AIP Applied Physics Letters

# Effect of nonhydrostaticity on the pressure induced phase transformation of rhombohedral boron nitride

T. Taniguchi, T. Sato, W. Utsumi, T. Kikegawa, and O. Shimomura

Citation: Applied Physics Letters **70**, 2392 (1997); doi: 10.1063/1.118882
View online: http://dx.doi.org/10.1063/1.118882
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/70/18?ver=pdfcov
Published by the AIP Publishing

---

---

# Effect of nonhydrostaticity on the pressure induced phase transformation of rhombohedral boron nitride

T. Taniguchi[a] and T. Sato
*National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan*

W. Utsumi
*Department of Synchrotron Radiation Facilities Project, Kansai Research Establishment, Japan Atomic Energy Research Institute, Spring-8 Kamigori, Hyogo 678-12, Japan*

T. Kikegawa and O. Shimomura
*Photon Factory, National Institute for High Energy Physics, Ooho, Tsukuba, Ibaraki 306, Japan*

(Received 27 January 1997; accepted for publication 7 March 1997)

An *in situ* x-ray diffraction study of room-temperature compression of rhombohedral boron nitride (rBN) was performed up to 10 GPa. Although no phase transformation of rBN was observed in a liquid pressure transmitting medium, the structure of rBN changed to become disordered within the layered stacking sequence at less than 1 GPa with the solid-state pressure transmitting medium. Further transformation to the wurtzite structure (wBN) was observed at 6 GPa and was unquenchable upon the release of pressure at room temperature. The orientation relationship of the phase transformation of rBN to wBN was compared with that of hexagonal BN to wBN. © *1997 American Institute of Physics.* [S0003-6951(97)03118-5]

Pressure induced phase transformations of low-pressure polymorphs of boron nitride (BN) and carbon have been the subject of study for many years.[1–5] It was expected, in particular, that two types of stacking sequences of a hexagonal network with twofold and threefold structures may transform into different dense modifications of wurtzite and zincblende structures, respectively. At room temperature and high pressure (HP), hexagonal boron nitride (hereafter denoted as hBN) and graphite, with a twofold layered structure, are known to transform to wurtzite type BN (hereafter denoted as wBN)[1,2] and hexagonal diamond (hereafter denoted as h-diamond),[3–5] respectively.

In the case of the threefold layered structure of the rhombohedral form, although a significant amount of rhombohedral graphite has not yet been obtained for detailed study, rhombohedral BN (hereafter denoted as rBN) has been synthesized by several methods.[6–11] According to the previous studies, rBN included in pyrolytic BN transformed to wBN at HP and high temperature (HT) using a solid-state pressure transmitting medium (hereafter denoted as PTM).[8,10–12] In order to explain the phase transformation from rBN to wBN, the buckling mechanism of the basal plane, which was proposed to explain graphite/h-diamond transformation was introduced.[3,4,11] Graphite was known to transform to h-diamond at HP and room temperature and was unquenchable upon the release of pressure.[3,4] On the contrary, the phase transformation to wBN from rBN was not shown at room-temperature compression using the liquid phase PTM.[9] It can be seen that the nature of the pressure involving shear stress should play an important role for the diffusionless shear mechanism in the idea of the buckling mechanism for rBN. In the previous studies, however, attention was not adequately paid to the state of PTM, which may significantly affect the nature of the pressure.

In this letter we will report on an *in situ* x-ray diffraction study for pressure induced phase transformation of pure rBN synthesized by the chemical reaction of sodium tetrahydroborate ($NaBH_4$) and ammonium chloride ($NH_4Cl$).[6] In this study, two types of PTM, liquid and solid phases, were used to make clear the effect of nonhydrostaticity on phase transformation behavior. The phase transformation feature of rBN was also compared with that of hBN under static HP up to 12 GPa.

High-pressure *in situ* x-ray diffraction with the energy dispersive method was performed using a cubic anvil-type HP apparatus[13] at the Photon Factory in the National Institute for High Energy Physics. The sample was typically embedded in a 6 mm face-cube-shaped gasket made of a mixture of boron and epoxy resin (4:1 in weight ratio), which was squeezed isotropically by six anvils with a truncation of 4 mm. Two samples were compressed by different PTM in each experiment. At one side, the rBN sample was directly embedded into the boron–epoxy 4:1 gasket as a solid-state PTM, while the other sample was embedded in a Teflon capsule with a mixture of methanol and ethanol of a 4:1 volume ratio as a liquid phase PTM at the other side. Between the samples, sodium chloride (NaCl) was embedded as a pressure marker, which was surrounded by the boron–epoxy gasket. Furthermore, in order to make clear the difference of the compression behavior between rBN and hBN, the hBN sample (DENKA Co., type GP) was also studied in the same way as the rBN sample using a solid-state PTM.

Figure 1 shows the x-ray diffraction profiles of rBN at ambient pressure and under static HP with the liquid phase PTM. No phase transformation has been observed up to 7.2 GPa, and the sample after releasing the pressure was quite similar to that of the starting condition, as shown in Fig. 1. The relative lattice parameters $a/a_0$ and $c/c_0$ of rBN were evaluated as a function of pressure. The compression of the $a$ axis was the intermediate between the reported value for hBN[14] and rBN.[15] Applying the pressure–volume relationship into the first-order Murnaghan equation of state, the isothermal bulk modulus and its first pressure derivative for

---

[a] Electronic mail: taniguch@nirim.go.jp

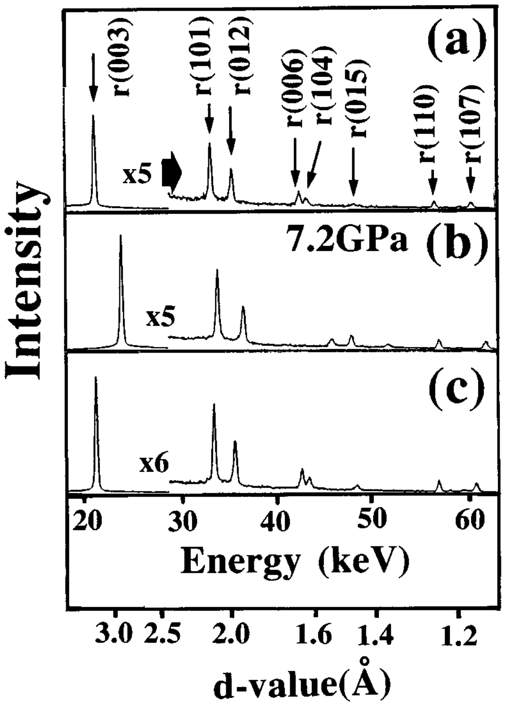

FIG. 1. X-ray diffraction profiles of rBN at ambient pressure and under static HP by using liquid phase PTM at room temperature. 2$\theta$:10°. (a) Starting condition, (b) 7.2 GPa, and (c) release of the pressure to ambient pressure.

the rBN sample at 298 K were calculated as 38.2±0.5 GPa and 5.4±0.2, respectively.

Figure 2 shows the variation of the x-ray diffraction profiles of rBN under static HP up to 9.5 GPa with a solid-state PTM. Comparing to the compression behavior using a liquid phase PTM, as shown Fig. 1, a significant difference was the degradation of peaks particularly shown in those of rBN(101) and rBN(012) at a pressure range of less than 1 GPa [see Fig. 2(b)]. The half-width of the diffraction peak of rBN(003) became approximately two times larger during the compression while that in the liquid phase PTM was not changed. Those may be attributed to the disorder of layered stacking sequence of the rBN structure due to the compression with the solid-state PTM. At 6 GPa, a new peak, which can be assigned wBN(100) appeared [Fig. 2(d)]. The formation of wBN was clearly seen at 9.5 GPa [Fig. 2(f)], but was unquenchable upon the release of pressure. At atmospheric pressure, the recovered rBN sample showed the broadened peaks of rBN(101) and rBN(012) [Fig. 2(i)], which was similar to the profile observed at 5 GPa [Fig. 2(c)]. The wBN formed at 9.5 GPa showed the strong peak denoted as wBN(100) [Fig. 2(f)], implying that the appeared wBN phase had an oriented feature of the *a* axis and was parallel to the *c* axis of rBN, which was preferentially oriented at the starting condition.

Figure 3 shows the variation of the x-ray diffraction profiles of hBN under static HP up to 12 GPa with solid-state PTM. At 10 GPa, hBN began to transform to wBN as has been previously studied[1,2,13] [Fig. 3(c)]. The wBN formed from hBN was quenchable and coexisted with residual hBN at ambient pressure, as shown in Fig. 3(g). It is noticed that the wBN transformed from hBN showed a strong peak of wBN(002), implying that the *c* axis of wBN transformed from hBN was parallel to the *c* axis of hBN, which was also preferentially oriented at the starting condition. This orientation relationship of the phase transformation of hBN to wBN was explained with the martensitic transformation mechanism via puckering of the basal plane along the *c* axis.

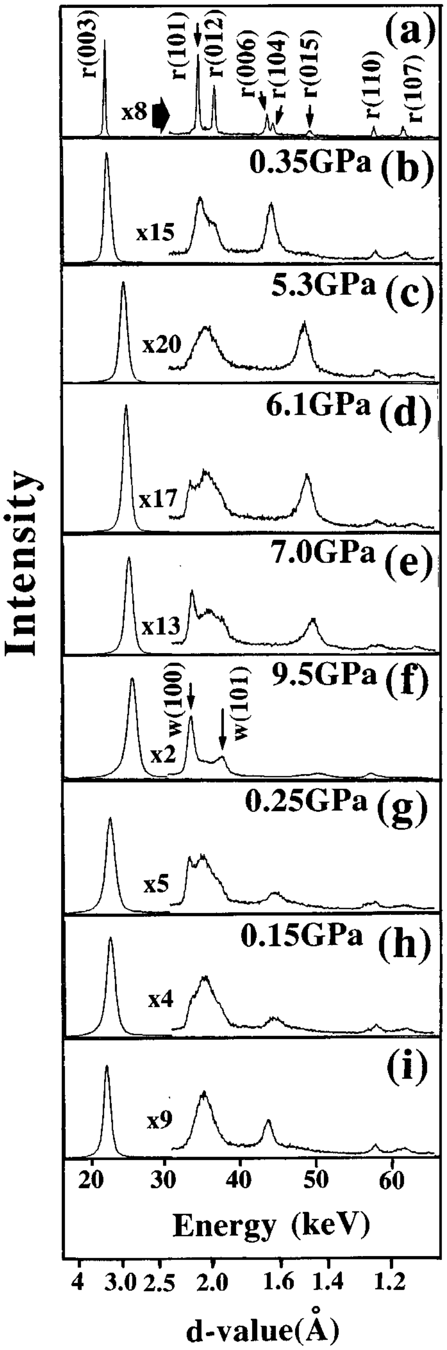

FIG. 2. The variation of the x-ray diffraction profiles of rBN with pressure by using solid-state PTM at room temperature. 2$\theta$:10°. (a) Starting condition, (b) 0.35 GPa, (c) 5.3 GPa, (d) 6.1 GPa, (e) 7.0 GPa, (f) 9.5 GPa, (g) release of the pressure to 0.25 GPa, (h) 0.15 GPa, and (i) ambient pressure.

On the other hand, in the phase transformation to h-diamond from graphite, the *a* axis of the h-diamond becomes parallel to the *c* axis of graphite via buckling the hexagon of the basal plane.[3,4] This orientation relationship is quite similar to that of rBN to wBN with the solid-state PTM

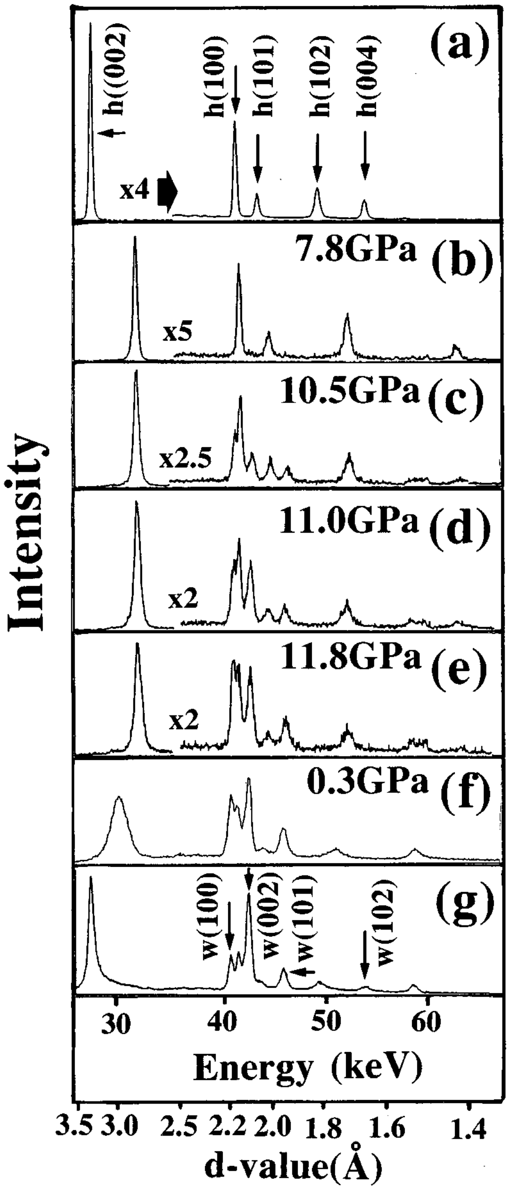

FIG. 3. The variation of x-ray diffraction profiles of hBN with pressure by using solid-state PTM at room temperature. $2\theta$:8°. (a) Starting condition, (b) 7.8 GPa, (c) 10.5 GPa, (d) 11.0 GPa, (e) 11.8 GPa, (f) release of the pressure to 0.3 GPa, and (g) ambient pressure.

as described above. In this study, the stacking sequence of the rBN structure was found to have changed to give broader peaks of rBN(101) and rBN(012) by the shear stress, while it did not change under hydrostatic pressure. The microstructural analysis with high-resolution transmission electron microscopy gave evidence of the formation of a 2H layered structure in the recovered rBN compressed up to 8 GPa at room temperature.[16] This fact may introduce the existence of the *A*-*B*-*A*-*B* stacking sequence similar to graphite, implying that the formation of wBN from rBN resulted from a similar transformation feature of graphite/h-diamond, as suggested by the previous study.[11]

Comparing the stacking order of hexagons in rBN with those of graphite and hBN, centers of hexagons in the basal planes of rBN and graphite are ordered to overlap with up and downward atoms, while the hexagon of hBN is ordered to overlap with the adjacent hexagon completely by each layer with rotation by 60° in the plane. Therefore, the idea of the similarity of the phase transformation mechanism between rBN/wBN and graphite/h-diamond might be acceptable in view of the structural similarity of rBN and graphite. To achieve such phase transformation in rBN, however, shear stress may play an important role in changing the rBN structure to the 2H type similar to graphite.

It should be noticed that wBN transformed from rBN was unquenchable, while wBN transformed from hBN was quenchable upon the release of pressure at room temperature. This result implies that the wBN formed from a different orientation relationship under HP results in the forms having different phase stability upon the release of pressure. Although the structural instability of wBN transformed from rBN has been studied with respect to thermal stability,[12] further investigation for the structural stability of wBN transformed from rBN is important for future work involving more detailed assessment of the effect of shear stress on the structure change. When the phase transformation mechanism of rBN to wBN is similar to that of graphite to h-diamond, it can be seen that the well-known difference of the phase stability of h-diamond and wBN, which transformed from hBN, may be attributed to the difference of the orientation relationship under phase transformation from low pressure phases.

The authors would like to thank Dr. K. Kusaba of Tohoku University for his help in the HP experiments. Dr. S. Yamaoka of NIRIM and Dr. D. Dobson of the University College of London are also acknowledged for their useful comments and critical readings of the manuscript.

[1] F. R. Corrigan and F. P. Bundy, J. Chem. Phys. **63**, 3812 (1975).
[2] F. P. Bundy and R. H. Wentorf, Jr., J. Chem. Phys. **38**, 1144 (1963).
[3] F. P. Bundy and J. S. Kasper, J. Chem. Phys. **46**, 3437 (1967).
[4] T. Yagi, W. Utsumi, M. Yamakata, T. Kikegawa, and O. Shimomura, Phys. Rev. B **46**, 6031 (1992).
[5] K. Lonsdale and H. J. Milledge, Miner. Mag. **32**, 185 (1959).
[6] T. Sato, Proc. Jpn. Acad. **61**, 459 (1985).
[7] T. Sato, T. Ishii, and N. Setaka, J. Am. Ceram. Soc. **65**, 162 (1982).
[8] A. Onodera, K. Inoue, H. Yoshihara, H. Nakane, T. Matsuda, and T. Hirai, J. Mater. Sci. **25**, 4279 (1990).
[9] M. Ueno, K. Hasegawa, R. Oshima, A. Onodera, O. Shimomura, T. Kikegawa, H. Nakae, T. Matsuda, and T. Hirai, Phys. Rev. B **45**, 10 226 (1992).
[10] V. F. Britun, A. V. Kurdyumov, and I. A. Petrusha, J. Mater. Sci. **28**, 6575 (1993).
[11] A. V. Kurdyumov, V. F. Britun, and I. A. Petrusha, Diam. Relat. Mater. **5**, 1229 (1996).
[12] V. L. Solochenko, I. A. Petrusha, and A. A. Svirid, High Press. Res. **12**, 347 (1994).
[13] O. Shimomura, W. Utsumi, T. Taniguchi, T. Kikegawa, and T. Nagashima, in *High-Pressure Research in Mineral Physics: Application to Earth and Planetary Sciences*, edited by Y. Shono and M. H. Manghnani (TERRAPUB, Tokyo, 1992), p. 3.
[14] V. L. Solochenko, G. Will, and F. Elf, Solid State Commun. **96**, 1 (1995).
[15] V. L. Solochenko, G. Will, H. Hupen, and F. Elf, Solid State Commun. **90**, 65 (1994).
[16] L. L. He, S. Horiuchi, T. Taniguchi, and T. Sato (unpublished).