of carbon presented by Bundy (Ref. 16). The *P-T* conditions in which *c*-diamond was formed from graphite in the present study is included in the region where *h*-diamond was formed by Bundy and Kasper (Ref. 2). The conditions for *c*-diamond obtained by Wentorf (Ref. 17) and Higashi (Ref. 18) are also shown.

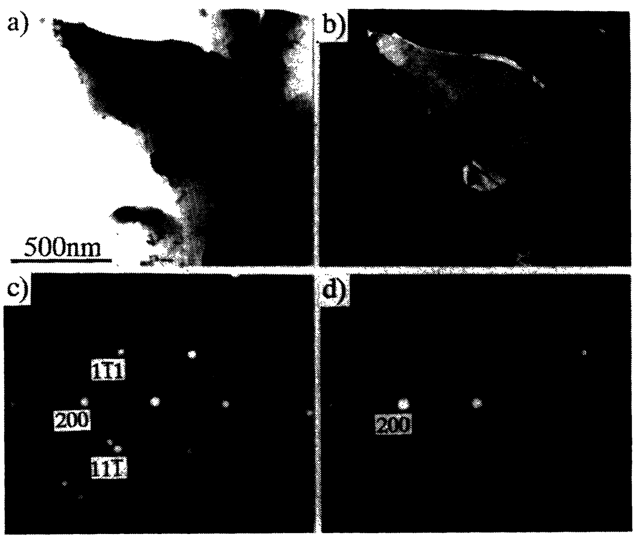

FIG. 6. Formation of *n*-diamond in the sample recovered from 14 GPa and 1200 °C. (a) A TEM micrograph, (b) a dark field electron micrograph taken from the 200 spot of (d), (c) a selected area diffraction pattern of a grain of (a), and (d) an electron-diffraction pattern showing a strong excitation of the 200 reflection after a slight rotation about the [100] axis of (c).

compression up to 18 GPa. Their results are obviously different from those reported here, although their experiment was performed with a multianvil similar to ours. The appearance of *h*-diamond may be ascribed to the fact that the powdered kish graphite had a strong preferred orientation when it was compacted into a cylindrical shape by a piston-cylinder-type jig before their experiment.

B. Formation of "*n*-diamond"

Under TEM, grains identified as neither *c*-diamond nor graphite were found together with a large amount of *c*-diamond in the sample recovered from 14 GPa and 1200 °C. Examples of TEM images and the electron-diffraction pattern of a grain of ~ 1 μm are shown in Figs. 6(a)–6(d). The pattern of Fig. 6(c) is of an fcc structure for the electron beam in the [011] direction, and the *d* values agree with those of *c*-diamond. However, a forbidden spot of *c*-diamond, 200, is clearly observed in Fig. 6(c). When two 111 reflections are simultaneously excited, a double reflection may result in the appearance of a 200 reflection. Thus, the specimen was rotated along the 100 axis not so as to satisfy the diffraction condition of 111 reflections, however, the strong 200 reflection remained as seen in Fig. 6(d). Therefore, it is concluded that the 200 reflection in Fig. 6 is not a multiple reflection, but is real. In addition, another forbidden reflection for *c*-diamond, 222, was confirmed in the same sample.

These characteristics of the electron-diffraction pattern agree with those of the "*n*-diamond" named to a new carbon phase by Hirai and Kondo,[19] who quenched it from 65 GPa and 3700 K by shock-wave compression accompanied by rapid cooling. They considered that *n*-diamond may be transformed martensitically from graphite and may be a metastable intermediate phase appearing before the transition to *c*-diamond. They also suggested the structure and the chemical bonds based upon various models.[20] A similar phase has been synthesized by chemical vapor deposition and physical vapor deposition methods.[21,22] However, the present study is a synthesis

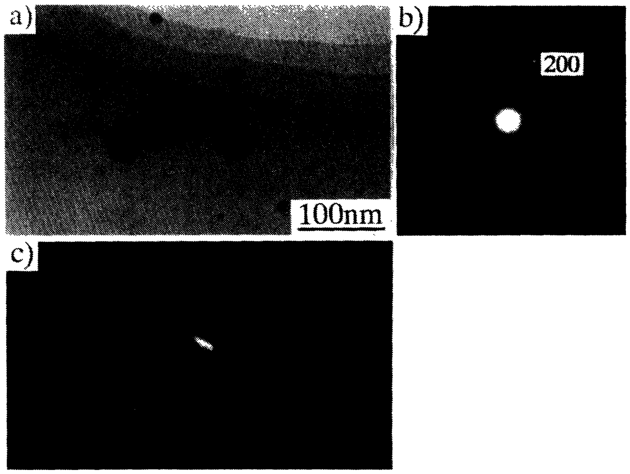

FIG. 7. TEM micrographs and an electron-diffraction pattern showing the formation of *n*-diamond in the sample recovered from 40 GPa at room temperature. (a) A TEM image, (b) an electron-diffraction pattern of (a) showing a sharp 200 spot of *n*-diamond, and (c) a dark field image taken from the 200 spot of (b).

TABLE I. Electron-diffraction data of n-diamond formed by the present static compression and the shock compression. Intensities are classified as strong (s), medium (m), or weak (w).

Reflection	Static compression 14 GPA 1200 °C		40 GPa 25 °C		Shock compression^a 65 GPa 3700 K	
hkl	d (Å)	I	d (Å)	I	d (Å)	I
111	2.06	s	2.06	s	2.06	s
200^b	1.789	s	1.80	s	1.78	s
220	1.274	s	1.261	s	1.26	$s \sim m$
311	1.073	m	1.064	m	1.07	$s \sim m$
222^b	1.040	w	1.029	w	1.04	$m \sim w$
400	0.902	w	0.890	w	0.898	w
331	0.822	w	0.820	w	0.818	w
420^b					0.796	m

^{a}Reference 19.

^{b}Reflection forbidden for c-diamond ($Fd3m$).

of n-diamond by static compression of graphite. While the grain size of the n-diamond formed by Hirai and Kondo was $\sim 0.1\ \mu$m, ours was in the order of 1 μm, which gives the diffraction pattern with clear spots as shown in Figs. 6(c) and 6(d). However, the amount of n-diamond in the sample recovered from 14 GPa and 1200 °C is very small as shown in the x-ray-diffraction patterns of Fig. 3, where the diffraction line of n-diamond, 200, is not apparent.

Furthermore, another result was obtained by using the Drickamer cell. The n-diamond grains of $0.05 \sim 0.1\ \mu$m were recovered from 40 GPa and room temperature. Figures 7(a)–7(c) are the TEM images and the electron-diffraction pattern of a polygonal grain smaller than $\sim 0.1\ \mu$m. The diffraction data of the n-diamond formed under our condition of static compression are listed in Table I, together with those of the shock-wave experiment by Hirai and Kondo.[19] Thus, we showed that n-diamond is formed by static compression of graphite even at room temperature.

The n-diamond, however, may not be the main phase appearing under high pressure at room temperature, because n-diamond is quenchable to ambient conditions and the amount formed by static compression is too small.

V. CONCLUSION

Natural polycrystalline graphite was compressed using a multianvil and a Drickamer cell, and the following results were obtained.

(i) The so-called hexagonal diamond was not found in all the samples recovered from high pressures and temperatures.

(ii) Instead, diamond was formed in the P-T region of $14 \sim 20$ GPa and $800 \sim 1200$ °C, which almost agrees with that for the graphite→hexagonal diamond transition previously reported by Bundy and Kasper.[2]

(iii) 800 °C is probably the lowest temperature among those hitherto reported for a direct graphite → diamond transition.

(iv) n-diamond is formed under conditions of 40 GPa, room temperature, and 14 GPa, 1200 °C. We report the formation of n-diamond from the static compression of graphite.

(v) The attempt to confirm the structure of the high-pressure phase that appeared at room temperature, was unsuccessful.

ACKNOWLEDGMENTS

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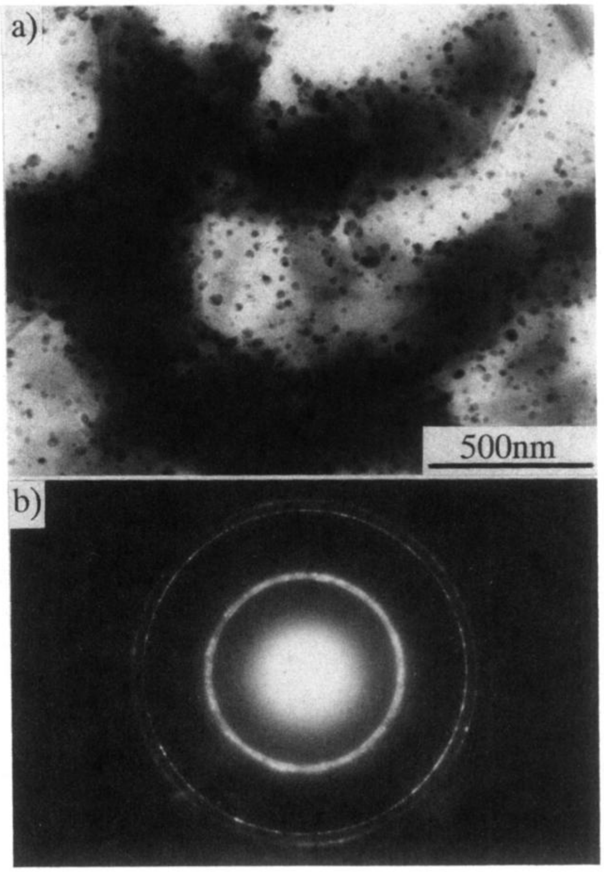


FIG. 4. A transmission-electron micrograph (a) and an electron-diffraction pattern (b), showing the formation of *c*-diamond in a sample recovered from 20 GPa and 800 °C.

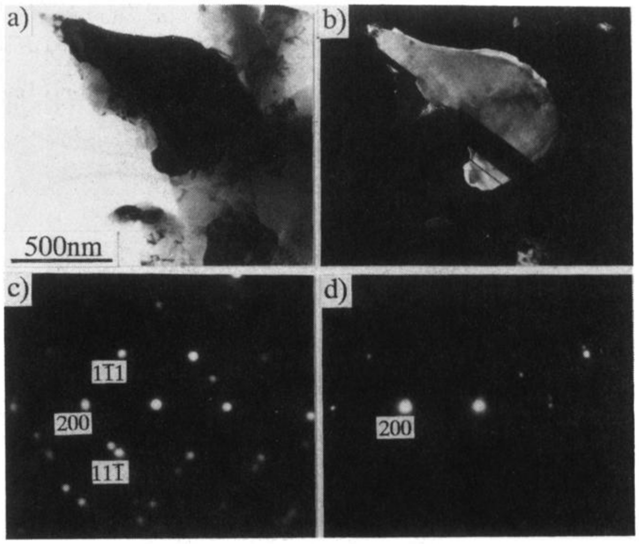
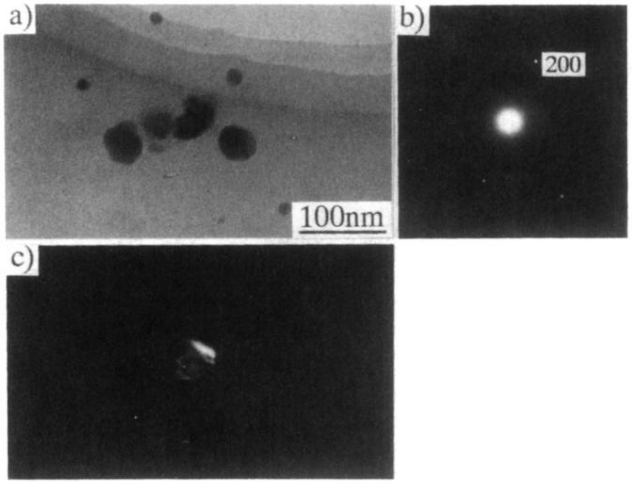


FIG. 6. Formation of *n*-diamond in the sample recovered from 14 GPa and 1200 °C. (a) A TEM micrograph, (b) a dark field electron micrograph taken from the 200 spot of (d), (c) a selected area diffraction pattern of a grain of (a), and (d) an electron-diffraction pattern showing a strong excitation of the 200 reflection after a slight rotation about the [100] axis of (c).



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