substance: boron compounds, general properties
property: α-rhombohedral boron structure group

The types of unit cells of the members of this structure group are shown in Fig. 1.

In the basic structure of α-rhombohedral boron, the vertices of the rhombohedral unit cell are occupied by one B_{12} icosahedron, each, being slightly distorted in consequence of the static Jahn-Teller effect (for details see Landolt-Börnstein Vol. III/41C). In the hexagonal representation of the structure one of the trigonal symmetry axes of the icosahedron coincides with the main diagonal of the rhombohedral unit cell, which is orientated parallel to the crystallographic *c* axis. The six boron atoms (B(2)) forming the top and bottom triangles of this orientated icosahedron are called polar, the six remaining ones (B(1)) are called equatorial because they are arranged slightly above and below the equatorial plane of the icosahedron, which is perpendicular to the crystallographic *c* axis. The unit cell of the α-rhombohedral modification of elementary boron does not contain further atoms. The inter-icosahedral bonds of the polar atoms along the edges of the rhombohedral unit cell are largely covalent, while the equatorial atoms of three neighboring icosahedra form weak electron-deficient three-center bonds approximately orientated perpendicular to the crystallographic *c* axis.

The unit cells of binary compounds attributed to the α-rhombohedral boron structure group contain 2 or 3 additional atoms, which – at least in most cases – are arranged on the main diagonal of the rhombohedral unit cell. They usually saturate the equatorial bonds of the icosahedra and exchange the weak three-center bonds of α -rhombohedral boron by strong bonds thus considerably hardening the whole structure. Two kinds of such compounds with two atoms on the main diagonal are to be distinguished, (i) those with chain atoms forming bonds in between and (ii) those with two unbounded atoms. A peculiarity are Al atoms, which are sideways shifted from the center of the unit cell.

$B_{12}Be$ [66K] and $B_{12}S$ [61M] were initially assumed to be isostructural compounds to α-rhombohedral boron as well, but with only one additional atom accommodated in the center of the unit cell. However a more recent analysis of the original X-ray data [91L] suggests to attribute these compounds to the $B_{12}X_2$ structures with the X sites being only partly occupied.

In general, the aspect of unoccupied sites in the two- or three-atom chains seems to be important. For boron-rich boron carbide the existence of a considerable concentration of chain-free unit cells was proved [92K2, 92K1]. These were shown to be at disposal for the accommodation of Si atoms in ternary compounds [94W]. A similar situation was assumed for $B_{12}P_2$ as well [96W, 97W]. Accordingly, it is possible to have complete and chainless unit cells side by side instead of unit cells with single chain sites remaining unoccupied.

All the representatives of the α-rhombohedral boron structure group are semiconductors or insulators.

Representatives of the α-rhombohedral boron structure group.

Chemical formula	Structural formula (idealized)	attributed ternary compound (doped binary compound)	
B (α-rhombohedral boron)	B_{12}		LB 41C
B + n*Li (n =1,2, 3)		(stable according to ab initio calc.)	94G
$B_{12}X_2$ (X_2 chain of bounded atoms)			
B_6P	$B_{12}P_2$		67B, 86M, 87L, 94Y, 95Y
		$B_{12}P_2$ + Si	96W, 97W
B_6As	$B_{12}As_2$		87L1, 87M
	$B_{12}Se_{2-x}B_x$		93B
$B_{\sim 3}Si$ [3])	$(B_{12-x}Si_x)Si_2$		97A, 98A, 62M.
(2 unbounded X atoms)			
B_6O	$B_{12}O_2$		87L, 62R
$B_{12}Be$[1])[2])	$B_{12}Be_2$		66K, 91L
$B_{12}S$[2])	$B_{12}S_2$		87L, 61M
B_6N	$B_{12}N_2$		76C, 93S, 94L, 96L
$B_{12}XY$			
$B_{13}Se$	$B_{12}Se_{2-x}B_x$		93B, 94L
$B_{12}X_3$			
$B_{4.3}C$	$(B_{12})_{1-x}(B_{11})_x$ (C-B-C)$_y$ (C-B-B)$_z$ (y+z ≤ 1)		92K2, 92K1
$B_4C - B_{\sim 11}C$			85S, 90T
		boron carbide + Si	94W
		boron carbide + Al	97S
$(B_{11}X)Y_2$			
$B_{4.9(3)}Be_{0.5(1)}N$	$(B_{11}Be)N_2$		97G2

[1]) The same formula holds for a member of the α-tetragonal boron structure group as well.

[2]) This chemical formula means that the two sites of the chain atoms are only partly occupied. Initially it was assumed that there are unit cells with one chain atom only. However, based on recent results on boron carbide and $B_{12}P_2$ (see there) it seems more probable that there are unit cells with two chain atoms and unit cells without chain atoms side by side.

[3]) In principle, $B_{2.89}$ Si belongs to this structure group as well. However, there is a qualitative difference, because the relatively large Si atoms substitute for icosahedral boron atoms as well and this enlarges the unit cell volume considerably (see Fig. 2 [93B]).

Calculated overlap populations

(A) Intraicosahedral bonding, (B) Intericosahedral bonding, (C) interchain bonding 95L

Bond	Type	α-rh. B	$B_{13}C_2$	$B_{11}C(CBC)$	$B_{12}P_2$	$B_{12}As_2$
B(1)-B(1)	(A)	0.12(6)	0.13(6)	0.13(4)	0.11(6)	0.12(6)
B(1)-B(2)	(A)	0.12(18)	0.13(12)	0.13(10)	0.11(12)	0.13(12)
	(A)		0.11(6)	0.12(5)	0.09(6)	0.19(6)
B(2)-B(2)	(A)	0.14(6)	0.14(6)	0.11(6)	0.11(6)	0.13(6)
B(1)-C	(A)			0.11(2)		
B(2)-C	(A)			0.12(2)		
	(A)			0.11(1)		
B(1)-B(1)	(B)	0.24(6)	0.24(6)	0.24(4)	0.27(6)	0.25(6)
B(2)-B(2)	(B)	0.05(12)				
B(2)-P(As)	(B)				0.27(6)	0.21(6)
B(1)-C	(B)			0.22(2)		
B(2)-C’	(B)		0.20(6)	0.21(6)		
P-P, As-As	(C)				0.15(1)	0.15(1)
B’-C’	(C)		0.28(2)	0.27(2)		

Comparative discussion and group theoretical determination of the lattice vibrations of the α-rhombohedral boron structure group in [87W].

Unit cell structures of α-rhombohedral boron type crystals are assumed to be able to form quasicrystal structures (real prolate and hypothetical oblate arrangements of icosahedra in the unit cells) [93K].

Boron K edges of several representatives of the α-rhombohedral boron structure group in Fig. 3 [97G1].

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Fig. 1.

α-rhombohedral boron structure group, Unit cells of the α-rhombohedral boron structure family. **(a)** α-rhombohedral boron; **(b)** $B_{12}X_2$ structure; **(c)** $B_{12}X_3$ structure. Closed circles: polar atoms of the icosahedra forming covalent inter-icosahedral bonds; open circles: equatorial atoms of the icosahedra forming the weak three-center bonds in **(a)** and strong bonds to the chain end atoms of the chains in **(b)** and **(c)**.

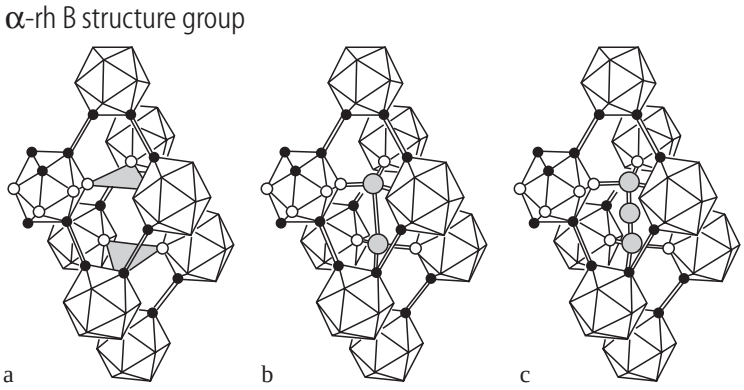

Fig. 2.
α-rhombohedral boron structure group. Unit cell volume vs. radius of non-boron element [91L, 93B].

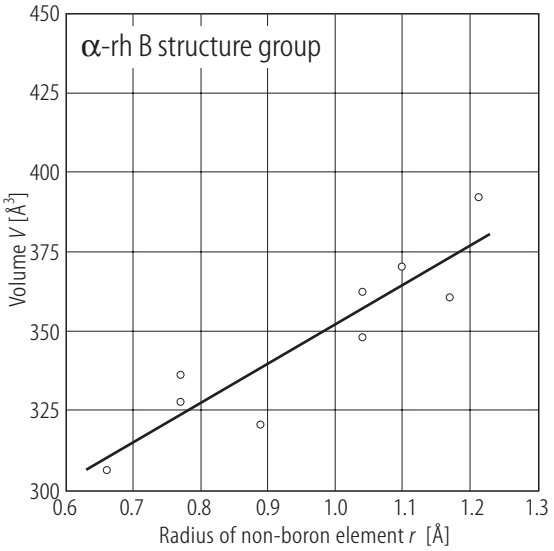

Fig. 3.

α-rhombohedral boron structure group. Boron K edges of some α-rh B-bearing material. The edges are divided into the energy-loss near-edge structure (ELNES) and the extended electron-loss fine sructure (EXELFS). The ELNES for the B K edges can be divided into π* and σ* regions [97G1].