Boron

General:

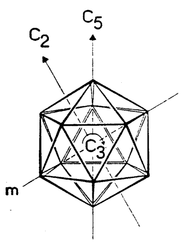
PSE group 13, non-metal, small atoms (80-90 pm), high ionization energy (3660 kJ/mol), high tendency towards covalency, but only 3 valence electrons and four orbitals, therefore electron-deficient, high melting, very hard, band gap ca. 1.6 eV, annual world production 100 tons (Industrial) synthesis from B_2O_3 and Mg or BCl_3 and H_2 or by thermal decomposition of B_2H_6; B_2O_3 from boric acid (H_3BO_3) or borate minerals like borax, kernite (Turkey, U.S.A.)

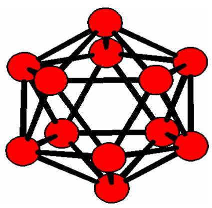
Modifications:

- up to 16 discussed plus high-pressure phases
- existence of three modifications (α-rhombohedral-B_{12}, β-rhombohedral-B_{105}, hp-γ-B_{28}) is confirmed/ensured
- α-tetragonal, β-tetragonal unconfirmed

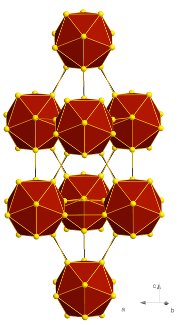
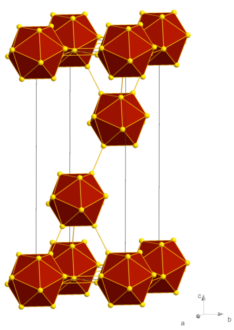
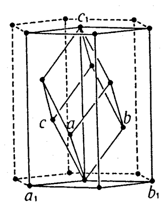
Structures:

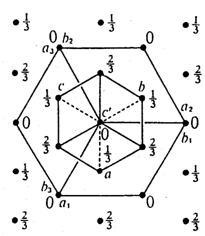
1) B_{12} icosahedron is building unit in all elemental modifications and some metal borides (like Na_2B_{29}) or boron-hydrogen compounds (like $K_2B_{12}H_{12}$), symmetry elements are 6x C5, 10x C3, 15x C2, 15x m, point group I_h





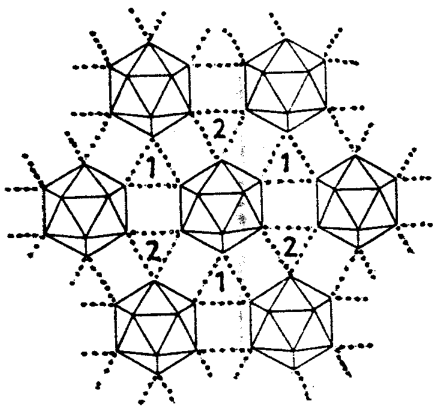
2) α-rhombohedral-B_{12} has a simple rhombohedral structure with 12 atoms per unit cell (one icosahedron at the corners of a simple rhombohedral unit cell) which can also described in R-centred hexagonal setting with 36 atoms per unit cell.

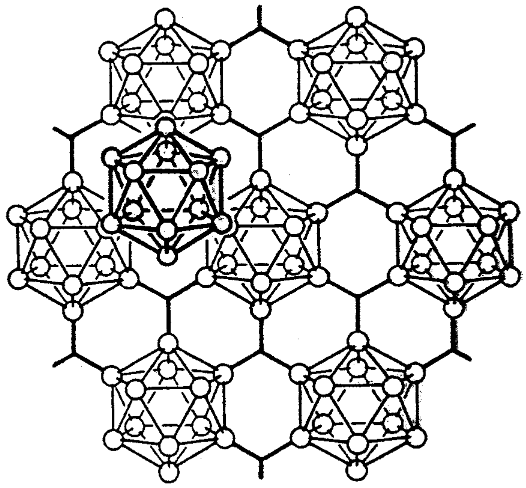






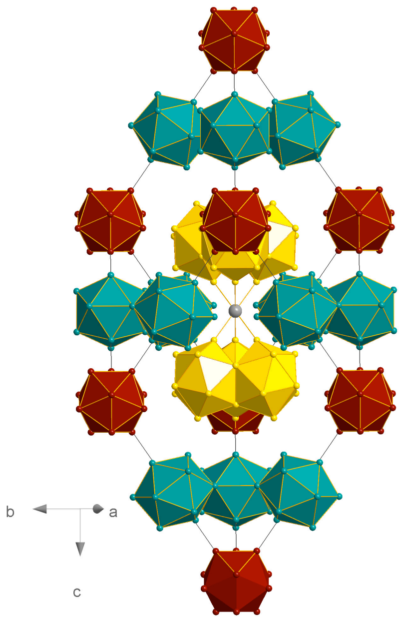
The icosahedra are packed with ABC sequence in a rhombohedrally distorted ccp arrangement, each icosahedron therefore has 12 icosahedra as neighbors.
You can apply WADE rules to count electrons: 2n+2 electrons (n = number of corners of the polyhedron) are required to stabilize closed (*closo*) polyhedron with multicentre

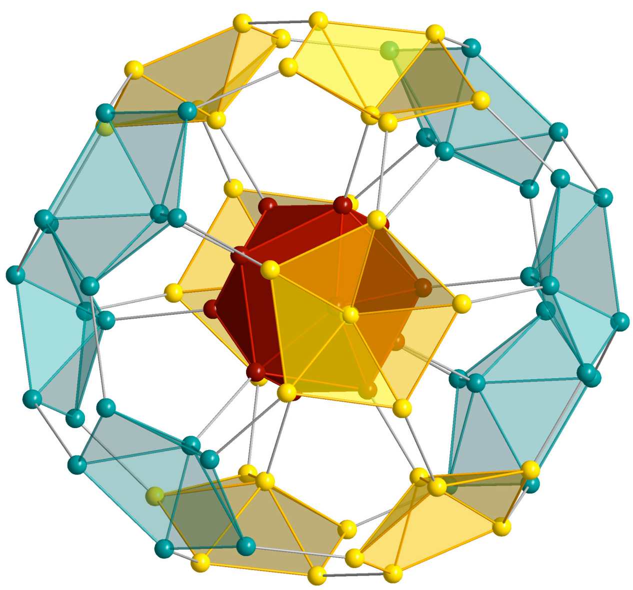
bonds, here 26. Since each boron atom contributes 3 valence electrons, 36 are available. That leaves 10 for the bonds between the icosahedra in α-rhombohedral-B. If you think of an ABC stacking of layers of icosaheda, you could count six 2e2c-bonds between an icosahedron in the B layer and its six neighbors in A and C, that leaves you four for the six 2e3c-bonds within the B layer (6x 2/3 = 4).



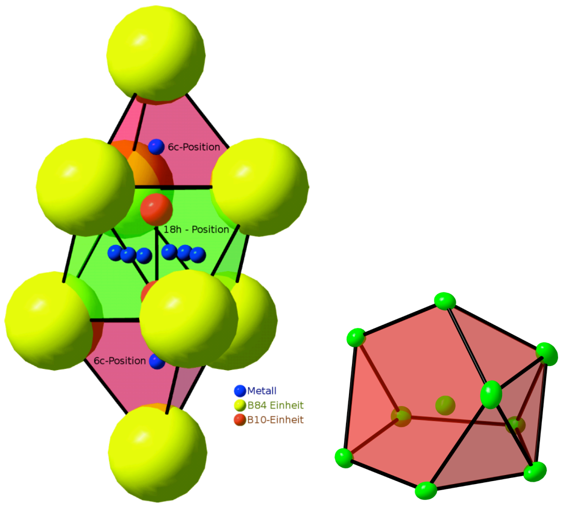


3) Space group of β-rhombohedral-B_{105} is the same ($R\bar{3}m$, no. 166) as that of α-rhombohedral-B_{12}, but there are 105 to 107 atoms in the rhombohedral cell (or 315 321 in the hexagonal; icosahedra are located on the corners and in the middle of the edges of the rhombohedral cell, and there are two B_{28} units in the body diagonal [111] of the rhombohedral cell and a single boron atom in the center of the cell (12 + 3x 12 + 2x 28 + 1 = 105 atoms). Each of the B_{28} units consists of three condensed icosahedra. In addition, there are positions in the cell where you can place disordered boron atoms or – in case of doping – metal atoms.



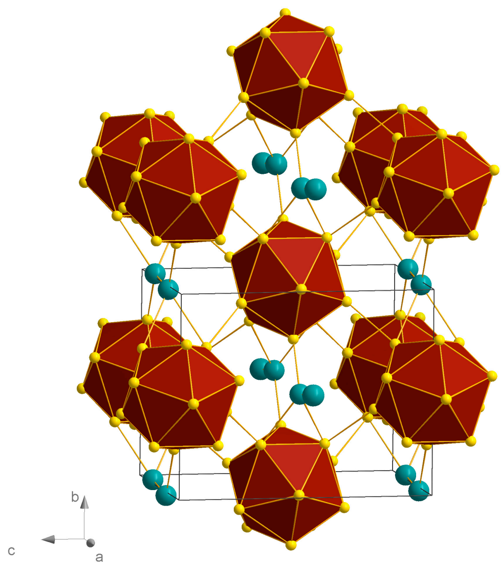


If you add two more shells of boron atoms to each (red) icosahedron at the corners of the rhombohedral cell, you get a B_{84} unit (B12-B12-B60). The outer shell resembles to C_{60} (note that a C_{60} fullerene has the same point group symmetry as an icosahedron). These B_{84} units consist of the icosahedron at the corner plus 6 halves of icosahedra from the edges and 6 halves of icosahedra from the B_{28} units. They are located at the corners of a simple rhombohedral cell, thus again forming something like a rhombohedrally distorted ccp arrangement of B_{84} units. The remaining atoms from the former B_{28} units now form two B_{10} units.



This picture also shows the positions were there are additional (disordered) boron atoms in β-rhombohedral-B_{105} (blue positions, they can also be occupied by metal atoms).

4) High pressure-γ-B_{28} was not found but only recently. It is a distorted cubic packing of icosahedra with B2 dumbbells in the pseudo-octahedral gaps. It was called "ionic" boron.



Further reading: Barbara Albert, Harald Hillebrecht, Angew. Chem. Int. Ed. 48 (2009) 8640-8668