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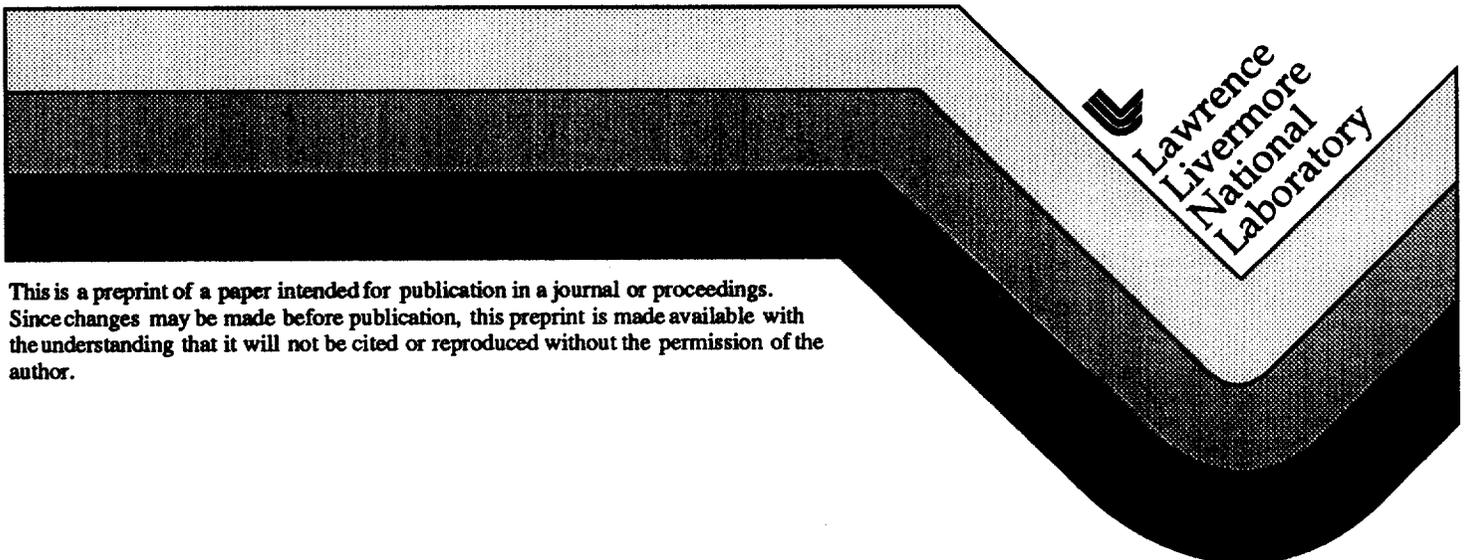
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M. Nicol
C.-S. Yoo
J. Akella
H. Cynn

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Boron Nitrides Synthesized Directly from the Elements
at High Pressures and Temperatures

Malcolm Nicol

Department of Chemistry and Biochemistry, University of California,
Los Angeles, CA 90095-1569 USA and
Ceramic Material and Structures Laboratory, Tokyo Institute of Technology,
Nagatsuta, Midori, Yokohama 226, Japan

Choong-Shik Yoo, Jagannath Akella, and Hyunchoe Cynn
Lawrence Livermore National Laboratory, University of California,
Livermore, CA 94551, USA

ABSTRACT

We use angle-resolved synchrotron x-ray diffraction, laser sample heating, and diamond-anvil cells to follow *in-situ* chemical reactions directly between elemental boron and nitrogen. The structures of the solid reaction products vary with pressure. Below 10 GPa, hexagonal BN is the product; cubic or wurzite BN form at higher pressures. Under nitrogen-rich conditions, another hexagonal allotrope occurs which seems to be a new highly transparent, low density h'-BN. No direct reactions occur at ambient temperature even at pressures as high as 50 GPa, implying that a large activation barrier limits the kinetics of these exothermic processes. Laser heating overcomes the large kinetic activation barrier and initiates spontaneous, self-sustaining exothermic reactions even at moderate pressures.

Many important materials composed of the elements, boron, carbon, nitrogen, oxygen, aluminum, and silicon are hard and have covalently-bonded three-dimensional structures. Examples include diamond and cubic boron nitride, c-BN. The networks of these materials contrast with softer molecular forms of the same elements like graphite, N₂ and O₂. Although they have strong intramolecular covalent bonds, only weak van der Waals attractions operate between molecules. Localizing electrons in molecular covalent bonds minimizes their potential energy, makes the bonds extremely stable, and acts as a barrier to reactions leading to network structures. Applying pressure raises the kinetic energies of the electrons by $\rho^{2/3}$, where ρ is the density. This is faster than the potential energy increases; it grows as $\rho^{1/3}$. High pressures are, therefore, inimical to local covalent bonds. At high densities, electrons eventually delocalize, converting molecular solids to more closely packed network structures and eventually to metals.

Many experiments support these ideas. Most unsaturated organic molecules polymerize at pressures of the order of 10 GPa.¹ Layered covalent solids like graphite and h-BN transform at high pressures to dense, three-dimensional network materials, diamond and c-BN.² The proposed superhard material,³ β -C₃N₄, also may have a covalently bonded network structure. Many diatomic molecules, halogen, and inert gases even metallize at the pressures of 100 GPa.^{4, 5} However, large activation barriers often limit the rates of achieving these stable high pressure products. Synthetic diamond grows only at substantially higher than the equilibrium transition temperature⁶ or under kinetic control.

The standard enthalpies of formation in Table I show the stabilities of some first- and second-row oxides, nitrides, and carbides. Even the boron-nitrogen reaction leading to h-BN is very exothermic. In contrast, formation of many hydrides or a theoretical nitrogen polymer⁷ consume energy. Despite the thermodynamic stability of the product, boron and nitrogen do not react with each other at ambient temperature even at 50 GPa, the highest pressure of our

experiments. Most syntheses of these materials follow more complex routes.

We recently combined diamond-anvil cells, laser-heating, and synchrotron x-ray diffraction to overcome activation barriers for synthesis at high pressures⁸ and to follow the processes *in-situ*. Here, we discuss using these methods for the direct reactions of nitrogen with boron yielding three forms of boron nitride: c-BN, h-BN, and what we believe is a new hexagonal form, h'-BN. We do the synthesis-diffraction experiments at the UC-National Laboratories PRT beamline at SSRL using a modified Merrill-Bassett high pressure cell.⁹

For the diffraction work, we isolate the 20-KeV output from the wiggler with a Si(220) double-crystal monochromator and focus it through a slot in a maraging steel seat behind one diamond. The focus intersects the sample at the focus of the laser-heating system. The steel restricts transmission of unwanted x-rays while the slot allows easy optical and x-ray access to the sample. A 30- μm radius Pt pinhole placed about 5 cm before the sample restricts the size of the incident x-ray beam. However, the x-ray beam is larger than the hot spot, whose radius is 15-to-25 μm depending upon the temperature. Thus, x-rays sample the full range of temperatures which can be very large. A Be seat backed the other diamond anvil. The low x-ray absorption of the Be allows us to collect angle-resolved diffraction patterns around the entire ϕ cone to quit high 2θ 's using image plates. With a 20-by-40 cm image plate 20 cm from the sample, we collect features to 2θ of 26° along all directions on the plate and up to 45° along the long dimension. We read the images with a Fuji BAS2000 scanner at 100 μm resolution.

The samples consist of boron powder prepressed between diamond anvils and a few pieces of ruby dust for pressure measurement. We place these solids in a 150- μm diameter hole in a spring steel or rhenium gasket and add nitrogen as a liquid by immersion. We heat the samples with a cw Nd:YAG laser microfocussed along an axis about 30 degrees from the normal to the diamond culets and collect the thermal emission with a chromatically corrected, Leitz 20x

objective along an axis about 15 degrees from the normal (and 45 degrees from the laser axis). With a 75- μm diameter pinhole, we limit the field of view of the collection optics to the central 4 μm of the heated area. A single-core 200- μm diameter fiber couples the thermal emission to a spectrometer with a cooled CCD detector. Temperatures were determined by fitting the thermal emission spectrum to a gray-body expression. However, these are only upper limits for the hottest spot of the sample and should not be overinterpreted. The x-ray beam samples a wider range of temperatures. Transient temperature excursions during the rapid stages of these very exothermic reactions also make precise temperature measurements even less realistic.

The reactions go in several stages: (1) Before heating, the boron is opaque in the nearly transparent nitrogen. (2) Boron strongly absorbs infrared radiation so by slowly adjusting the power of the Nd:YAG 1.06- μm output, we can change its temperature in small steps. Above about 1300 K, thermal emission makes evident the hot areas of the sample. As long as the highest temperature is limited, however, the sample does not change appearance. It remains dark when the laser power is reduced or turned off. (3) Above a threshold laser power and temperature, the intensity of the thermal emission suddenly increases as evident by bright flashes of nearly white light as the sample burns. For boron and nitrogen, this threshold is approximately 1800 K. The peak temperatures during reaction were not measured. (4) After combustion, the intensity of the emission drops rapidly; and the sample loses luminosity even for higher laser powers because very transparent products form. These were recovered at ambient temperature and pressure. We collected angle-resolved x-ray diffraction patterns at steps (1), (2), and (4); that is, before, during, and after reaction. We also collected patterns of quenched samples were collected at the National Synchrotron Light Source by energy dispersive methods.¹⁰

A typical diffraction pattern before heating consists of diffuse features with d- spacings of about 0.2 and 0.3 nm from amorphous boron and/or fluid nitrogen and, occasionally, diffraction

rings from the gasket. During heating above the threshold temperature, the diffuse features weaken or disappear; and new sharp diffraction rings arise. The new rings remain after combustion, clearly showing that the sample changes irreversibly. The transparency of the quenched product also shows that a chemical reaction occurs at high temperatures.

For lower pressure reactions, the new rings are readily indexed in terms of hexagonal h-BN. Table II shows the indexing for the pattern of sample recovered after heating at 6 GPa to ignition at approximately 2100 K. The density and lattice parameters are nearly identical to literature values.¹¹ The sharpness and relative intensities of the rings imply that the h-BN is highly crystalline, unlike the distorted h-BN or turbostratic t-BN produced by other chemical methods.^{12,13} All the h-BN synthesized here was of similarly high crystallinity. Thus, direct high-pressure processing may be a way to make highly pure, single phase h-BN and to control its crystallinity.

The crystal structure of final BN products changes with pressure. Above 10 GPa, the direct reaction yields cubic, c-BN. Table II summarizes the indexing of the diffraction pattern of the BN at 14.6 GPa and ambient temperature after quenching from about 2300 K. The major features of this pattern and the computed density of c-BN is 3.596 g/cm³ are within 0.5% of the measured equation of state of c-BN at 14.6 GPa, 3.614 g/cm³.¹⁴ We attribute the difference to distortions introduced during quenching. The lattice parameter of δ -N₂, $a=569.2$ pm also is consistent with literature values extrapolated to the same pressure, 569.9 nm.¹⁵ Other weak peaks at 223, 198 and 114 pm probably arise from the (100), (101), and (200) reflections of w-BN,¹⁶ although the spring steel gasket may also contribute to these peaks. Weak diffused features at 223 and 188 pm have not been indexed. A complete report of these patterns will be published elsewhere.¹⁷

The composition of the charge seems to influence the crystal structure of the final products. Fig. 1 shows energy-dispersive x-ray diffraction patterns of a N₂-rich mixtures at 15 GPa after quenching from 1800 K (upper trace) and at 2 GPa after quenching from 1300 K (lower trace).

The 25.84, 29.96, and 42.32-KeV features in the upper trace closely match the expected positions of the (111), (200), and (220) lines of c-BN. The bands at 24.76, 25.89, and 27.80 KeV match the (100), (002) and (101) patterns of w-BN.¹ Weak features at 18.60, 21.11 and 22.99 keV in the upper trace can be indexed as the strong (200), (210), and (211) reflections of δ -N₂.¹⁵

We index seven other features as parts of the pattern of a hexagonal structure, probably a boron nitride. We designate this as h'-BN to distinguish it from the familiar h-BN. Features attributed to h'-BN also appear in patterns of products made at lower pressures like that in the lower trace. The unit cell volume of h'-BN is much larger than that of h-BN; see Table I.

h'-BN seems to result only from N₂-rich charges. When large amounts of boron powder are used, the reaction typically produces either nearly pure h-BN at low pressures or c-BN above 10 GPa. h'-BN is highly transparent and can be recovered as white polycrystals at ambient pressure. Scanning electron micrographs of recovered h'-BN and h-BN show that both products have plate-like structures, typical of layered hexagonal materials. However, h'-BN has many microholes that may be the escaped routes for excess nitrogen in the sample or captured in the BN lattice. We have not seen h'-BN convert to other forms of boron nitride at ambient condition, although it appears unstable when exposed to high power lasers. h'-BN probably is a nitrogen-rich metastable B_xN_y. Its low density and morphology support this interpretation. Further studies are needed to learn its crystal structure, stoichiometry, and stability.

Thus, we find that thermodynamic stability at the synthesis pressure dictates the structure of the BN product. Samples with comparable initial amounts of boron and nitrogen yield only h-BN below 7.5 GPa. c-BN is the product above 10 GPa. This is consistent with the reported stability fields.⁶ We found no diffraction lines of the low-pressure rhombohedral (r-BN) or h-BN at high pressures, nor c- or w-BN at low pressures. These observations are consistent with the hypothesis that the reaction between elemental boron and nitrogen leading to c-BN at high

pressures does not go through an h-BN intermediate. Instead, c-BN forms directly from the reacting elements. c-BN has typically been synthesized from h-BN at high P,T conditions.^{6, 18} We believe that this is the first direct synthesis of c-BN from its elements.

In summary, we have found a new synthetic route for c-BN and h-BN, directly reacting the elements at high pressures and temperatures. Similar reactions can be used to synthesize other technologically important materials made of first and second row elements.¹⁹ Furthermore, since the crystal structures of direct reaction products depend largely on pressure, it may be feasible to engineer the final product based on its thermodynamic stability at various pressure-temperature conditions.

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FIGURE CAPTION

Fig. 1. Energy-dispersive x-ray diffraction patterns of the BN reaction products in nitrogen-rich conditions at 15 GPa quenched from 1800 K (upper pattern) and at 2 GPa quenched from 1300 K (lower pattern). The data were obtained at $E_d = 5.4754$ KeV nm.

Table I. Standard enthalpies of formation of some oxides, nitrides, carbides, and hydrides for comparison.*

Compound	$\Delta H^\circ_{f, 298} / (\text{KJ/FW})$	Compound	$\Delta H^\circ_{f, 298} / (\text{KJ/FW})$
B_2O_3	-1253.28 ^a	TiC	-184.11 ^a
TiO_2 (rutile)	- 994.79 ^a	SiC	- 77.22 ^a
SiO_2 (quartz)	- 910.90 ^a	$\text{CH}_4(\text{g})$	- 74.5 ^a
Si_3N_4	- 744.77 ^a	B_4C	- 71.3 ^b
C_3N_4	- 666.5 ^b	$\text{B}_{(\text{s})}, \text{C}_{\text{gr}}, \text{N}_{2(\text{g})}$	0
$\text{CO}_2(\text{g})$	- 393.5 ^a	$\text{O}_{2(\text{g})}, \text{Si}_{(\text{s})}$	0
TiN	- 337.67 ^a	C_{dia}	~ 1
BN	- 250.92 ^a	$\text{B}_2\text{H}_6(\text{g})$	+36 ^a
H_2O (Ice I)	- 242.74 ^a	Poly- N_2	313.8 ^c

^a NIST Chemistry NetBook, NIST Standard Reference Database Number 69,

<http://webbook.nist.gov/chemistry/> (accessed October 30, 1996).

^b *Handbook of Chemistry and Physics*, D.R. Lide, Jr., ed. (CRC Press, Boca Raton, Florida, 1996).

^c C. Mailhot, L. H. Yang, and A. K. McMahan, *Phys.Rev. B* 46, 14419 (1992).

Table II. X-ray diffraction patterns of h-BN and h'-BN at ambient condition of material synthesized by direct reactions of elemental boron and nitrogen initiated at the indicated high pressures and temperatures.

h-BN quenched from 2100 K, 6.0 GPa				h' -BN quenched from 1300 K, 2.0 GPa			
(hkl)	d_{cal}/pm	d_{obs}/pm	$\Delta d/\text{pm}$	(hkl)	d_{cal}/pm	d_{obs}/pm	$\Delta d/\text{pm}$
002	334.2	334.1	0.1	100	285.4	285.4	0.0
100	218.6	218.6	0.0	002	252.9	252.7	0.2
102	183.0	183.0	0.0	102	189.2	189.2	0.0
004	167.1	167.2	0.1	110	164.7	164.3	0.4
104	132.8	133.2	0.4	200	142.6	142.8	0.2
110	126.2	126.3	0.1	112	138.0	138.5	0.5
112	118.1	117.9	0.2	201	124.2	124.2	0.0
114	100.7	104	115.7	115.7	0.0

a =

b =	252.4±2.0 pm	c = 668.4±2.0 pm	a = b = 329.5± 2.0 pm	c = 505.5±2.0 pm
	250.4 pm [°]	666.1 pm [°]		
c/a =	2.648		c/a =	1.534
	2.660 [°]			
$\nabla/(\text{BN}) =$	$9.22 \times 10^{-30} \text{ m}^3$		$\nabla/(\text{BN}) =$	$11.89 \times 10^{-30} \text{ m}^3$

[°] After R.S. Pease, Acta Cryst. 5, 356 (1952).

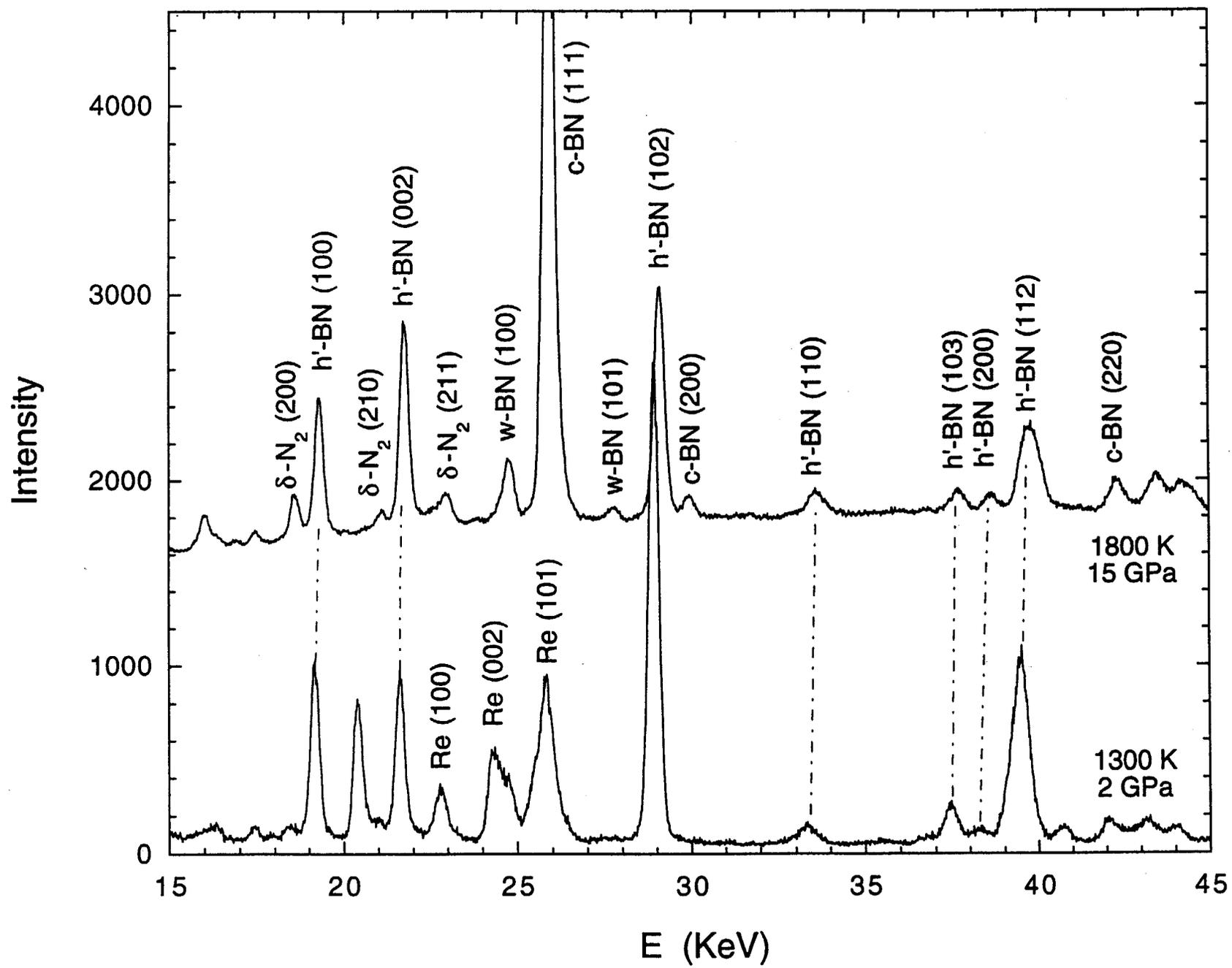
Table III. The crystal structure of c-BN synthesized directly from its elements at 14.6 GPa and about 2300 K. The diffraction pattern was obtained at 14.6 GPa and ambient temperature.*

Material (h,k,l)	d_{obs}/nm	I_{obs}^{\dagger}	d_{cal}/nm	$I_{\text{cal}}^{\ddagger}$	$\Delta d/\text{nm}$
$\delta\text{-N}_2(200)$	284.60	25	284.60	89	0.00
$\delta\text{-N}_2(210)$	254.40	75	254.55	100	0.15
$\delta\text{-N}_2(211)$	232.32	57	232.37	91	0.05
w-BN(100)	223.06	28	213.82	33	
c-BN(111), w-BN(002)	206.59	100	206.60	100	0.01
w-BN(101), $\alpha\text{-Fe}(101)$	197.80	62			
c-BN(200)	179.80	46	178.9	8	0.9
	178.09	51			
c-BN(220), w-BN(110)	126.54	49	126.50	33	0.04
w-BN(200), $\alpha\text{-Fe}(211)$	114.46	15			
c-BN(311)	107.96	13	107.90	20	0.06

* The calculations assume for $\delta\text{-N}_2$: $a = 569.20$ nm, and for c-BN: $a = 357.82$ nm, $\nabla/(\text{BN}) = 0.2781$ cm^3/mol , $\rho = 3.5958$ g/cm^3 (cf, $\rho = 3.4678$ g/cm^3 at 1 atm).

\dagger The intensities are in arbitrary units, normalized to the intensity of the c-BN(111) reflection.

\ddagger The calculated intensities for c-BN and $\delta\text{-N}_2$, are normalized to the (111) reflection for c-BN and the (210) for $\delta\text{-N}_2$.



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