inorganic compounds

Rhombohedral boron subnitride, B$_{13}$N$_2$, by X-ray powder diffraction

Oleksandr O. Kurakevych and Vladimir L. Solozhenko*

LPMTM-CNRS, 99 avenue J. B. Clement, 93430 Villetaneuse, France
Correspondence e-mail: vls@lpmtm.univ-paris13.fr

The structure of the title compound consists of distorted B$_{12}$ icosahedra linked by N—B—N chains. The compound crystallizes in the rhombohedral space group $R\bar{3}m$ (No. 166). The unit cell contains four symmetry-independent atom sites, three of which are occupied by boron [in the 18h, 18h (site symmetry m) and 3b (site symmetry $\bar{3}m$) Wyckoff positions] and one by nitrogen (in the 6c Wyckoff position, site symmetry 3m). Two of the B atoms form the icosahedra, while N atoms link the icosahedra together. The main feature of the structure is that the 3b position is occupied by the B atom, which makes the structure different from those of B$_6$O, for which these atom sites are vacant, and B$_{4+x}$C$_{1-x}$, for which this position is randomly occupied by both B and C atoms.

Comment

The fortunate combination of lightness, hardness, strength, chemical inertness and high cross section for neutron absorption has suited boron and boron-rich phases (B$_6$O, B$_{4+x}$C$_{1-x}$, *etc.*) to many technological applications (Emin, 1987; McMillan, 2002). Very recently, we have synthesized a new member of this group, boron subnitride, 'B$_6$N'. From the electron energy loss spectroscopy data, the stoichiometry of the phase has been determined to be B$_{6\pm1}$N, and from the X-ray study as B$_{13}$N$_2$. The phase has a structure similar in some respects to those of α-rhombohedral boron (Decker & Kasper, 1959), B$_{4+x}$C$_{1-x}$ (Kirfel *et al.*, 1979; Aselage *et al.*, 1997) and B$_6$O (Higashi *et al.*, 1991; Aselage *et al.*, 1997). However, the relative line intensities correspond to none of these three structures. The similarity is greatest to B$_{4+x}$C$_{1-x}$, which has the same unit cell, space group and atom sites as the nitride. Studies of the carbide by X-ray diffraction, Raman spectroscopy and, especially, ^{13}C and ^{11}B nuclear magnetic resonance revealed that a very complicated atomic distribution of carbon all over the lattice takes place *via* C/B disorder, resulting in C—C—C, B—B—C and C—B—C intericosa-hedral chains, as well as B$_{11}$C and B$_{12}$ icosahedra (Aselage *et al.*, 1997; Tallant *et al.*, 1989; Bullett, 1982; Lundstrom, 1997). In the case of 'B$_6$N', our Raman data have supported the suggestion that the 'B$_6$N' structure is similar to that of boron

carbide, B$_{4+x}$C$_{1-x}$, but with no evidence of N/B disorder of the type seen in the carbide. Thus, the nitride features N—B—N linkages, but no N—N—N linkages, which would be much less stable than the carbon analogues in any case.

In the present work, the structure of the new boron subnitride B$_{13}$N$_2$ has been determined by Rietveld refinement
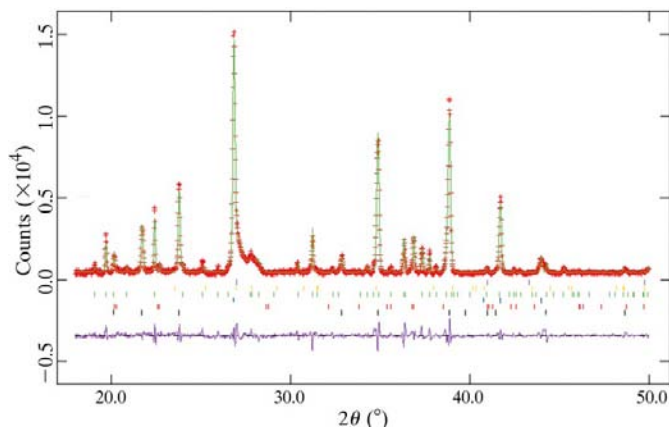

Figure 1
Rietveld full profile refinement of the X-ray powder diffraction pattern of B$_{13}$N$_2$.
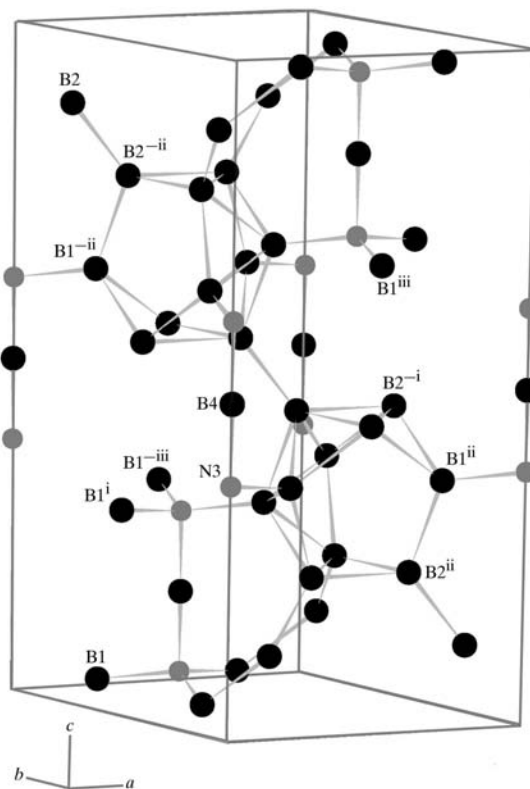

Figure 2
The unit cell of B$_{13}$N$_2$, containing four symmetry-independent atom sites, three of which are occupied by boron [*i.e.* B1, B2 and B4 in the 18h, 18h and 3b Wyckoff positions, respectively] and one by nitrogen (N3 in the 6c Wyckoff position). [Symmetry codes: (i) $y - x + \frac{1}{3}$, $-x + \frac{2}{3}$, $z + \frac{2}{3}$; ($-$i) $x - y + \frac{2}{3}$, $x + \frac{1}{3}$, $-z + \frac{1}{3}$; (ii) $x + \frac{2}{3}$, $y + \frac{1}{3}$, $z + \frac{1}{3}$; ($-$ii) $-x + \frac{1}{3}$, $-y + \frac{2}{3}$, $-z + \frac{2}{3}$; (iii) $x + \frac{1}{3}$, $x - y + \frac{2}{3}$, $z + \frac{2}{3}$; ($-$iii) $-x + \frac{2}{3}$, $y - x + \frac{1}{3}$, $-z + \frac{1}{3}$.]

of powder diffraction data collected at ambient conditions (Fig. 1). The Bragg lines of the compound have been indexed in the rhombohedral cell, with lattice parameters a = 5.4455 (2) Å and c = 12.2649 (9) Å. In order to check all possibilities of the atom type distribution over symmetry-independent site positions, we have performed a Rietveld refinement of several unit cells of the 'B$_6$N' compound. All the cells contained atoms B1 and B2 (18h Wyckoff position), while the 6c and 3b Wyckoff positions were allowed to be occupied by either B or N atoms. Satisfactory refinement was achieved only in the case of the starting unit cell containing two symmetry-independent B atoms of the 18h Wickoff position, one independent N atom in the 6c position and one B atom in the 3b position (Fig. 2). The site occupancies of the atoms of each crystallographic type are close to unity, so the synthesized phase has the B$_{13}$N$_2$ stoichiometry.

Experimental

Boron subnitride, B$_{13}$N$_2$, was synthesized from a B–BN melt at 5 GPa using the multianvil X-ray system MAX80 at beamline F2.1, HASYLAB–DESY. The experimental setup has been described elsewhere (Solozhenko & Peun, 1997). The starting materials, β-rhombohedral boron (β-rh B) and hexagonal boron nitride (hBN), were mixed in the 5:1 molar ratio that corresponds to the B$_6$N stoichiometry, compressed to 5 GPa, heated to 2500 K and then quenched to ambient conditions. Since the B$_{13}$N$_2$ phase crystallizes by peritectic reaction, the title compound has always been found in a mixture with β-rh boron, an I-tetragonal (I-t) boron-like phase (Ploog et al., 1972) and hBN. According to the Rietveld refinement, the sample contains about 22 vol% B$_{13}$N$_2$.

Phase 1

Crystal data

B$_{13}$N$_2$	c = 12.2649 (9) Å
M_r = 168.54	V = 314.97 (4) Å^3
Trigonal, $R\bar{3}m$	Z = 3
a = 5.4455 (2) Å	

Phase 2

Crystal data

BN$_x$	c = 5.037 (3) Å
M_r = 10.81	V = 389.91 Å^3
Tetragonal, $P\bar{4}n2$	Z = 50
a = 8.7979 (18) Å	

Phase 3

Crystal data

BN	c = 6.6357 (2) Å
M_r = 24.82	V = 35.87 (1) Å^3
Hexagonal, $P\bar{6}m2$	Z = 2
a = 2.49824 (8) Å	

Phase 4

Crystal data

B	c = 10.1398 Å
M_r = 10.81	V = 823.05 Å^3
Trigonal, $R\bar{3}mr$	Z = 105
α = 65.351 (3)°	

Phase 5

Crystal data

H$_3$BO$_3$	c = 9.600 (10) Å
M_r = 58.81	V = 412.67 Å^3
Trigonal, $P3_2$	Z = 6
a = 7.0453 Å	

Phase 6

Crystal data

BN	c = 6.598 (3) Å
M_r = 24.82	V = 36.86 Å^3
Hexagonal, $P\bar{6}m2$	Z = 2
a = 2.54 Å	

All phases

Crystal data

Cu $K\alpha$ radiation	Specimen prepared at 2400 K
T = 297 K	Fine powder, black
Specimen prepared at 5 GPa	

Data collection

Inel G3000 TEXT diffractometer	Scan method: fixed

Refinement

R_p = 0.100	S = 3.97
R_{wp} = 0.136	14 parameters
R_{exp} = 0.034	$(\Delta/\sigma)_{max}$ = 0.21

The necessity of Rietveld analysis of the powder diffraction pattern that contains six phases (five with already established structures and one new) has complicated the structure refinement. The 2θ interval for the profile fitting (Fig. 1) was chosen so that the main lines of boron subnitride B$_{13}$N$_2$ were not overlapped by the lines of other phases. The profile fitting of all the phases except B$_{13}$N$_2$ was performed employing both LeBail and Rietveld procedures using the literature data on the structures of corresponding phases.

Six phases were employed for profile fitting: B$_{13}$N$_2$ (phase 1), 'B$_{50}$N$_2$' (phase 2), hBN (phase 3), β-rhombohedral boron (phase 4), boric acid H$_3$BO$_3$ (phase 5) and phase 6, which has the same structure as phase 3 but a slightly different cell parameter c. Phase 6 was added to adjust the profile asymmetry of the 002 line due to a slight nonhomogeneity in the degree of ordering of hBN (Franklin, 1950, 1951). This has improved the fitting of the most intensive line of hBN (2θ = 24–26°) and has not influenced fitting out of this range. The only line of phase 5 belongs to this 2θ range and does not affect the structure refinement of the principal phase. Phases 2 and 4 have some lines overlapping with the lines of B$_{13}$N$_2$, but these lines are noticeably narrower than those of phase 1; this fact much facilitated the intensity extraction.

The sample contains approximately 22 vol% B$_{13}$N$_2$, 37 vol% hBN and about 41 vol% boron. The boron content (both β-rhombohedral boron and a I-t boron-like phase) was estimated using the values of phase fractions for B$_{13}$N$_2$ and hBN and the total composition of the starting mixture (5B + BN). A very small amount of boric acid (0.001 vol%) was also observed. Its formation may be attributed to hBN hydrolysis that cannot be avoided in the high-pressure experiments.

Data collection: *SYMPHONIX* (Inel, 2006); cell refinement: *GSAS* (Larson & Von Dreele, 2000); data reduction: *SYMPHONIX*; program(s) used to solve structure: *GSAS*; program(s) used to refine structure: *GSAS*; molecular graphics: *POWDERCELL* (Kraus & Nolze, 1996); software used to prepare material for publication: *GSAS*.

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