BORON – NITROGEN – OXYGEN

The boron takes the second place after diamond in firmness. Many compounds of boron with other elements are used as heat-resistant and abrasive materials.

The natural boron consist of two isotopes: ^{10}B=19.57% and ^{11}B=80.43%. The average atomic mass is 10.811u. Temperature of melting is 2573K, temperature of boiling is 3931K. The temperature factor of linear expansion in a range of temperatures 273-1300K is changeable also and changes in limits $(4.8\text{-}7.0)\times10^{-6}$ 1/K.

Boron has more than 10 crystal modifications. Formation of one or another modification and their mutual transitions are determined by temperature, at which receive boron. Some parameters of the steadiest allotropic modifications of boron are below adduced.

At temperature 800-1100K it is formed amorphous boron with density 2350kg/m^3. The volume for one atom of boron in its amorphous modification is equal 7.639Å^3.

Crystal lattices of others modifications of boron are constructed from icosahedrons and made of the big number of atoms (from 12 up to 324). We have chosen crystal cells, which contain 12, 105 and 50 atoms for modeling.

At temperature 1100-1300K are formed red crystals of α-B with rhombohedral lattice (a=506pm, α=58.06°), with density 2450-2460 kg/m^3. The volume for one atom is equal 7.327–7.298Å^3. In reference books it is underlined, that this crystal cell contains 12 atoms. Corresponding calculation shows, that for one atom the volume of crystal 9.166Å^3 falls on. It in 25% is more, than shows calculation on density for given modification of boron. If to allow, that in a cell 15 atoms are located, then the volume of crystal for one atom will be equal 7.333 Å^3, that fully suitable with calculation on density.

At temperature 1300-1500K the steadiest modification β-B is formed with rhombohedral cell (a=1014.5pm, α=65.2°), with density 2310-2350 kg/m^3. The volume of crystal for one atom is equal 7.771–7.639Å^3. The given cell contains 105 atoms. Corresponding calculation shows, that for one atom the volume of crystal 9.029Å^3 falls on. It in 17% is more, than shows calculation on density for given modification of boron. If to allow, that in a cell 124 atoms are located, then the volume of crystal for one atom will be equal 7.647Å^3, that more corresponds to reality.

At temperature 1500-1800K it is formed modification with tetragonal lattice (a=875pm, c=506pm), with density 2360-2370 kg/m^3. The volume of crystal for one atom is equal 7.607–7.575Å^3. The given cell contains 50 atoms. Corresponding calculation shows, that for one atom the volume of crystal 7.748Å^3. If to locate in a cell 51 atoms, then the volume of crystal for one atom will be equal 7.596Å^3.

The reduced comparison of volumes of atom of boron speaks that the statement about cells-icosahedrons is erroneous.

Boron (especially crystal) is chemically inert element. With H_2 boron directly does not react. The acids, which are not being oxidizers, with boron also do not react. The concentrated nitric acid HNO_3 and nitrohydrochloric acid oxidize it up to boric acid H_3BO_3.

Boric (ortho-boric) acid has layered triclinic lattice (a=b=704pm, c=656pm, α=101.10° , β=92.30°, γ=120.00°, the distance between layers is 318pm). Density of H_3BO_3 is equal 1460 kg/m^3; temperature of melting 444K; the decomposition of acid begins at temperature of melting. The volume for one molecule of acid in cell is equal 70.326 Å^3, at calculation on density, and 68.983Å^3, at calculation on parameters of crystal lattice (in a cell 4 molecules are located).

In fig.1 the crystal structure of orto-boric acid is shown. The crystal is made of molecules of boron (lilac color), molecules of hydrogen (blue color) and molecules of oxygen (dark blue color). The directions of main crystallographic axes of all three grades of molecules coincide. Molecules of boron are draw up by correct lines along the main axis with alternation one molecule through one vacancy.

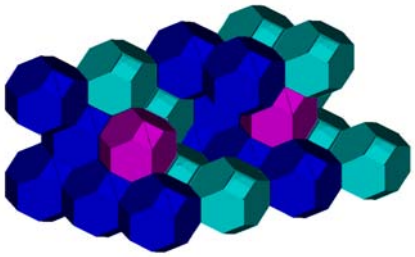

Fig.1
The crystal structure of ortho-boric acid H_3BO_3

Molecules of hydrogen and oxygen also are draw up by correct lines along the main axis with alternation one by one. Molecules of boron in the neighboring lines are displaced along the main axis on one step, therefore layers of molecules of boron are located in relation to the main axis of crystal under angle 50.5°. Accordingly, the angle between criss-cross layers is equal 101° that corresponds to crystallographic angle α. The volume for one molecule, in view of vacancies between molecules of boron, is equal 68.924Å^3.

At temperature 380.6K (107.5°C) ortho-boric acid H_3BO_3 changes into more dense meta-boric acid HBO_2 (fig.2). Meta-boric acid HBO_2 represents colorless crystals of three modifications.

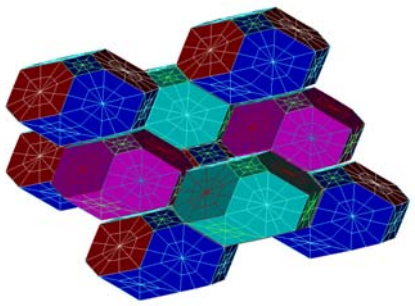

Рис.2
The crystal structure of meta-boric acid HBO_2

The steadiest is γ-modification with a cubic lattice (a=887pm, number of molecules in a cell 24). The temperature of melting HBO_2 is equal 509K (236°C). Density is 2486 kg/m^3. The volume for one molecule of acid in a cell is equal 29.268 Å^3, at calculation on density, and 29.078Å^3, at calculation on parameters of crystal lattice.

Besides exist α-modification with a rhombic lattice (temperature of melting 449K (176°C), density 1784 kg/m^3) and β-modification with a monoclinic lattice (temperature of melting 474K (200.9°C), density 2045 kg/m^3). All crystal modifications HBO_2, decompose at temperature of melting.

Meta-boric acid HBO_2 actively reacts with water and turns into ortho-boric H_3NO_3.

At temperature 433K (160°C) α-modification HBO_2 changes into β-modification.

At the same temperature (433K) ortho-boric H_3BO_3 changes into oxide of boron B_2O_3 (fig.3). Besides, oxide of boron can be manufactured by heating of boron in atmosphere of air up to temperature 1000K.

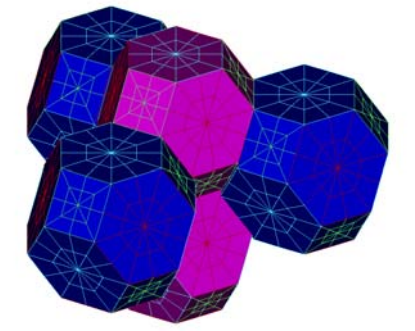

Fig.3
The crystal structure of molecule of oxide of boron B_2O_3

Oxide of boron B_2O_3 represents colorless vitreous or crystal substance of bitter taste. Vitreous oxide B_2O_3 has density 1812 kg/m^3, also possesses with high mechanical firmness. Temperature of melting is 600-700K. Structure of vitreous oxide of boron is layered, with distance between layers 185pm. The volume for one molecule in vitreous oxide of boron is equal 63.801Å^3. In vitreous modification B_2O_3 always there is a plenty of vacancies of the various sizes.

Crystal B_2O_3 can be manufactured by means of cautious extracting of water from α-modification HBO_2.

Under usual conditions it is steady crystal modification with hexagonal lattice (a=433pm, c=832pm, number of molecules in a cell 3), with density 2460 kg/m^3.

The volume for one molecule α-HBO_2 in a cell is equal 46.995Å^3, at calculation on density, and 51.997Å^3, at calculation on parameters of crystal lattice. Our calculations have shown, that in crystal of α-HBO_2 between each three cells one vacancy for a molecule boron is formed.

At temperature 673K (400°C) and at pressure 2200 MPa α-HBO_2 is transform into monoclinic modification with higher density and temperature of melting.

Oxide of boron B_2O_3 is a firm and heat-resistant material. It is used as an additive by manufacture of special glasses, ceramics, enamels.
At temperature 1300K, at the presence of coal, oxide of boron reacts with molecular nitrogen and forms boron nitride BN (fig.4). Boron nitride is formed also at heating of boron above 1500K in an atmosphere of nitrogen or ammonia NH_3.

Fig.4
Molecule of boron nitride BN

In fig.4 the atom of boron is arranged from four disks of lilac color, the atom of nitrogen – from four disks of brown color.
Under usual conditions boron nitride exists as steady graphite-like α-modification, with temperature of melting about 3300K.
At temperature higher 1600K and at pressure 6-13 GPa from α-BN black crystals β–BN are formed; at pressure higher 13GPa metastable modification γ-BN is formed.
Others physical and chemical properties of boron nitride are adduced in the table 1.

Table 1

Properties of crystal	Crystal modification boron nitride		
	α-BN	β-BN	γ-BN
Color	White	Black	Grey
Crystal lattice	Hexagonal	Cubic	Hexagonal
Parameters of lattice	a=250.4 pm c=666.1 pm	a=361.5 pm –	a=255.0 pm c=423.0 pm
Number of molecules in a cell	z=2	z=4	z=2
Volume for one molecule on crystal cell, Å^3	18.085	11.810	11.910
Density, kg/m^3	2290	3450	3400
Volume for one molecule on density, Å^3	17.996	11.945	12.121
Linear expansion coefficient, 1/K on an axis “a” on an axis “c”	 $2.9*10^{-6}$ $40.5*10^{-6}$	 $2.8*10^{-6}$ –	 $2.7*10^{-6}$ $3.7*10^{-6}$

Design volume of truncated bipyramid for a molecule α-BN is equal 18.23Å^3.
In crystal lattice of boron nitride layers of molecules BN are located mirror to each other – cones of atoms of boron of one layer are located in hollows between cones of atoms of boron in in mirror layer, accordingly, cones of atoms of nitrogen of one layer are located in hollows between cones of atoms of nitrogen in mirror layer.
Boron nitride possesses the big anisotropy of mechanical properties, therefore at high pressure, molecules are flattened in the direction of the main axis of crystal and their volumes are essentially decreased.

Three-dimensional modeling and mathematical calculation of the above crystal lattices have allowed to calculate diameter of boron polytron D_B=188.772pm.
Atom of nitrogen in molecule α-BN has the same form, as well as in a free molecule of nitrogen. In a solid state, at usual pressure, nitrogen exists in two modification: below 35K it is steady α-form with a cubic lattice (a=566.7pm, density 1026.5 kg/m^3); higher 35K it is steady β-form with hexagonal lattice (a=393pm, c=650pm, density 0.8792 kg/m^3). The molecule of nitrogen has the same form, as well as the molecule of hydrogen, but diameter of nitric polytron is little bit more D_N=218.000pm.
Energy of thermal dissociation of molecules N_2 is equal 941.64 kJ/mol = 9.759eV/molecule, therefore dissociation becomes appreciable only at very high temperatures. So, at temperature of melting of boron nitride (3300K) and at normal pressure a degree of dissociation of nitrogen makes only 0.1 % of molecules. The big energy of dissociation of molecular nitrogen is the reason of its low reactionary ability. Only with some active metals (Li, Cs) nitrogen reacts at low temperatures.
According to the standard theory of structure of atoms and molecules, diatomic molecule of nitrogen has bond length between atoms N≡N 110pm.
We have executed modeling for several diatomic molecules and came to the conclusion, that this parameter depends on temperature, therefore bond length cannot be used in calculations as base size. We use at calculations the diameters of polytrons and crystallographic angles. These parameters allow creating more real models of complex chemical compounds and their crystal lattices.
In polytronic model, the connection of atoms and molecules with each other can be provided, at least, with four types of bonds.
The strongest bond is realized in that case, when the atom or molecule of the greater size absorbs atom or molecule of the smaller size. This type of bond we could modeling by the examples of formation of hydride of lithium and oxide of lithium.
The second type of bond (less strong, than the first) is realized in that case, when polytrons of two neighboring atoms are located on one axis and are gravitate to each other due to the electromagnetic moments of polytrons. Resonant vibration of polytrons prevents with junction of two polytrons in one and at the same time promotes to sliding of sides of polyhedrons relatively each other.
The following, the third type of bond is realized in that case, when free nodes of four polytrons of one atom incorporate with free nodes of four polytrons of other atom. By means of these bonds, diatomic molecules of one element, and also such linear structures, as hydrogen shanks in crystals of ice are formed.
The fourth, weakest type of bond is realized in that case, when one node on an edge of one atom-polyhedron incorporates with one node on an edge of other atom-polyhedron.
For formation of the above compounds of boron, oxygen and nitrogen the nature uses two types of connection – the second and the third.
We assume, that at creation of the living matter and, in particular, for the information exchange between subjects of the living matter, the nature uses the fourth type of connection.