Boron

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Black - brown.

1– Introduction :

Boron is the chemical element with atomic number 5 and the chemical symbol **B**. Boron is a metalloid. Because boron is not produced by stellarnucleo synthesis, it is a low- abundance element in both the solar system and the Earth's crust. However, boron is concentrated on Earth by the water-solubility of its more common naturally occurring compounds, the borate minerals. These are mined industrially as evaporate ores, such as borax and kernite.

Chemically uncombined boron is not found naturally on Earth. Industrially, very pure isolated boron is produced with difficulty, as boron tends to form refractory materials containing small amounts of carbon or other elements. Several allotropes of boron exist: amorphous boron is a brown powder and crystalline boron is black, extremely hard (about 9.5 on Mohs' scale), and a poor conductor at room temperature. Elemental boron is used as a dopant in the semiconductor industry.

The major industrial-scale uses of boron compounds are in sodium per borate bleaches, and the borax component of fiberglass insulation. Boron polymers and ceramics play specialized roles as high-strength lightweight structural and refractory materials. Boron compounds are used in silica-based glasses and ceramics to give them resistance to thermal shock. Boron-containing reagents are used for the synthesis of organic compounds, as intermediate in the synthesis of fine chemicals. A few boron-containing organic pharmaceuticals are used, or are in study. Natural boron is composed of two stable isotopes, one of which (boron-10) has a number of uses as a neutron-capturing agent.

In biology, borates have low toxicity in mammals (similar to table salt), but are more toxic to arthropods and are used as insecticides. Boric acid is mildly anti microbial, and a natural boron - containing organic antibiotic is known. Boron is essential to life. Small amounts of boron compounds play a strengthening role in the cell walls of all plants, making boron necessary in soils. Experiments indicate a role for boron as an ultra trace element in animals, but the nature of its role in animal physiology is unknown.

Name, Symbol, Number	Boron, B, 5
Element category	metalloid
Group, period, block	13, 2, p
Standard atomic weight	11
Electron configuration	[He] $2s^2 2p^1$
Electrons per shell	2, 3
Phase	solid
Liquid density at m.p.	$2.08 \text{ g} \cdot \text{cm}^{-3}$
Melting point	2076 °C
Boiling point	3927 °С
Heat of fusion	$50.2 \text{ kJ} \cdot \text{mol}^{-1}$
Heat of vaporization	$480 \text{ kJ} \cdot \text{mol}^{-1}$
Molar heat capacity	$11.087 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Oxidation states	3, 2, 1 (mildly acidic oxide)
Electro negativity	2.04 (Pauling scale)
Ionization energies	1^{st} : 800.6 kJ·mol ⁻¹
(more)	2^{nd} : 2427.1 kJ·mol ⁻¹
	3^{rd} : 3659.7 kJ·mol ⁻¹
Atomic radius	90 pm
Covalent radius	$84 \pm 3 \text{ pm}$

Van der Waals radius	192 pm		
Magnetic ordering	diamagnetic		
Electrical resistivity	$(20 \ ^{\circ}C) \sim 10^{6} \ \Omega \cdot m$		
Thermal conductivity	$27.4 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$		
Thermal expansion	(25 °C) (β form) 5–7 ^[3] μ m·m ⁻¹ ·K ⁻¹		
Speed of sound (thin rod)	(20 °C) 16,200 m·s ⁻¹		
Mohs hardness	~9.5		
Most stable isotopes			
Main article: Isotopes of bo	oron		
iso NA half-lit 10 B 19.9 % * 10 B is 11 B 80.1 % * 11 B is	feDMDE (MeV)DPstable with 5 neutronsstable with 6 neutrons		
*Boron -10 content may be as low as 19.1% and as high as 20.3 % in natural samples. Boron-11 is the remainder in such cases.			

2 - History and etymology

The name boron originates from the Arabic word بورق buraq or the Persian word بوره burah ; which are names for the mineral borax .



Sassolite

Boron compounds were known thousands of years ago. Borax was known from the deserts of western Tibet, where it received the name of *tincal*, derived from the Sanskrit. Borax glazes were used in China from AD300, and some tincal even reached the West, where the Persian alchemist Jābir ibn Hayyān seems to mention it in 700.

Marco Polo brought some glazes back to Italy in the 13th century. Agricola, around 1600, reports the use of borax as a flux in metallurgy. In 1777, boric acid was recognized in the hot springs (soffioni) near Florence, Italy, and became known as *sal sedativum*, with mainly medical uses. The rare mineral is called sassolite, which is found at Sasso, Italy. Sasso was the main source of European borax from 1827 to 1872, at which date American sources replaced it. Boron compounds were relatively rarely used chemicals until the late 1800s when Francis Marion Smith's Pacific Coast Borax Company first popularized these compounds and made them in volume and hence cheap

Boron was not recognized as an element until it was isolated by Sir Humphry Davy and by Joseph Louis Gay - Lussac and Louis Jacques Thénard In 1808 Davy observed that electric current sent through a solution of borates produced a brown precipitate on one of the electrodes. In his subsequent experiments he used potassium to reduce boric acid instead of electrolysis. He produced enough boron to confirm a new element and named the element *boracium*. Gay-Lussac and The nard use iron to reduce boric acid at high temperatures. They showed by oxidizing boron with air that boric acid is a oxidation product of boron . Jöns Jakob Berzelius identified boron as an element in 1824 . Pure boron was arguably first produced by the American chemist Ezekiel Weintraub in 1909 .

3 – Characteristics :

3–1 - Allotropes :

Boron is similar to carbon in its capability to form stable covalently bonded molecular networks. Even nominally disordered (amorphous) boron contains regular boron icosahedra which are, however, bonded randomly to each other without long-range order. Crystalline boron is a very hard, black material with a high melting point of above 2000 °C. It exists in four major polymorphs: α , β , γ and T. Whereas α , β and T phases are based on B₁₂ icosahedra, the γ -phase can be described as a rock salt - type arrangement of the icosahedra and B₂ atomic pairs.^[20] It can be produced by compressing

other boron phases to 12–20 GPa and heating to $1500 - 1800 \,^{\circ}$ C; it remains stable after releasing the temperature and pressure. The T phase is produced at similar pressures, but higher temperatures of $1800 - 2200 \,^{\circ}$ C. As to the α and β phases, they might both coexist at ambient conditions with the β phase being more stable. Compressing boron above 160 GPa produces a boron phase with an as yet unknown structure, and this phase is a super conductor at temperatures $6 - 12 \,^{\circ}$ K.

Boron phase	α	β	Γ	Τ
Symmetry	Rhombohedral	Rhombohedral	Orthorhombic	Tetragonal
Atoms/unit cell	12	~105	28	
Density (g/cm ³)	2.46	2.35	2.52	2.36
Vickers hardness (GPa)	42	45	50–58	
Bulk modulus (GPa)	185	224	227	
Bandgap (eV)	2	1.6	2.1	

3 – 2 - Chemistry of the element :

Elemental boron is rare and poorly studied because the material is extremely difficult to prepare. Most studies on "boron" involve samples that contain small amounts of carbon. Chemically, boron behaves more closely to silicon than to aluminium. Crystalline boron is chemically inert and resistant to attack by boiling hydrofluoric or hydrochloric acid. When finely divided, it is attacked slowly by hot concentrated hydrogen peroxide, hot concentrated nitric acid, hot sulfuric acid or hot mixture of sulfuric and chromic acids.^{[16][32]}

The rate of oxidation of boron depends upon the crystallinity, particle size, purity and temperature. Boron does not react with air at room temperature, but at higher temperatures it burns to form boron trioxide :

 $4 B + 3 O_2 \rightarrow 2 B_2 O_3$

Boron undergoes halogenations to give tri halides, for example:

$$2 B + 3 Br_2 \rightarrow 2 BBr_3$$

These tri halides in practice are usually made from the oxides.

3 – 2 - 1 - Chemical compounds :

In its most familiar compounds, boron has the formal oxidation state III. These include oxides, sulfides, nitrides, and halides.

The tri halides adopt a planar trigonal structure. These compounds are Lewis acids in that they readily form adducts with electron - pair donors, which are called Lewis bases. For example, fluoride (F) and boron tri fluoride (BF_3) combined to give the tetra fluoro borate anion, BF_4 . Boron tri fluoride is used in the petrochemical industry as a catalyst. The halides react with water to form boric acid.

Boron is found in nature on Earth entirely as various oxides of B(III), often associated with other elements. The more than one hundred borates all feature boron in oxidation state +3. These mineral resemble silicates in some respect, although boron is often found not only in a tetrahedral coordination with oxygen, but also in a trigonal planar configuration. Unlike silicates, the boron minerals never feature boron with coordination number greater than four. A typical motif is exemplified by the tetra borate anions of the common mineral borax, shown at left. The formal negative charge of the tetrahedral

borate centers is balanced by metal cations in the minerals, such as the sodium (Na^+) in borax.

The **boron nitrides** are notable for the variety of structures that they adopt. They adopt structures analogous to various allotropes of carbon, including graphite, diamond, and nano tubes. In the diamond - like structure called cubic boron nitride (trade name Borazon), boron atoms exist in the tetrahedral structure of carbons atoms in diamond, but one in every four B - N bonds can be viewed as a coordinate covalent bond, wherein two electrons are donated by the nitrogen atom which acts as the Lewis base to a bond to the Lewis acidic boron (III) centre . Cubic boron nitride, among other applications, is used as an abrasive, as it has a hardness comparable with diamond (the two substances are able to produce scratches on each other). In the BN compound analogue of graphite, hexagonal boron nitride (h-BN), the positively-charged boron and negativelycharged nitrogen atoms in each plane lie adjacent to the oppositely charged atom in the next plane. Consequently graphite and h-BN have very different properties: both are lubricants, as these planes slip past each other. However, h-BN is a relatively poor electrical and thermal conductor in the planar direction.

3 – 2 - 1 - 1 - Organo boron chemistry :

A large number of organo boron compounds are known and many are useful in organic synthesis. Organo boron (III) compounds are usually tetrahedral or trigonal planar, for example, tetra phenyl borate $(B(C_6H_5)_4)$ vs tri phenyl borane $(B(C_6H_5)_3)$. Many are produced from hydro boration, which employs diborane (B_2H_6) .

3-2-1-2-Compounds of B (I) and B (II)

Although these are not found on Earth naturally, boron forms a variety of stable compounds with formal oxidation state less than three. As for many covalent compounds, formal oxidation states are often of little meaning in boron hydrides and metal borides. The halides also form derivatives of B(I) and B(II). BF, iso electronic with N_2 , is not isolable in condensed form, but B_2F_4 and B_4Cl_4 are well characterized .

Binary metal - boron compounds, the metal borides, feature boron in oxidation state less than III. Illustrative is magnesium di boride (MgB₂). Each boron has a formal -1 charge and magnesium is assigned a formal charge of 2+. In this material, the boron centers are trigonal planar, with an extra double bond for each boron, with the boron atoms forming sheets akin to the carbon in graphite. However, unlike the case with hexagonal boron nitride which by comparison lacks electrons in the plane of the covalent atoms, the delocalized electrons in the plane of magnesium di boride allow it to conduct electricity similar to iso electronic graphite. In addition, in 2001 this material was found to be a high-temperature super conductor.

Certain other metal borides find specialized applications as hard materials for cutting tools.

From the structural perspective, the most distinctive chemical compounds of boron are the hydrides. Included in this series are the cluster compounds do deca borate $(B_{12}H_{12}^{2-})$, deca borane $(B_{10}H_{14})$, and the carboranes such as $C_2B_{10}H_{12}$. Characteristically such compounds feature boron with coordination numbers greater than four.

3–3 - Isotopes



Ball-and-stick model of superconductor magnesium di boride. Boron atoms lie in hexagonal aromatic graphite-like layers, with a charge of -1 per boron. Magnesium (II) ions lie between layers

Boron has two naturally occurring and stable isotopes, ^{11}B (80.1 %) and ^{10}B (19.9 %). The mass difference results in a wide range of $\delta^{11}B$ values, which are defined as a fractional difference

between the ¹¹B and ¹⁰B and traditionally expressed in parts per thousand, in natural waters ranging from -16 to +59. There are 13 known isotopes of boron, the shortest-lived isotope is ⁷B which decays through proton emission and alpha decay. It has a half-life of 3.5×10^{-22} s. Isotopic fractionation of boron is controlled by the exchange reactions of the boron species B(OH)₃ and [B(OH)₄]⁻. Boron isotopes are also fractionated during mineral crystallization, during H₂O phase changes in hydrothermal systems, and during hydrothermal alteration of rock. The latter effect results in preferential removal of the ¹⁰B(OH)₄ ion onto clays. It results in solutions enriched in ¹¹B(OH)₃ and therefore may be responsible for the large ¹¹B enrichment in seawater relative to both oceanic crust and continental crust; this difference may act as an isotopic signature. The exotic ¹⁷B exhibits a nuclear halo, i.e. its radius is appreciably larger than that predicted by the liquid drop model.

The ¹⁰B isotope is good at capturing thermal neutrons . Natural boron is about 20% ¹⁰B and 80 % ¹¹B. The nuclear industry enriches natural boron to nearly pure ¹⁰B. The less-valuable by-product, depleted boron, is nearly pure ¹¹B.

3-3-1 - Commercial isotope enrichment

Because of its high neutron cross-section, boron-10 is often used to control fission in nuclear reactors as a neutron-capturing substance. Several industrial-scale enrichment processes have been developed, however only the fractionated vacuum distillation of the di methyl ether adduct of boron tri fluoride (DME-BF₃) and column chromate graphy of borates are being used.

3-**3** - **2** - **Enriched boron** (boron -10)

Enriched boron or ¹⁰B is used in both radiation shielding and in boron neutron capture therapy. In the latter, a compound containing ¹⁰B is attached to a muscle near a tumor. The patient is then treated with a relatively low dose of thermal neutrons. This causes energetic and short range alpha radiation from the boron to bombard the tumor.



Neutron cross section of boron (top curve is for ${}^{10}B$ and bottom curve for ${}^{11}B$)

In nuclear reactors, ¹⁰B is used for reactivity control and in emergency shutdown systems. It can serve either function in the form of borosilicate control rods or as boric acid. In pressurized water reactors, boric acid is added to the reactor coolant when the plant is shut down for refueling. It is then slowly filtered out over many months as fissile material is used up and the fuel becomes less reactive.

In future manned interplanetary spacecraft, ¹⁰B has a theoretical role as structural material (as boron fibers or BN nano tube material) which would also serve a special role in the radiation shield. One of the difficulties in dealing with cosmic rays, which are mostly high energy protons, is that some secondary radiation from interaction of cosmic rays and spacecraft materials is high energy spallation neutrons. Such neutrons can be moderated by materials high in light elements such as poly ethylene, but the moderated neutrons continue to be a radiation hazard unless actively absorbed in the shielding. Among light elements that absorb thermal neutrons, ⁶Li and ¹⁰B appear as potential spacecraft structural materials which serve both for mechanical reinforcement and radiation protection.

3-**3** - **3** - **Depleted boron** (boron -11)

Cosmic radiation will produce secondary neutrons if it hits spacecraft structures. Those neutrons will be captured in ¹⁰B, if it is

present in the spacecraft's semi conductors, producing a gamma ray, an alpha particle, and a lithium ion. These resultant decay products may then irradiate nearby semiconductor 'chip' structures, causing data loss (bit flipping, or single event upset). In radiation hardened semiconductor designs, one countermeasure is to use **depleted boron** which is greatly enriched in ¹¹B and contains almost no ¹⁰B. ¹¹B is largely immune to radiation damage. Depleted boron is a by-product of the nuclear industry.

¹¹B is also a candidate as a fuel for aneutronic fusion. When struck by a proton with energy of about 500 keV, it produces three alpha particles and 8.7 MeV of energy. Most other fusion reactions involving hydrogen and helium produce penetrating neutron radiation, which weakens reactor structures and induces long term radioactivity thereby endangering operating personnel. Whereas, the alpha particles from ¹¹B fusion can be turned directly into electric power, and all radiation stops as soon as the reactor is turned off.

3-3-4- NMR spectroscopy :

Both ¹⁰B and ¹¹B possess nuclear spin. The nuclear spin of ¹⁰B is 3 and that of ¹¹B is 3/2. These isotopes are, therefore, of use in nuclear magnetic resonance spectroscopy; and spectrometers specially adapted to detecting the boron-11 nuclei are available commercially. The ¹⁰B and ¹¹B nuclei also cause splitting in the resonances of attached nuclei.

3-4- Occurrence



Borax crystals

Boron is a relatively rare element in the Earth's crust, representing only 0.001 %. The worldwide commercial borate deposits are estimated at 10 million tones . Turkey and the United States are the world's largest producers of boron . Turkey has almost 72 % of the world's boron reserves . Boron does not appear on Earth in elemental form but is found combined in borax , boric acid , colemanite , kernite , ulexite and borates. Boric acid is sometimes found in volcanic spring waters .

Ulexite is one of over a hundred borate minerals; it is a fibrous crystal where individual fibers can guide light like optical fibers.

Economically important sources of boron are rasorite (kernite) and tincal (borax ore). They are both found in the Mojave Desert of California, but the largest borax deposits are in Central and Western Turkey including the provinces of Eskişehir, Kütahya and Balıkesir.

4 - Production

The production of boron compounds does not involve formation of elemental boron, but exploits the convenient availability of borates.

The earliest routes to elemental boron involved reduction of boric oxide with metals such as magnesium or aluminium. However the product is almost always contaminated with metal borides. Pure boron can be prepared by reducing volatile boron halides with hydrogen at high temperatures. Ultrapure boron, for the use in semiconductor industry, is produced by the decomposition of diborane at high temperatures and then further purified with the zone melting or Czochralski processes.

4 – 1 - Market trend

Estimated global consumption of boron rose to a record 1.8 million tones of B_2O_3 in 2005, following a period of strong growth in demand from Asia, Europe and North America. Boron mining and refining capacities are considered to be adequate to meet expected levels of growth through the next decade.

The form in which boron is consumed has changed in recent years. The use of ores like colemanite has declined following concerns over arsenic content. Consumers have moved towards the use of refined borates and boric acid that have a lower pollutant content. The average cost of crystalline boron is \$5/g.

Increasing demand for boric acid has led a number of producers to invest in additional capacity. Eti Mine Company of Turkey opened a new boric acid plant with the production capacity of 100,000 tones per year at Emet in 2003. Rio Tinto Group increased the capacity of its boron plant from 260,000 tones per year in 2003 to 310,000 tones per year by May 2005, with plans to grow this to 366,000 tones per year in 2006. Chinese boron producers have been unable to meet rapidly growing demand for high quality borates. This has led to imports of sodium tetra borate (borax) growing by a hundredfold between 2000 and 2005 and boric acid imports increasing by 28 % per year over the same period.

The rise in global demand has been driven by high growth rates in fiber glass and borosilicate production. A rapid increase in the manufacture of reinforcement-grade fiberglass in Asia with a consequent increase in demand for borates has offset the development of boron-free reinforcement-grade fiberglass in Europe and the USA. The recent rises in energy prices may lead to greater use of insulation-grade fiberglass, with consequent growth in the boron consumption. Roskill Consulting Group forecasts that world demand for boron will grow by 3.4 % per year to reach 21 million tonnes by 2010. The highest growth in demand is expected to be in Asia where demand could rise by an average 5.7 % per year.

5 - Applications

Nearly all boron ore extracted from the Earth is destined for refinement into boric acid and sodium tetra borate penta hydrate . In the United States, 70 % of the boron is used for the production of glass and ceramics.

5 - 1 - Glass and ceramics :



Borosilicate glassware. Displayed are two beakers and a test tube.

Borosilicate glass , which is typically $12-15 \% B_2O_3$, $80 \% SiO_2$, and $2 \% Al_2O_3$, has a low coefficient of thermal expansion giving it a good resistance to thermal shock. Duran and Pyrex are two major brand names for this glass, used both in laboratory glass ware and in consumer cook ware and bake ware , chiefly for this resistance.

Boron filaments are high - strength, light weight materials that are used chiefly for advanced aerospace structures as a component of composite materials, as well as limited production consumer and sporting goods such as golf clubs and fishing rods. The fibers can be produced by chemical vapor deposition of boron on a tungsten filament.

Boron fibers and sub-millimeter sized crystalline boron springs are produced by laser-assisted chemical vapor deposition. Translation of the focused laser beam allows to produce even complex helical structures. Such structures show good mechanical properties (elastic modulus 450 GPa, fracture strain 3.7 % , fracture stress 17 GPa) and can be applied as reinforcement of ceramics or in micromechanical systems.

5 - 2 - Detergent formulations and bleaching agents :

Borax is used in various household laundry and cleaning products, including the well - known "20 Mule Team Borax" laundry

booster and "Boraxo" powdered hand soap. It is also present in some tooth bleaching formulas.

Sodium per borate serves as a source of active oxygen in many detergents, laundry detergents, cleaning products, and laundry bleaches. However, despite its name, "Bora teem" laundry bleach no longer contains any boron compounds, using sodium percarbonate instead as a bleaching agent.

5 - 3 - Insecticides

Boric acid is used as an insecticide , notably against ants, fleas, and cockroaches.

5 - 1 - Semi conductors

Boron is a useful dopant for such semiconductors as silicon, germanium, and silicon carbide. Having one fewer valence electron than the host atom, it donates a hole resulting in p-type conductivity. Traditional method of introducing boron into semiconductors is via its atomic diffusion at high temperatures. This process uses either solid (B_2O_3), liquid (BBr₃), or gaseous boron sources (B_2H_6 or BF₃). However, after 1970s, it was mostly replaced by ion implantation, which relies mostly on BF₃ as a boron source.^[71] Boron trichloride gas is also an important chemical in semiconductor industry, however not for doping but rather for plasma etching of metals and their oxides. Tri ethyl borane is also injected into vapor deposition reactors as a boron source. Examples are the plasma deposition of boron-containing hard carbon films, silicon nitride - boron nitride films, and for doping of diamond film with boron.

5 - 5 – Magnets :

Boron is a component of neodymium magnets $(Nd_2Fe_{14}B)$, which are the strongest type of permanent magnet. They are found in a variety of domestic and professional electromechanical and electronic devices, such as magnetic resonance imaging (MRI), various motors and actuators, computer HDDs, CD and DVD players, mobile phones, timer switches, speakers, and so on.

5 - 6 - High - hardness and abrasive compounds



Boron carbide is used for inner plates of ballistic vests

Several boron compounds are known for their extreme hardness and toughness.

Boron carbide and cubic boron nitride powders are widely used as abrasives. Metal borides are used for coating tools through chemical vapor deposition or physical vapor deposition. Implantation of boron ions into metals and alloys, through ion implantation or ion beam deposition, results in a spectacular increase in surface resistance and micro hardness. Laser alloying has also been successfully used for the same purpose. These borides are an alternative to diamond coated tools, and their (treated) surfaces have similar properties to those of the bulk boride.

5-6-1 - Boron carbide

Boron carbide is a ceramic material which is obtained by decomposing B_2O_3 with carbon in the electric furnace :

 $2 B_2 O_3 + 7 C \rightarrow B_4 C + 6 CO$

Boron carbide's structure is only approximately B_4C , and it shows a clear depletion of carbon from this suggested stoichiometric ratio. This is due to its very complex structure. The substance can be seen with empirical formula $B_{12}C_3$ (i.e., with B_{12} dodecahedra being a motif), but with less carbon as the suggested C_3 units are replaced with B-C chains, and there are smaller (B_6) octahedra present as well. The repeating polymer plus semi - crystalline structure of boron carbide gives it great structural strength per weight. It is used in tank armor, bullet proof vests, and numerous other structural applications.

Boron carbide's ability to absorb neutrons without forming longlived radio nuclides (especially when doped with extra boron-10) makes the material attractive as an absorbent for neutron radiation arising in nuclear power plants. Nuclear applications of boron carbide include shielding, control rods and shut-down pellets. Within control

Mechanical properties of BCN solids and ReB ₂						
Material	Diamond	cubic- BC ₂ N	cubic- BC ₅	cubic- BN	B ₄ C	ReB ₂
Vickers hardness (GPa)	115	76	71	62	38	22
Fracture toughness (MPa m ^{1/2})	5.3	4.5	9.5	6.8	3.5	

rods, boron carbide is often powdered, to increase its surface area.^[75]

5 – **6** - **2** - **Other super hard boron compounds**

• Hetero diamond (also called BCN);

• Boron nitride. This material is isoelectronic to carbon. Similar to carbon, it has both hexagonal (soft graphite-like h-BN) and cubic (hard, diamond-like c-BN) forms. h-BN is used as a high temperature component and lubricant. c-BN, also known under commercial name borazon, is a superior abrasive. Its hardness is only slightly smaller, but chemical stability is superior to that of diamond.

• Rhenium di 5 - 6 - 1 - boride can be produced at ambient pressures, but is rather expensive because of rhenium. The hardness of ReB₂ exhibits considerable anisotropy because of its hexagonal

layered structure. Its value is comparable to that of tungsten carbide, silicon carbide, titanium di boride or zirconium diboride.

• $AlMgB_{14} + TiB_2$ composites possess high hardness and wear resistance and are used in either bulk form or as coatings for components exposed to high temperatures and wear loads.

5 – 7 - Shielding in nuclear reactors :

Boron shielding is used as a control for nuclear reactors, taking advantage of its high cross-section for neutron capture.

5 – 8 - Other non medical uses



Boron - containing emergency flare



Launch of Apollo 15 Saturn V rocket, using tri ethyl borane ignitor

• Because of its distinctive green flame, amorphous boron is used in pyrotechnic flares . Starch and casein - based adhesives contain sodium tetra borate deca hydrate ($Na_2B_4O_7$ •10 H₂O)

• Some anti - corrosion systems contain borax .

• Sodium borates are used as a flux for soldering silver and gold and with ammonium chloride for welding ferrous metals.^[82] They are also fire retarding additives to plastics and rubber articles.^[83]

- Boric acid (also known as ortho boric acid) H_3BO_3 is used in the production of textile fiberglass and flat panel displays and in many PVAc and PVOH based adhesives.

• Tri ethyl borane is a substance which ignites the JP-7 fuel of the Pratt & Whitney J58 turbojet/ramjet engines powering the Lockheed SR-71 Blackbird. It was also used to ignite the F-1 Engines on the Saturn V Rocket utilized by NASA's Apollo and Skylab programs from 1967 until 1973. Tri ethyl borane is suitable for this because of its pyrophoric properties, especially the fact that it burns with a very high temperature. Tri ethyl borane is an industrial initiator in radical reactions, where it is effective even at low temperatures.

5 – 9 - Research areas

Magnesium di boride is an important super conducting material with the transition temperature of 39 K . Mg B_2 wires are produced with the powder-in-tube process and applied in superconducting magnets.

Amorphous boron is used as a melting point depressant in nickel - chromium braze alloys .

Hexagonal boron nitride forms atomically thin layers, which have been used to enhance the electron mobility in graphene devices . It also forms nano tubular structures (BNNTs), which have with high strength, high chemical stability, and high thermal conductivity, among its list of desirable properties.

6 - Biological role :

There is a boron-containing natural antibiotic , boro mycin , isolated from streptomyces . Boron is an essential plant nutrient, required primarily for maintaining the integrity of cell walls. Conversely, high soil concentrations of > 1.0 ppm can cause marginal and tip necrosis in leaves as well as poor overall growth performance. Levels as low as 0.8 ppm can cause these same symptoms to appear in plants particularly sensitive to boron in the soil. Nearly all plants, even those somewhat tolerant of boron in the soil, will show at least some symptoms of boron toxicity when boron content in the soil is

greater than 1.8 ppm. When this content exceeds 2.0 ppm, few plants will perform well and some may not survive. When boron levels in plant tissue exceed 200 ppm symptoms of boron toxicity are likely to appear.

As an ultra trace element, boron is necessary for the optimal health of rats, although it is necessary in such small amounts that ultra purified foods and dust filtration of air is necessary to induce boron deficiency, which manifest as poor coat or hair quality. Presumably, boron is necessary to other mammals. No deficiency syndrome in humans has been described. Small amounts of boron occur widely in the diet, and the amounts needed in the diet would, by analogy with rodent studies, be very small. The exact physiological role of boron in the animal kingdom is poorly understood.

Boron occurs in all foods produced from plants. Since 1989 its nutritional value has been argued. It is thought that boron plays several biochemical roles in animals, including humans . The U.S. Department of agriculture conducted an experiment in which postmenopausal women took 3 mg of boron a day. The results showed that supplemental boron reduced excretion of calcium by 44%, and activated estrogen and vitamin D, suggesting a possible role in the suppression of osteoporosis. However, whether these effects were conventionally nutritional, or medicinal, could not be determined. The US National Institutes of Health quotes this source:

Total daily boron intake in normal human diets ranges from 2.1 - 4.3 mg boron / day.

6 – 1 - Analytical quantification :

For determination of boron content in food or materials the colorimetric curcumin method is used. Boron has to be transferred to boric acid or borates and on reaction with curcumin in acidic solution, a red colored boron - chelate complex, rosocyanine, is formed .

7 - Boron pharmaceuticals and biologicals

Boric acid has antiseptic, antifungal, and antiviral properties and for this reasons is applied as a water clarifier in swimming pool water treatment. Mild solutions of boric acid have been used as eye antiseptics.

A number of potential boronated pharmaceuticals using boron -10, have been prepared for use in boron neutron capture therapy (BNCT).

Some boron compounds show promise in treating arthritis, though none have as yet been generally approved for the purpose.

Boron is used as an intermediate in pharmaceutical synthesis, but it appeared as an active element in its first-approved organic pharmaceutical in bortezomib, a new class of drug called proteasome inhibitors, which are active in myeloma and one form of lymphoma. The boron atom in bortezomib binds the catalytic site of the 26S proteasome with high affinity and specificity.

7 - 1 - Health issues

Elemental boron, boron oxide , boric acid , borates, and many organo boron compounds are non - toxic to humans and animals (approximately similar to table salt) . The LD₅₀ (dose at which there is 50 % mortality) for animals is about 6 g per kg of body weight. Substances with LD₅₀ above 2 g are considered non-toxic. The minimum lethal dose for humans has not been established, but an intake of 4 g / day was reported without incidents, and medical dosages of 20 g of boric acid for neutron capture therapy caused no problems. Fish have survived for 30 min in a saturated boric acid is more toxic to insects than to mammals, and is routinely used as an insecticide.

The boranes and similar gaseous compounds are quite poisonous. As usual, it is not an element that is intrinsically poisonous, but toxicity depends on structure .

The boranes (boron hydrogen compounds) are toxic as well as highly flammable and require special care when handling. Sodium boro hydride presents a fire hazard due to its reducing nature, and the liberation of hydrogen on contact with acid. Boron halides are corrosive.

Congenital endothelial dystrophy type 2, a rare form of corneal dystrophy, is linked to mutations in SLC4A11 gene that encodes a transporter reportedly regulating the intracellular concentration of boron.

Allotropes of boron



Contents

- 1 Introduction
- 2 Summary of properties
- 3α rhombo hedral boron
- 4β rhombo hedral boron
- 5 γ boron
- 6 Tetragonal boron phases
- 7 High pressure super conducting phase
- 8 Amorphous boron

1 – Introduction :

Elemental boron can exist in several allotropes, the most common of which are crystalline boron and brown amorphous boron. Crystalline boron has four major polymorphs: α , β , γ and T. Whereas the β phase is most stable and others are metastable, the transformation rate is negligible at room temperature, and thus all those phases can exist at ambient conditions.

Crystalline boron is a very hard (Vickers hardness comparable to that of cubic boron nitride), black, diamagnetic material with a melting point of 2080 °C. Pure elemental boron is difficult to extract.

The earliest methods involved reduction of boric oxide with metals such as magnesium or aluminum. However the product is almost always contaminated with metal borides. Pure boron can be prepared by reducing volatile boron halides with hydrogen at high temperatures . Very pure boron, for the use in semiconductor industry, is produced by the decomposition of diborane at high temperatures and then further purified with the zone melting or Czochralski processes. Even more difficult is to prepare pure single crystals of pure boron phases, because of polymorphism, reactivity of boron with impurities, etc.; typical crystal size is ~0.1 mm.

2 - Summary of properties :

Boron phase	α	β	Г	т
Symmetry	Rhombohedral	Rhombohedral	Orthorhombic	Tetragonal
Atoms/unit cell	12	~105	28	192
Density (g/cm ³)	2.46	2.35	2.52	2.36
Vickers hardness (GPa)	42	45	50–58	
Bulk modulus (GPa)	224	184	227	
Bandgap (eV)	2	1.6	2.1	



A fragment of phase diagram of boron reproduced from

		2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
Structure of y-boron	Structure of β -boron	Structure of a-boron

3 - *α* **- rhombohedral boron :**

 α -rhombohedral boron has a unit cell of twelve boron atoms. The structure consists of B₁₂ icosahedra in which each boron atom has five nearest neighbors within the icosahedrons . If the bonding were the conventional covalent type then each boron would have donated 5 electrons. However, boron has only 3 valence electrons, and it is thought that the bonding in the B₁₂ icosahedra is achieved by the so-called 3-center electron-deficient bonds where the electron charge is accumulated at the center of a triangle formed by 3 adjacent atoms.^[12]

The isolated B_{12} icosahedra are not stable; thus boron is not a molecular solid, but the icosahedra in it are connected by strong covalent bonds.

4 - β - rhombohedral boron

 β - rhombohedral boron has a sub cell containing 105–108 atoms — or a unit cell of 320 atoms. Many atoms form B₁₂ icosahedra, but there are also a large number of non-icosahedral atoms as well. For long time, it was unclear whether the α or β phase is most stable at ambient conditions; however, gradually a consensus was reached that β phase as the thermodynamically stable allotrope.

5 - γ – boron :



 γ -boron: Comparison of X-ray diffraction data of Wentorf^[7] (bottom) with the modern data

The γ - phase can be described as a Na Cl - type arrangement of two types of clusters, B_{12} icosahedra and B_2 pairs . It can be produced

by compressing other boron phases to 12–20 GPa, heating to 1500–1800 0C and is quenchable to ambient conditions . There is evidence of significant charge transfer from B_2 pairs to the B_{12} icosahedra in this structure ; in particular, lattice dynamics suggests the presence of significant long - range electrostatic interactions.

This phase was reported by Wentorf in 1965, however neither structure nor chemical composition were established. The structure was solved using *ab initio* crystal structure prediction calculations and confirmed using single crystal X - ray diffraction.

6 - Tetragonal boron phases :

Two tetragonal phases have been reported, T-50 (or α -tetragonal boron) and T-192 (or β -tetragonal boron) with 50 and 192 atoms in the unit cell, respectively. Whereas T-50 has been assigned to a compound (nitride (B₅₀N₂) or carbide (B₅₀C₂)), T-192 is a genuine pure boron phase. It was produced in 1960 by hydrogen reduction of BBr₃ on hot tungsten, rhenium or tantalum filaments at temperatures 1270 –1550 °C (i.e. chemical vapor deposition). Further studies have reproduced the synthesis and confirmed the absence of impurities in this phase.

7 – High - pressure super conducting phase :

Compressing boron above 160 GPa produces a boron phase with an as yet unknown structure. Contrary to other phases, which are semi conductors, this phase is a metal and becomes a super conductor with a critical temperature increasing from 4 K at 160 GPa to 11 K at 250 GPa . This structural transformation occurs at pressures at which theory predicts the icosahedra to dissociate.

8 - Amorphous boron :

Amorphous boron contains B_{12} regular icosahedra that are randomly bonded to each other without long range order. Pure amorphous boron can be produced by thermal decomposition of diborane at temperatures below 1000 °C. Annealing at 1000 °C converts amorphous boron to β -rhombohedral boron. Amorphous boron nano wires (30 –60 nm thick) or fibers can be produced by magnetron sputtering and laser-assisted chemical vapor deposition, respectively; and they also convert to β -rhombohedral boron nano wires upon annealing at 1000 °C.

Boron Ore

Important Boron Ore are :

- I . Borane
- II . Borax
- III . Kernite

I - Borane



Contents :

- 1 Introduction
- 2 Generic formula of boranes
- 3 Naming conventions
- 4 Cluster types
- 5 Bonding in boranes
- 6 Chemistry of boranes
 - 6.1 Properties and reactivity trends
 - 6.2 Synthesis and general reactivity
- 7 History

1 – Introduction :

In chemistry, a **borane** is a chemical compound of boron and hydrogen. The boranes comprise a large group of compounds with the generic formulae of B_xH_y . These compounds do not occur in nature. Many of the boranes readily oxidize on contact with air, some

violently. The parent member BH_3 is called borane, but it is known only in the gaseous state, and dimerises to form di borane, B_2H_6 . The larger boranes all consist of boron clusters that are poly hedral, some of which exist as isomers. For example, isomers of $B_{20}H_{26}$ are based on the fusion of two 10-atom clusters.

The most important boranes are diborane B_2H_6 , penta borane B_5H_9 , and deca borane $B_{10}H_{14}$.

The development of the chemistry of boron hydrides led to new experimental techniques and theoretical concepts. Boron hydrides have been studied as potential fuels, for rockets and for automotive uses . Over the past several decades, the scope of boron hydride chemistry has grown to include cages containing atoms other than boron, such as carbon in the carboranes and metals in the metalla boranes , wherein one or more boron atoms are substituted by metal atoms.

2 - Generic formula of boranes :

The four series of single-cluster boranes have the following general formulae, where "n" is the number of boron atoms:

Туре	formula	notes
closo-	$B_n H_n^{2-}$	No neutral B_nH_{n+2} boranes are known
nido–	$B_{n}H_{n+4}$	
arachno-	B_nH_{n+6}	
hypho-	B_nH_{n+8}	only adducts established

There also exists a series of substituted neutral *hypercloso* - boranes that have the theoretical formulae B_nH_n . Examples include $B_{12}(OCH2Ph)_{12}$, which is a stable derivative of *hypercloso*- $B_{12}H_{12}$.

3 - Naming conventions :

The naming of neutral boranes is illustrated by the following examples, where the Greek prefix shows the number of boron atoms and the number of hydrogen atoms is in brackets :

- B_5H_9 penta borane (9)
- B_6H_{12} hexa borane (12)

The naming of anions is illustrated by the following, where the hydrogen count is specified first followed by the boron count, and finally the overall charge in brackets:

• $B_5H_8^-$ octa hydro penta borate (1–)

Optionally *closo- nido-* etc. (see above) can be added :-

- B_5H_9 , *nido*-penta borane (9)
- B_4H_{10} , *arachno*-tetra borane (10)
- $B_6H_6^{2-}$, hexa hydro-*closo*-hexa borate (2-)

Under stand ably many of the compounds have abbreviated common names.

4 - Cluster types :

It was realized in the early 1970s that the geometry of boron clusters are related and that they approximate to deltahedra or to deltahedra with one or more vertices missing. The deltahedra that are found in borane chemistry are (using the names favoured by most chemists)

deltahedron	vertices
Trigonal bipyramid	5
Octahedron	6
Pentagonal bipyramid	7
Dodecahedron	8
Tri capped trigonal prism	9
Bi capped square antiprism	10
Octa deca hedron	11
Icosahedron	12

One feature of these deltahedra is that boron atoms at the vertices may have different numbers of boron atoms as near neighbors

For example, in the pentagonal bipyramid, 2 borons have 3 neighbors, 3 have 4 neighbors, whereas in the octahedral cluster all vertices are the same, each boron having 4 neighbors. These differences between the boron atoms in different positions are important in determining structure, as they have different chemical shifts in the ¹¹B NMR spectra.





 B_6H_{10} is a typical example. Its geometry is, in essence, a 7boron framework (pentagonal bipyramid), missing a vertex that had the highest number of near neighbors, e.g., a vertex with 5 neighbors The extra hydrogen atoms bridge around the open face. A notable exception to this general scheme is that of B_8H_{12} , which would be expected to have a *nido-* geometry (based on $B_9H_9^{2-}$ missing 1 vertex), but is similar in geometry to B_8H_{14} , which is based on $B_{10}H_{10}^{2-}$.

The names for the series of boranes are derived from this general scheme for the cluster geometries:-

• *Hyper closo* - (from the Greek for "over cage") a closed complete cluster, e.g., B_8Cl_8 is a slightly distorted dodecahedron

• *closo*- (from the Greek for "cage") a closed complete cluster, e.g., icosa hedral $B_{12}H_{12}^{2-}$

• *nido* - (from the Latin for "nest") B occupies n vertices of an n+1 deltahedron, e.g., B_5H_9 an octahedron missing 1 vertex

• *arachno*- (from the Greek for "spiders web") B occupies n vertices of an n+2 deltahedron e.g. B_4H_{10} an octahedron missing 2 vertices

• *hypho*- (from the Greek for "net") B occupies n vertices of an n+3 deltahedron possibly B_8H_{16} has this structure, an octahedron missing 3 vertices

• *conjuncto-* 2 or more of the above are fused together, eg., the edge or two vertex fused $B_{19}H_{22}^{1-}$, face or three vertex fused $B_{21}H_{18}^{1-}$, and four vertex fused $B_{20}H_{16}$

5 - Bonding in boranes :

Boranes are electron - deficient and pose a problem for conventional descriptions of covalent bonding that involves shared electron pairs. BH₃ is a trigonal planar molecule (D_{3h} molecular symmetry). Diborane has a hydrogen - bridged structure, see the diborane article. The description of the bonding in the larger boranes formulated by William Lipscomb involved:

- 3-center 2-electron B-H-B hydrogen bridges
- 3-center 2-electron B-B-B bonds
- 2-center 2-electron bonds (in B-B, B-H and BH₂)

The styx number was introduced to aid in electron counting where s = count of 3-center B-H-B bonds; t = count of 3-center B-B-B bonds; y = count of 2-center B-B bonds and x = count of BH₂ groups. Lipscomb's methodology has largely been superseded by a molecular orbital approach, although it still affords insights. The results of this have been summarized in a simple but powerful rule, PSEPT, often known as Wade's rules, that can be used to predict the cluster type, *closo-*, *nido-*, etc. The power of this rule is its ease of use and general applicability to many different cluster types other than boranes. There are continuing efforts by theoretical chemists to improve the treatment of the bonding in boranes — an example is Stone's tensor surface harmonic treatment of cluster bonding. A recent development is fourcenter two - electron bond.

6 - Chemistry of boranes :

6 - 1 - Properties and reactivity trends :

Boranes are all colourless and diamagnetic. They are reactive compounds and some are pyrophoric. The majority are highly poisonous and require special handling precautions.

closo-

There is no known neutral closo borane. Salts of the closo anions, $B_n H_n^{2-}$ are stable in neutral aqueous solution, and their stabilities increase with size. The salt $K_2 B_{12} H_{12}$ is stable up to 700°.

nido-

Penta borane (9) and deca borane (14) are the most stable *nido*-boranes, in contrast to *nido* – B_8H_{12} that decomposes above - 35° .

arachno –

Generally these are more reactive than *nido*-boranes and again larger compounds tend to be more stable.

6 - 2 - Synthesis and general reactivity

Borane BH₃

This is an important intermediate in the pyrolosis of diborane to produce higher boranes.

Diborane B_2H_6 and higher boranes

Diborane is made industrially by the reduction of BF_3 , and is the starting point for preparing the higher boranes. It has been studied extensively.

General reactivity :

Typical reactions of boranes are :

* electrophilic substitution

- * nucleophilic substitution by Lewis bases
- * deprotonation by strong bases
- * cluster building reactions with boro hydrides
- * reaction of a *nido* borane with an alkyne to give a carborane cluster

Boranes can act as ligands in coordination compounds. Hapticities of η^1 to η^6 have been found, with electron donation involving bridging H atoms or donation from B - B bonds. For example, *nido*-B₆H₁₀ can replace ethene in Zeise's salt to produce Fe (η^2 -B₆H₁₀) (CO)₄.

Boranes can react to form hetero – boranes , e.g., carboranes or metalloboranes (clusters that contain boron and metal atoms).

7 – History :

The development of the chemistry of boranes posed two challenges to chemists. First, new laboratory techniques had to be developed to handle these very reactive compounds; second, the structures of the compounds challenged the accepted theories of chemical bonding.

The German chemist Alfred Stock first characterized the series of boron-hydrogen compounds. His group developed the glass vacuum line and techniques for handling the compounds. However, exposure to mercury (used in mercury diffusion pumps and float valves) caused Stock to develop mercury poisoning, which he documented in the first scientific papers on the subject. The chemical bonding of the borane clusters was investigated by Lipscomb and his co-workers. Lipscomb was awarded the Nobel prize in Chemistry in 1976 for this work. PSEPT, (Wades rules) can be used to predict the structures of boranes .

Interest in boranes increased during World War II due to the potential of uranium borohydride for enrichment of the uranium isotopes. In the US, a team led by Schlesinger developed the basic chemistry of the boron hydrides and the related aluminium hydrides. Although uranium borohydride was not utilized for isotopic separations, Schessinger's work laid the foundation for a host of boron hydride reagents for organic synthesis, most of which were developed by his student Herbert C. Brown. Borane - based reagents are now widely used in organic synthesis. For example, sodium borohydride is the standard reagent for converting aldehydes and ketones to alcohols. Brown was awarded the Nobel prize in Chemistry in 1979 for this work.^[2] In the 1950s and early '60s, the US and USSR investigated boron hydrides as high-energy fuels (ethyl boranes , for example) for high speed aircraft, such as the XB-70 Valkyrie. The development of advanced surface-to-air missiles made the fast aircraft redundant, and the fuel programs were terminated, although tri ethyl borane (TEB) was later used to ignite the engines of the SR-71 Blackbird.
II - Borax



IUPAC name : Sodium tetra borate dec	a hydrate
Molecular Formula	$Na_{2}B_{4}O_{7} \cdot 10 \text{ H}_{2}O \text{ or}$ $Na_{2}[B_{4}O_{5}(OH)_{4}] \cdot 8H_{2}O$
Molar Mass	381 (deca hydrate)
Appearance	white solid
Density	1.73 g / cm ³ (solid)
Melting point	743 °C (anhydrous)
Boiling point	1575 °C



Old steam tractor and Borax wagons, Death Valley

Contents

- 1 Introduction
- 2 Uses
 - 2.1 House hold products
 - 2.2 Buffer

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- 2.5 Small scale mining
- 2.6 Putty
- $_{\circ}$ 2.7 Food additive
- \circ 2.8 Other uses
- 3 Natural sources
- 4 Toxicity
- 5 Chemistry

1 – Introduction :

Borax, also known as **sodium borate**, **sodium tetra borate**, or **disodium tetra borate**, is an important boron compound, a mineral, and a salt of boric acid. It is usually a white powder consisting of soft colorless crystals that dissolve easily in water.

Borax has a wide variety of uses. It is a component of many detergents, cosmetics, and enamel glazes. It is also used to make buffer solutions in biochemistry, as a fire retardant, as an anti-fungal compound for fiber glass, as an insecticide, as a flux in metallurgy, a texturing agent in cooking, and as a precursor for other boron compounds.

The term *borax* is used for a number of closely related minerals or chemical compounds that differ in their crystal water content, but usually refers to the deca hydrate. Commercially sold borax is usually partially dehydrated.

The word *borax* is Persian and originates in the Middle-Persian *būrak*.

Borax first came into common use in the late 19th century when Francis Marion Smith's Pacific Coast Borax Company began to market and popularize a large variety of applications under the famous 20 Mule Team Borax trademark, named for the method by which borax was originally hauled out of the California and Nevada deserts in large enough quantities to make it cheap and commonly available.

2 - Uses :

2 – 1 - House hold products :

Borax is used in various household laundry and cleaning products, including the "20 Mule Team Borax" laundry booster and "Boraxo" powdered hand soap. However, despite its name, "Borateem" laundry bleach no longer contains borax or other boron compounds.

Borax is also present in some tooth bleaching formulas.

2 – 2 - Buffer

Sodium borate is used in biochemical and chemical laboratories to make buffers, e.g. for gel electrophoresis of DNA, such as TBE or the newer SB buffer or BBS (borate buffered saline) in coating procedures. Borate buffers (usually at pH 8) are also used as preferential equilibration solution in DMP-based crosslinking reactions.

2 - 3 -Co - complexing

Borax as a source of borate has been used to take advantage of the co - complexing ability of borate with other agents in water to form complex ions with various substances. Borate and a suitable polymer bed are used to chromatograph non - glycosylated hemoglobin differentially from glycosylated hemoglobin (chiefly HbA1c), which is an indicator of long term hyperglycemia in diabetes mellitus. Borate and a proprietary synthetic amino acid, Deselex (from Henkel) have been used to complex water "hardness" cations to make a non - precipitating water "softener". Borate alone does not have a high affinity for "hardness" cations, although it has been used for that purpose.

2-4-Flux:

A mixture of borax and ammonium chloride is used as a flux when welding iron and steel. It lowers the melting point of the unwanted iron oxide (*scale*), allowing it to run off. Borax is also used mixed with water as a flux when soldering jewelry metals such as gold or silver. It allows the molten solder to flow evenly over the joint in question. Borax is also a good flux for 'pre - tinning' tungsten with zinc - making the tungsten soft - solder able .

2 – 5 - Small - scale mining :

Borax is replacing mercury as the preferred method for extracting gold in small - scale mining facilities. The method is called the borax method and is used in the Philippines .

2-6-Putty:

A rubbery polymer some times called **flubber**, **gluep** or **glurch** can be made by cross linking polyvinyl alcohol with a borax. Making flubber from polyvinyl acetate based glues, such as Elmer's Glue, and borax is a common elementary education experiment.

2-7 – Food additive :

Borax, given the E number *E285*, is used as a food additive in some countries but is banned in the United States. As a consequence, certain foods, such as caviar, produced for sale in the U.S. contain higher levels of salt to assist preservation . Its use as a cooking ingredient is to add a firm rubbery texture to the food, or as a preservative. In oriental cooking it is mostly used for its texturing properties. In Asia, Borax (Chinese : pinyin : $péng sh\bar{a}$) was found to have been added to some Chinese foods like the hand - pulled noodles *lamian* and some rice noodles like Shahe fen, Kway Teow, and Chee Cheong Fun recipes . In Indonesia it is a common, but forbidden, additive to such foods as noodles, bakso (meat balls), and steamed rice. The country's Directorate of Consumer Protection warns of the risk of liver cancer with high consumption over a period of 5–10 years.

2 – 8 – Other uses :

- Ingredient in enamel glazes
- Component of glass , pottery , and ceramics

• Borax can be used as an additive in ceramic slips and glazes to improve fit on wet, green ware, and bisque.

• Fire retardant

• Anti - fungal compound for fiber glass and cellulose insulation

- Moth proofing 10 % solution for wool
- Anti fungal foot soak
- Physical insecticide to kill ants, cockroaches and fleas

• Precursor for sodium per borate mono hydrate that is used in detergents, as well as for boric acid and other borates

• Tackifier ingredient in casein , starch and dextrin based adhesives

• Precursor for Boric acid, a tackifier ingredient in polyvinyl acetate, polyvinyl alcohol based adhesives

• Treatment for thrush in horses' hooves

• Used to make indelible ink for dip pens by dissolving shellac into heated borax

• Curing agent for snake skins

• Curing agent for salmon eggs, for use in sport fishing for salmon

• Swimming pool buffering agent to control the pH

• Neutron absorber, used in nuclear reactors and spent fuel pools to control reactivity and to shut down a nuclear chain reaction

• As a micronutrient fertilizer to correct boron-deficient soils.

- To clean the brain cavity of a skull for mounting
- To color fires with a green tint

• Was traditionally used to coat dry - cured meats such as hams to protect them from becoming fly - blown during further storage.

- Is found in some commercial vitamin supplements
- For stopping car radiator and engine block leaks
- As an important component in Slime

3 - Natural sources :

Borax occurs naturally in evaporite deposits produced by the repeated evaporation of seasonal lakes. The most commercially important deposits are found in Turkey; Boron, California; and Searles Lake, California. Also, it has been found at many other locations in the Southwestern United States, the Atacama desert in Chile, and in Tibet and Romania. Borax can also be produced synthetically from other boron compounds. Naturally occurring Borax, (known by the trade name Rasorite - 46 in USA and many other countries) is refined by a process of re-crystallization.

4 – Toxicity :

Borax , sodium tetra borate deca hydrate , is not acutely toxic. Its LD_{50} (median lethal dose) score is tested at 2.66 g / kg in rats: a significant dose of the chemical is needed to cause severe symptoms or death. The lethal dose is not necessarily the same for humans.

Sufficient exposure to borax dust can cause respiratory and skin irritation. Ingestion may cause gastrointestinal distress including nausea, persistent vomiting, abdominal pain, and diarrhea. Effects on the vascular system and brain include headaches and lethargy, but are less frequent. "In severe poisonings, a beefy red skin rash affecting palms, soles, buttocks and scrotum has been described. With severe poisoning, erythematous and exfoliative rash, unconsciousness, respiratory depression, and renal failure".

A reassessment of boric acid/borax by the United States Environmental Protection Agency Office of Pesticide Programs found potential developmental toxicity (especially effects on the testes).^[21] Boric acid solutions used as an eye wash or on abraded skin are known to be particularly toxic to infants, especially after repeated use, because of the slow elimination rate . At a recent European Diagnostics Manufacturing Association (EDMA) meeting, several new additions to the Substance of Very High Concern (SVHC) candidate list in relation to the Registration, Evaluation, Authorization and restriction of Chemicals Regulations 2007 (REACH) were discussed. The registration and review completed as part of REACH has changed the classification of Sodium Tetraborate CAS 1303-96-4 to *toxic for reproduction*.

5 - Chemistry :

The term *borax* is often used for a number of closely related minerals or chemical compounds that differ in their crystal water content :

- Anhydrous borax (Na₂B₄O₇)
- Borax penta hydrate $(Na_2B_4O_7 \cdot 5H_2O)$
- Borax deca hydrate ($Na_2B_4O_7 \cdot 10H_2O$)

Borax is generally described as $Na_2B_4O_7 \cdot 10H_2O$. How ever, it is better formulated as $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$, since borax contains the $[B_4O_5(OH)_4]^{2^-}$ ion. In this structure, there are two four-coordinate boron atoms (two BO_4 tetra hedra) and two three-coordinate boron atoms (two BO_3 triangles).

Borax is also easily converted to boric acid and other borates, which have many applications. Its reaction with hydrochloric acid to form boric acid is :

 $Na_2B_4O_7 \cdot 10H_2O + 2HCl \rightarrow 4 B(OH)_3 [or H_3BO_3] + 2NaCl + 5H_2O$

The "deca hydrate" is sufficiently stable to find use as a primary standard for acid base titrimetry.

When borax is added to a flame, it produces a yellow green color. This property has been tried in amateur fire works, but borax in this use is not popular because its waters of hydration inhibit combustion of compositions and make it an inferior source of the boron that is responsible for most of the green color, and that is overwhelmed by the yellow contributed to the flame by sodium.

How ever, commercially available borax can be mixed with flammables such as methanol to give the characteristic green flame of boron when ignited, which then slowly gives way to the characteristic yellow - orange flame of the sodium.

III - Kernite

Category	Inoborates	
Chemical formula	$Na_2B_4O_6(OH)_2 \cdot 3(H_2O)$	
Molar mass	290	
Color	Colorless, white	
Crystal habit	Crystalline - Coarse - Occurs as well -	
	formed coarse sized crystals	
Crystal system	Monoclinic,	
Mohs scale hardness	2.5 - 3	
Luster	Vitreous - Pearly	
Streak	white	
Specific gravity	1.9 - 1.92, Average = 1.91	
Optical properties	Biaxial (-), 2V=80	
Refractive index	$n\alpha = 1.454,$	
	$n\beta = 1.472,$	
	$n\gamma = 1.488$	
Birefringence	δ=0.0340	
Other characteristics	Non - radioactive, non-fluorescent,	
	non - magnetic	

Kernite, also known as **rasorite** is a hydrated sodium borate hydroxide mineral with formula $Na_2B_4O_6(OH)_2 \cdot 3H_2O$. It is a colorless to white mineral crystallizing in the monoclinic crystal system typically occurring as prismatic to acicular crystals or granular masses. It is relatively soft with Mohs hardness of 2.5 to 3 and light with a specific gravity of 1.91. It exhibits perfect cleavage and a brittle fracture. Kernite is used to produce borax which can be used in a variety of soaps.

The mineral was discovered in 1926 in Kern County, California and later named for the county. Kern County was the only known source of kernite for many years, but kernite is now also mined in Argentina, Spain, and Turkey. It occurs in sedimentary evaporite deposits in arid regions. The largest documented single crystal of kernite measured 2.44 x 0.9 x 0.9 m³ and weighed ~3.8 tons.

Borazon or Cubic Boron Nitride (CBN)

1 – Introduction :

Borazon is a brand name of a cubic form of boron nitride (CBN). It is one of the hardest known materials, along with various forms of diamond and boron nitride. Borazon is a crystal created by heating equal quantities of boron and nitrogen at temperatures greater than 1800 °C at 7 GPa (1 million lbf / in²). Borazon is the only substance other than those listed above that can scratch a diamond. A diamond will also scratch Borazon.

Borazon was first produced in 1957 by Robert H. Wentorf, Jr., a physical chemist working for the General Electric Company.^[2] In 1969, General Electric adopted the name Borazon as its trade mark for the material.

2 - Uses and production ;

Prior to the production of Borazon, diamond was the preferred abrasive used for grinding very hard super alloys but it could not be used effectively on steels because carbon tends to dissolve in iron at high temperatures. Aluminium oxide was the conventional abrasive used on hardened steel tools.

Borazon replaced aluminium oxide for grinding hardened steels due to its far superior abrasive properties, comparable to that of diamond . Borazon is used in industrial applications to shape tools, as it can withstand temperatures greater than 2000 °C , much higher than that of a pure diamond at 871 °C . Other uses include jewellery designing , glass cutting and laceration of diamonds .

CBN - coated grinding wheels, referred to as Borazon wheels, are routinely used in the machining of hard ferrous metals, cast irons, and nickel - base and cobalt - base super alloys . They can grind more material , to a higher degree of accuracy , than any other abrasive. The limiting factor in the life of such tools is typically determined not by wear on the cutting surface but by its break - down and separation from the metal core resulting from failure of the bonding layer .





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1 – Introduction :

Boric acid, also called **hydrogen borate** or **boracic acid** or **ortho boric acid** or **acidum boricum**, is a weak acid of boron often used as an antiseptic, insecticide, flame retardant, as a neutron absorber, and as a precursor of other chemical compounds. It exists in the form of colorless crystals or a white powder and dissolves in water. It has the chemical formula H_3BO_3 , sometimes written $B(OH)_3$. When occurring as a mineral, it is called sassolite.

IUPAC Name : Boric acid ,Tri hydroxide boron Other Names : Ortho boric acid , Boracic acid ,

Sassolite , Optibor , Borofax				
Molecular formula	$H_3 BO_3$			
Molar mass	62 g mol^{-1}			
Appearance	White crystalline solid			
Density	$1.435 \text{ g} / \text{cm}^3$			
Melting point	170.9 °C			
Boiling point	300 °C			
Solubility in water	2.52 g / 100 mL (0 °C) 4.72 g / 100 mL (20 °C) 5.7 g / 100 mL (25 °C) 19.10 g / 100 mL (80 °C) 27.53 g / 100 mL (100 °C)			
Solubility in other solvents	Soluble in lower alcohols moderately soluble in pyridine very slightly soluble in acetone			
Acidity (pK_a)	9.24			
Molecular shape	Trigonal planar			
Dipole moment	Zero			
Hazards				
EU classification	Harmful (Xn)			
Flash point	Non - flammable.			
LD ₅₀	2660 mg / kg, oral (rat)			
Thermodynamic data	Phase behaviour Solid , liquid , gas			
Spectral data	UV, IR, NMR, MS			

2 - Occurrence :

The free acid is found native in certain volcanic districts such as Tuscany, the Lipari Islands and Nevada, issuing mixed with steam from fissures in the ground; it is also found as a constituent of many minerals (borax , boracites , boronatrocaicite and colemanite). The presence of boric acid and its salts has been noted in seawater. It also exists in plants and especially in almost all fruits.

Boric acid was first prepared by Wilhelm Homberg (1652 – 1715) from borax, by the action of mineral acids, and was given the name *sal sedativum Hombergi* ("sedative salt of Homberg"). However Borates, including boric acid, have been used since the time of the Greeks for cleaning, preserving food, and other activities.

3 - Preparation :

Boric acid may be prepared by reacting borax (sodium tetra borate deca hydrate) with a mineral acid, such as hydrochloric acid :

Na₂B₄O₇ · 10H₂O + 2 HCl → 4 B(OH)₃ [or H₃BO₃] + 2 NaCl + 5 H₂O

4 - Properties

Boric acid is soluble in boiling water. When heated above 170 °C, it dehydrates, forming *meta boric acid* (HBO₂):

 $H_3BO_3 \rightarrow HBO_2 + H_2O$

Meta boric acid is a white, cubic crystalline solid and is only slightly soluble in water. Meta boric acid melts at about 236 °C, and when heated above about 300 °C further dehydrates, forming *tetra boric acid* or *pyro boric acid* ($H_2B_4O_7$) :

 $4 \text{ HBO}_2 \rightarrow H_2 B_4 O_7 + H_2 O$

The term *boric acid* may sometimes refer to any of these compounds. Further heating leads to boron trioxide.

 $H_2B_4O_7 \rightarrow 2 \ B_2O_3 + H_2O$

Boric acid does not dissociate in aqueous solution as a Brøn sted acid , but is a Lewis acid which interacts with water molecules to form the tetra hydroxy borate ion, as confirmed by Raman spectroscopy:

B (OH)₃ + H₂O
$$\rightleftharpoons$$
 B (OH) - 4 + H⁺
($K_a = 5.8 \times 10^{-10} \text{ mol} / 1$; p $K_a = 9.24$)

Poly borate anions are formed at pH 7 - 10 if the boron concentration is higher than about 0.025 mol/L. The best known of these is the *tetra borate* ion, found in the mineral borax:

$$4 \text{ B (OH)} - 4 + 2 \text{ H}^+ \rightleftharpoons B_4 O_2 - _7 + 9 \text{ H}_2 O_2$$

Boric acid makes an important contribution to the absorption of low frequency sound in seawater .

5 - Crystal structure

Crystalline boric acid consists of layers of $B(OH)_3$ molecules held together by hydrogen bonds. The distance between two adjacent layers is 318 pm.

6 - Toxicology

Based on mammalian median lethal dose (LD_{50}) rating of 2,660 mg / kg body mass, boric acid is poisonous if taken internally or inhaled in large quantities. The Thirteenth Edition of the Merck Index indicates that the LD_{50} of boric acid is 5.14 g/kg for oral dosages given to rats, and that 5 to 20 g/kg has produced death in adult humans. The LD_{50} of salt is reported to be 3.75 g / kg in rats according to the *Merck Index*.

Long term exposure to boric acid may be of more concern, causing kidney damage and eventually kidney failure (see links below). Although it does not appear to be carcinogenic, studies in dogs have reported testicular atrophy after exposure to 32 mg / kg bw / day for 90 days. This level is far lower than the LD_{50} .

According to boric acid IUCLID Dataset published by the European Commission, boric acid in high doses shows significant

developmental toxicity and teratogenicity in rabbit, rat, and mouse fetuses as well as cardiovascular defects, skeletal variations, mild kidney lesions, As a consequence, in August 2008, in the 30th ATP to EU directive 67 / 548 / EEC, the EC decided to amend its classification as reprotoxic category 2 and to apply the risk phrases R60 (may impair fertility) and R61 (may cause harm to the unborn child).

7 - Uses :

7 - 1 - Medicinal:

Boric acid solutions used as an eye wash or on abraded skin are known to be especially toxic to infants, especially after repeated use because of its slow elimination rate.

Boric acid can be used as an antiseptic for minor burns or cuts and is sometimes used in dressings or salves. Boric acid is applied in a very dilute solution as an eye wash in a 1.5 % solution (1 tbsp per quart or 15 cm^3 per L) of sterilized water. Boric acid eye wash, typically administered using an eye cup, relieves the eyes after they become irritated from long periods of swimming in the chlorinated water of a swimming pool.

As an anti - bacterial compound, boric acid can also be used as an acne treatment. Boric acid can be used to treat yeast and fungal infections such as candidiasis (vaginal yeast infections) by inserting a vaginal suppository containing 600 mg of boric acid daily for 14 days or for yeast infection of the male pubic region (jock-itch or strong genital odor) by applying the powder to the skin all over the pubic region for several days to a week. It is also used as prevention of athlete's foot, by inserting powder in the socks or stockings, and in solution can be used to treat some kinds of otitis externa (ear infection) in both humans and animals. The preservative in urine sample bottles (red cap) in the UK is boric acid.

7 - 2 - Laboratory:

Tris – borate - EDTA (TBE buffer) is widely used for the electro phoresis of nucleic acids and has a higher buffer capacity than a Tris – acetate - EDTA TAE buffer. It can be used for DNA and RNA poly acryl amide and agarose gel electro phoresis. Is used as a reagent and precursor of other substances, e.g. tetra acetyl di borate.

7-3-Insecticidal

Boric acid was first registered in the US as an insecticide in 1948 for control of cockroaches, termites, fire ants, fleas, silverfish, and many other insects. The product is generally considered to be safe to use in household kitchens to control cockroaches and ants. It acts as a stomach poison affecting the insects' metabolism, and the dry powder is abrasive to the insects' exoskeleton.

Boric acid is also made into a paste or gel form as a powerful and effective insecticide much safer to humans than many other insecticides. The paste or gel has attractants in it to attract insects. The boric acid slowly causes dehydration ,

7 – 4 – Preservation

In combination with its use as an insecticide, boric acid also prevents and destroys existing wet and dry rot in timbers. It can be used in combination with an ethylene glycol carrier to treat external wood against fungal and insect attack. It is possible to buy borate impregnated rods for insertion into wood via drill holes where dampness and moisture is known to collect and sit. It is available in a gel form and inject able paste form for treating rot affected wood without the need to replace the timber. Concentrates of borate-based treatments can be used to prevent slime, mycelium and algae growth, even in marine environments.

Boric acid is added to salt in the curing of cattle hides, calfskins and sheep skins. This helps to control bacteria development and helps to control insects.

7 – 5 – Lubrication

Colloidal suspensions of nano particles of boric acid dissolved in petroleum or vegetable oil can form a remarkable lubricant on ceramic or metal surfaces with a coefficient of sliding friction that decreases with increasing pressure to a value ranging from 0.10 to 0.02. Self - lubricating H_3BO_3 films result from a spontaneous chemical reaction between water molecules and B_2O_3 coatings in a humid environment. In bulk-scale, an inverse relationship exists between friction coefficient and Hertzian contact pressure induced by applied load.

Boric acid is used to lubricate carrom and novuss boards, allowing for faster play.

7 – 6 – Nuclear power :

Boric acid is used in nuclear power plants as a neutron poison to slow down the rate at which fission is occurring. Fission chain reactions are generally driven by the amount of neutrons present (as products from previous fissions). Natural boron is 20 % boron-10 and about 80% boron-11. Boron-10 has a high cross-section for absorption of low energy (thermal) neutrons. By adding more boric acid to the reactor coolant which circulates through the reactor, the probability that a neutron can survive to cause fission is reduced. Therefore, changes in boric acid concentration effectively regulate the rate of fission taking place in the reactor. This method is only used in pressurized water reactors (PWRs). Boron is also dissolved into the spent fuel pools containing used uranium rods. The concentration is high enough to keep neutron multiplication at a minimum.

7 – 7 – Industrial :

The primary industrial use of boric acid is in the manufacture of mono filament fiber glass usually referred to as textile fiber glass. Textile fiber glass is used to reinforce plastics in applications that range from boats, to industrial piping to computer circuit boards. In the jewelry industry, boric acid is often used in combination with denatured alcohol to reduce surface oxidation and fire scale from forming on metals during annealing and soldering operations.

Boric acid is used in the production of the glass in LCD flat panel displays.

In electro plating , boric acid is used as part of some proprietary formulas . One such known formula calls for about a 1 to 10 ratio of H_3BO_3 to NiSO₄, a very small portion of sodium lauryl sulfate and a small portion of H_2SO_4 .

It is also used in the manufacturing of ramming mass, a fine silica - containing powder used for producing induction furnace linings and ceramics.

Boric acid is one of the most commonly used substances that can neutralize active hydro fluoric acid (HF). It works by forcing the free F- anions into complex salts. This process defeats the extreme toxicity of hydro fluoric acid , particularly its ability to sequester ionic calcium from blood serum which can lead to cardiac arrest (amongst other things) ; such an event can occur from just minor skin contact with HF.

Boric acid is added to borax for use as welding flux by black smiths and farriers .

Boric acid, in combination with silicone oil, is used to manufacture Silly Putty.

7 – 8 – Pyrotechnics

It is used in pyrotechnics to prevent the amide - forming reaction between aluminium and nitrates. A small amount of boric acid is added to the composition to neutralize alkaline amides that can react with the aluminium .

Boric acid can be used as a colorant to make fire green. For example, when dissolved in methanol it is popularly used among fire jugglers and fire spinners to create a deep green flame.

Boron Arsenide

1 – Introduction :

Boron arsenide is a chemical compound of boron and arsenic. It is a cubic (sphalerite) semiconductor with a lattice constant of 0.4777 nm and an indirect band gap of roughly 1.5 eV. It can be alloyed with gallium arsenide.

Boron arsenide also occurs as an icosahedral boride , $B_{12}As_2$. It belongs to *R-3m* space group with a rhombohedral structure based on clusters of boron atoms and two - atom As - As chains. It's a wide band gap semiconductor (3.47 eV) with the extraordinary ability to "self-heal" radiation damage . This form can be grown on substrates such as silicon carbide.

Molecular Formula	B As or B_{12} As $_2$
Molar Mass	86 g / mol
Density	5.22 g / cm^3 , solid
Melting point	2027 °C
Solubility in water	Insoluble
Band gap	1.50 eV (B As) ; 3.47 eV (B ₁₂ As ₂)
Hazards	
EU classification	N/A

2 - Applications :

Solar cells can be fabricated from boron arsenide. It's also an attractive choice for devices exposed to radiation which can severely degrade the electrical properties of conventional semiconductors, causing devices to cease functioning. Among the particularly intriguing possible applications for B_{12} As₂ are beta cells, devices capable of producing electrical energy by coupling a radioactive beta emitter to a semiconductor junction, another space electronics.

Boron Carbide



Contents :

- 1 Introduction
- 2 Crystal structure
- 3 Properties
- 4 Preparation
- 5 Uses

1 – Introduction :

Boron carbide (chemical formula approximately B_4C) is an extremely hard boron–carbon ceramic material used in tank armor, bulletproof vests, and numerous industrial applications. With a Mohs hardness of above 9, it is one of the hardest materials known, behind cubic boron nitride and diamond.

Boron carbide was discovered in the 19th century as a byproduct of reactions involving metal borides, however, its chemical formula was unknown. It was not until the 1930s that the chemical composition was estimated as B_4C .^[1] There remained, however, controversy as to whether or not the material had this exact 4:1 stoichiometry, as in practice the material is always slightly carbondeficient with regard to this formula, and X-ray crystallography shows that its structure is highly complex, with a mixture of C-B-C chains and B_{12} icosahedra. These features argued against a very simple exact B_4C empirical formula . Because of the B_{12} structural unit, the chemical formula of "ideal" boron carbide is often written not as $B_4 C$, but as $B_{12} C_3$, and the carbon deficiency of boron carbide described in terms of a combination of the $B_{12} C_3$ and $B_{12} C_2$ units. The ability of boron carbide to absorb neutrons with out forming long lived radionuclides makes it attractive as an absorbent for neutron radiation arising in nuclear power plants. Nuclear applications of boron carbide include shielding, control rod and shut down pellets. Within control rods, boron carbide is often powdered, to increase its surface area.

IUPAC Name : Boron Carbide			
Other Names : Tetr	abor		
Molecular Formula	$B_4 C$		
Molar Mass	55 g/mol		
Appearance	dark gray or black powder, odorless		
Density	2.52 g/cm^3 , solid.		
Melting point	2763 °C		
Boiling point	3500 °C		
Solubility in water	insoluble		
Acidity (pK_a)	$6-7 (20 \ ^{\circ}C)$		
Crystal structure	Rhombohedral		

2 - Crystal structure :

Boron carbide has a complex crystal structure typical of icosahedron - based borides. There, B_{12} icosahedra form a rhombohedral lattice unit (space group: R3m (No. 166), lattice constants: a = 0.56 nm and c = 1.212 nm) surrounding a C - B - C chain that resides at the center of the unit cell, and both carbon atoms bridge the neighboring three icosahedra. This structure is layered: the B_{12} icosahedra and bridging carbons form a network plane that spreads parallel to the *c*-plane and stacks along the *c*-axis. The lattice has two basic structure units – the B_{12} icosahedron and the B_6 octahedron. Because of the small size of the B_6 octahedra , they

cannot interconnect. Instead, they bond to the B_{12} icosahedra in the neighboring layer, and this decreases bonding strength in the *c*- plane.

Because of the B_{12} structural unit, the chemical formula of "ideal" boron carbide is often written not as B_4C , but as $B_{12}C_3$, and the carbon deficiency of boron carbide described in terms of a combination of the $B_{12}C_3$ and $B_{12}C_2$ units.

3 – Properties :

Boron carbide is known as a robust material having high hardness, high cross section for absorption of neutrons (i.e. good shielding properties against neutrons), stability to ionizing radiation and most chemicals . Its Vickers hardness (38 GPa) and fracture toughness (3.5 MPa \cdot m^{1/2}) approach the corresponding values for diamond (115 GPa and 5.3 MPa \cdot m^{1/2}).

4 - Preparation :

Boron carbide was first synthesized by Henri Moissan in 1899, by reduction of boron trioxide either with carbon or magnesium in presence of carbon in an electric arc furnace. In the case of carbon, the reaction occurs at temperatures above the melting point of B_4 C and is accompanied by liberation of large amount of carbon monoxide

 $2 B_2 O_3 + 7 C \rightarrow B_4 C + 6 CO$

If magnesium is used, the reaction can be carried out in a graphite furnace, and the magnesium byproducts are removed by treatment with acid .

5 – Uses :

- Padlocks
- Personal and vehicle anti ballistic armor plating.
- Grit blasting nozzles.
- High pressure water jet cutter nozzles.
- Scratch and wear resistant coatings.
- Cutting tools and dies.

- Abrasives.
- Neutron absorber in nuclear reactors.
- Metal matrix composites.
- High energy fuel for solid fuel Ramjets.

Boron Mono Fluoride

Contents

- 1 Introduction
- 2 Structure
- 3 Preparation
- 4 Reactions
- 5 Ligand

1 – Introduction :

boron mono fluoride or **fluoro borylene** is a chemical compound with formula BF, one atom of boron and one of fluorine. It was discovered as an unstable gas and only in 2009 found to be a stable ligand combining with transition metals, in the same way as carbon monoxide. It is a sub halide , containing fewer than the normal number of fluorine atoms, compared with boron tri fluoride. BF is iso electronic with carbon monoxide and di nitrogen .

Other Names : Boron fluoride, Boron (I) fluoride,				
Fluoro boronene, Fluoro borylene				
Molecular formula	BF			
Molar mass	30 g mol^{-1}			
Std enthalpy of formation $\Delta_{\rm f} H^{\Theta}_{298}$	115.90 kJ mol ⁻¹			
Standard molar entropy S_{298}°	$200.48 \text{ J K}^{-1} \text{ mol}^{-1}$			

2 – Structure :

The experimental B - F bond length is 1.263 angstrom . One reported computed bond order for the molecule is 1.4.

3 - Preparation

Boron mono fluoride can be prepared by passing boron tri fluoride gas at 2000 °C over a boron rod. It can be condensed at liquid nitrogen temperatures (-196°).

4 - Reactions

BF can react with itself to form polymers of boron containing fluorine with between 10 and 14 boron atoms. BF reacts with BF₃ to form B_2F_4 . BF and B_2 F₄ further combine to form B_3F_5 . B_3F_5 is unstable above -50° and forms B_8F_{12} . This substance is a yellow oil.

BF reacts with acetylenes to make the 1,4-diboracyclohexadiene ring system. BF can condense with 2-butyne forming 1,4- di fluoro - 2,3,5,6 - tetra methyl -1,4- di bora cyclo hexadiene. Also it reacts with acetylene to make 1,4- di fluoro -1,4- di bora cyclo hexadiene.

5 – Ligand :

The first case of BF being a ligand on a transition element was demonstrated in 2009 with the compound $(C_5H_5)_2 Ru_2 (CO)_4 (\mu$ -BF). The BF was bound to both ruthenium atoms as a bridge . Vidovic and Aldridge reacted Na Ru $(CO)_2(C_5H_5)$ with (Et_2O) :BF₃. Note that the BF was formed in place rather than added on.

Earlier in 1968 K. Kämpfer , H. Nöth , W. Petz , and G. Schmid claimed that Fe (BF) $(CO)_4$ was formed in the reaction of B2F4 with Fe(CO)₅ , however this has not been reproduced .

Boron Nitrate

- Introduction :

Boron nitrate is a boron compound with the formula B $(NO_3)_3$. Like graphene, boron nitrate is a two - dimensional material.

IUPAC name : boron (3+) tri nitrate				
Molecular formula	B N ₃ O ₉			
Molar mass	197 g mol ^{-1}			

Boron Nitride

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1 – Introduction :

Boron nitride is a chemical compound with chemical formula BN, consisting of equal numbers of boron and nitrogen atoms. BN is isoelectronic to a similarly structured carbon lattice and thus exists in various crystalline forms. The hexagonal form corresponding to graphite is the most stable and softest among BN polymorphs, and is there fore used as a lubricant and an additive to cosmetic products. The cubic (sphalerite structure) variety analogous to diamond is called c-BN. Its hardness is inferior only to diamond, but its thermal and chemical stability is superior. The rare wurtzite BN modification is similar to lonsdaleite and may even be harder than the cubic form.

Boron nitride is not found in nature and is there fore produced synthetically from boric acid or boron trioxide. The initial product is amorphous BN powder, which is converted to crystalline h -BN by heating in nitrogen flow at temperatures above 1500 °C . c- BN is made by annealing h-BN powder at higher temperatures, under pressures above 5 GPa. Contrary to diamond, larger c-BN pellets can be produced by fusing (sintering) relatively cheap c-BN powders. As a result, c-BN is widely used in mechanical applications.

Because of excellent thermal and chemical stability, boron nitride ceramics are traditionally used as parts of high-temperature equipment. Boron nitride has a great potential in nanotechnology. Nano tubes of BN can be produced that have a structure similar to that of carbon nano tubes, i.e. graphene (or BN) sheets rolled on themselves, however the properties are very different: whereas carbon nanotubes can be metallic or semiconducting depending on the rolling direction and radius, a BN nano tube is an electrical insulator with a wide band gap of ~5.5 eV (same as in diamond), which is almost independent of tube chirality and morphology. Similar to other BN forms, BN nano tubes are more thermally and chemically stable than carbon nano tubes which favors them for some applications.

IUPAC Name : Boron Nitride	
Molecular Formula	B N
Molar Mass	25 g mol^{-1}
Appearance	Colorless crystals
Density	2.1 (hBN) g cm ^{-3} ; 3.45 (cBN) g cm ^{-3} ;
Melting point	2973 °C (sublimes (cBN))
Electron mobility	$200 \text{ cm}^2/(\text{V}\cdot\text{s}) \text{ (cBN)}$
Refractive index $(n_{\rm D})$	1.8 (hBN); 2.1 (cBN)
Crystal structure	hexagonal, sphalerite, wurtzite
Thermochemistry	

Std enthalpy of formation $\Delta_{f}H^{e}_{298}$ -250.91 kJ mol⁻¹ Standard molar entropy S^{e}_{298} 14.77 J K⁻¹ mol⁻¹ Hazards

2 – Structure :

Boron nitride has been produced in an amorphous (a-BN) and crystalline forms. The most stable crystalline form is the hexagonal one, also called h-BN, α -BN, or g-BN (graphitic BN). It has a layered structure similar to graphite. Within each layer, boron and nitrogen atoms are bound by strong covalent bonds, whereas the layers are held together by weak van der Waals forces. The interlayer "registry" of these sheets differs, however, from the pattern seen for graphite, because the atoms are eclipsed, with boron atoms lying over and above nitrogen atoms. This registry reflects the polarity of the B-N bonds. Still, h-BN and graphite are very close neighbors and even the BC₆N hybrids have been synthesized where carbon substitutes for some B and N atoms.

As diamond is less stable than graphite, cubic BN is less stable than h-BN, but the conversion rate between those forms is negligible at room temperature. The cubic form has the sphalerite crystal structure, same as diamond structure, and is also called β -BN or c-BN. The wurtzite BN form (w-BN) has similar structure as lonsdaleite rare hexagonal polymorph of carbon. In both c-BN and w-BN boron and nitrogen atoms are grouped into tetrahedra , but the angles between neighboring tetrahedra are different.



 α -BN, hexagonal β -BN, sphalerite structure BN, wurtzite structure

3 – Properties :

3-1 – Physical :

Properties of amorphous and crystalline BN, graphite and diamond. Some properties of h-BN and graphite differ within the basal planes (||) and perpendicular to them (=)

Material	a-BN	h-BN	c-BN	w-BN	graphite	diamond
Density (g/cm ³)	2.28	~2.1	3.45	3.49	~2.1	3.515
Mohs hardness		1–2	~10	~10	1–2	10
Knoop hardness (GPa)	10		45	34		100
Bulk modulus (GPa)	100	36.5	400	400	34	440
Thermal conductivity (W/cm K)	0.03	6∥; 0.3 ⊥	7.4		2–20∥; 0.02–0.8⊥	6–20
Thermal expansion $(10^{-6}/^{\circ}C)$		-2.7∥; 38⊥	1.2	2.7	$-1.5 \parallel;$ 25 \perp	0.8
Bandgap (eV)	5.05	5.2	6.4	4.5– 5.5	0	5.5
Refractive index	1.7	1.8	2.1	2.05		2.4
Magnetic susceptibility (µemu/g)		-0.48∥; -17.3⊥			-0.2 2.7∥; - 2028⊥	-1.6

The partly ionic structure of BN layers in h-BN reduces covalency and electrical conductivity, whereas the interlayer interaction increases resulting in higher hardness of h-BN relative to graphite. The reduced electron-delocalization in hexagonal-BN is also indicated by its absence of color and a large band gap. Very different bonding – strong covalent within the basal planes (planes where boron and nitrogen atoms are covalently bonded) and weak between them – causes high anisotropy of most properties of h-BN. For example, the hardness, electrical and thermal conductivity are much higher within the planes than perpendicular to them. On the contrary, the properties of c-BN and w-BN are more homogeneous.

Those materials are extremely hard, with the hardness of c-BN being slightly smaller and w-BN even higher than that of diamond.^[10] Because of much better stability to heat and metals, c-BN surpasses diamond in mechanical applications . The thermal conductivity of BN is among the highest of all electric insulators (see table).

Boron nitride can be doped p-type with Be and n-type with boron, sulfur, silicon or if co-doped with carbon and nitrogen.^[7] Both hexagonal and cubic BN are wide-gap semiconductors with a band gap energy corresponding to the UV region. If voltage is applied to h-BN or c-BN, then it emits UV light in the range 215–250 nm and therefore can potentially be used as light emitting diodes (LEDs) or lasers.

Little is known on melting behavior of boron nitride. It sublimates at 2973 °C at normal pressure releasing nitrogen gas and boron, but melts at elevated pressure.

3 – 2 - Thermal stability :

Hexagonal and cubic (and probably w-BN) BN show remarkable chemical and thermal stabilities. For example, h-BN is stable to decomposition in temperatures up to 1000 °C in air, 1400 °C in vacuum, and 2800 °C in an inert atmosphere. The reactivity of h-BN and c-BN is relatively similar, and the data for c-BN are summarized in the table below.

Reactivity of c-BN with solids			
Solid	Ambient	Action	Threshold T (°C)
Мо	10 ⁻² Pa vacuum	reaction	1360
Ni	10 ⁻² Pa vacuum	wetting	1360

Fe, Ni, Co	argon react		1400–1500
Al	10^{-2} Pa vacuum	wetting and reaction	1050
Si	10^{-3} Pa vacuum	wetting	1500
Cu, Ag, Au, Ga, In, Ge, Sn	10^{-3} Pa vacuum	no wetting	1100
В		no wetting	2200
$Al_2O_3 + B_2O_3$	10^{-2} Pa vacuum	no reaction	1360

Thermal stability of c-BN can be summarized as follows :

- In air or oxygen: B_2O_3 protective layer prevents further oxidation to ~1300 °C; no conversion to hexagonal form at 1400 °C.
- In nitrogen: some conversion to h-BN at 1525 °C after 12 h.
- In vacuum (10^{-5} Pa) : conversion to h-BN at 1550–1600 °C.

3 – 3 - Chemical stability :

Boron nitride is insoluble in usual acids, but is soluble in alkaline molten salts and nitrides, such as Li OH, K OH, Na OH, Na₂CO₃, NaNO₃, Li₃N, Mg₃N₂, Sr₃N₂, Ba₃N₂ or Li₃BN₂, which are therefore used to etch BN.

3-**4** - Thermal conductivity :

The theoretical thermal conductivity of hexagonal Boron nitride nano ribbons (BNNRs) can approach 1700–2000 W/(m·K), which has the same order of magnitude as the experimental measured value for graphene , and can be comparable to the theoretical calculations for graphene nano ribbons . Moreover, the thermal transport in the BNNRs is anisotropic. The thermal conductivity of zigzag - edged

BNNRs is about 20 % larger than that of armchair - edged nano ribbons at room temperature .

4 – Synthesis :

Boron nitride has not been found in nature and therefore is produced synthetically. The most common raw materials for BN synthesis, boric acid and boron trioxide are produced on industrial scales by treating minerals borax and colemanite with sulfuric acid or hydrochloric acid:

Boron trioxide is obtained by heating boric acid.

4 – 1 - Preparation and reactivity of hexagonal BN :

Hexagonal boron nitride is obtained by the reacting boron trioxide (B_2O_3) or boric acid $(B(OH)_3)$ with ammonia (NH_3) or urea $(CO(NH_2)_2)$ in nitrogen atmosphere :

$$\begin{split} &B_2O_3 + 2 \text{ NH}_3 \rightarrow 2 \text{ BN} + 3 \text{ H}_2O \text{ (T} = 900 \text{ °C)} \\ &B(OH)_3 + \text{NH}_3 \rightarrow \text{BN} + 3 \text{ H}_2O \text{ (T} = 900 \text{ °C)} \\ &B_2O_3 + CO(\text{NH}_2)_2 \rightarrow 2 \text{ BN} + CO_2 + 2 \text{ H}_2O \text{ (T} > 1000 \text{ °C)} \\ &B_2O_3 + 3 \text{ CaB}_6 + 10 \text{ N}_2 \rightarrow 20 \text{ BN} + 3 \text{ CaO} \text{ (T} > 1500 \text{ °C)} \end{split}$$

The resulting disordered (amorphous) boron nitride contains 92– 95 % BN and 5– 8 % B_2O_3 . The remaining B_2O_3 can be evaporated in a second step at temperatures > 1500 °C in order to achieve BN concentration > 98 %. Such annealing also crystallizes BN, the size of the crystallites increasing with the annealing temperature .

h-BN parts can be fabricated inexpensively by hot-pressing with subsequent machining. The parts are made from boron nitride powders adding boron oxide for better compressibility. Thin films of boron nitride can be obtained by chemical vapor deposition from boron tri chloride and nitrogen precursors . Combustion of boron powder in nitrogen plasma at 5500 $^{\circ}$ C yields ultrafine boron nitride used for lubricants and toners.

Boron nitride reacts with iodine fluoride in tri chloro fluoro methane at -30 °C to produce an extremely sensitive contact explosive, NI₃, in low yield .

4 – 2 - Intercalation of hexagonal BN :



Structure of hexagonal boron nitride intercalated with potassium (B_4N_4K)

Similar to graphite, various molecules, such as NH_3 or alkali metals , can be intercalated into hexagonal boron nitride, that is inserted between its layers. Both experiment and theory suggest the intercalation is much more difficult for BN than for graphite .

4-3 - Preparation of cubic BN :

Synthesis of c-BN uses same methods as that of diamond: Cubic boron nitride is produced by treating hexagonal boron nitride at high pressure and temperature, much as synthetic diamond is produced from graphite. Direct conversion of hexagonal boron nitride to the cubic form has been observed at pressures between 5 and 18 GPa and temperatures between 1730 and 3230 °C, that is similar parameters as for direct graphite-diamond conversion . The addition of a small amount of boron oxide can lower the required pressure to 4–7 GPa and temperature to 1500 °C. As in diamond synthesis, to further reduce the conversion pressures and temperatures, a catalyst is added, such as lithium, potassium, or magnesium, their nitrides, their fluoronitrides, water with ammonium compounds, or hydrazine.^{[30][31]} Other industrial synthesis methods, again borrowed from diamond growth, use crystal growth in a temperature gradient, or explosive

shock wave. The shock wave method is used to produce material called hetero diamond, a super hard compound of boron, carbon, and nitrogen.

Low-pressure deposition of thin films of cubic boron nitride is possible. As in diamond growth, the major problem is to suppress the growth of hexagonal phases (h-BN or graphite, respectively) . Whereas in diamond growth this is achieved by adding hydrogen gas, boron tri fluoride is used for c-BN. Ion beam deposition, plasmaenhanced chemical vapor deposition, pulsed laser deposition, reactive sputtering, and other physical vapor deposition methods are used as well.

4 – 4 - Preparation of wurtzite BN

Wurtzite BN can be obtained via static high - pressure or dynamic shock methods . The limits of its stability are not well defined. Both c-BN and w-BN are formed by compressing h-BN, but formation of w-BN occurs at much lower temperatures close to $1700 \ ^{\circ}$ C.

4 – 5 - Production statistics :

Where as the production and consumption figures for the raw materials used for BN synthesis, namely boric acid and boron trioxide, are well known , the corresponding numbers for the boron nitride are not listed in statistical reports. An estimate for the 1999 world production is 300 to 350 metric tons. The major producers and consumers of BN are located in the United States, Japan, China and Germany. In 2000, prices varied from about \$75 / kg to \$120 / kg for standard industrial - quality h-BN and were about up to \$200 – \$400 / kg for high purity BN grades .

5 - Applications :

5 – 1 - Hexagonal BN :

Hexagonal BN is the most widely used polymorph. It is a good lubricant at both low and high temperatures (up to 900 °C, even in an

oxidizing atmosphere). h-BN lubricant is particularly useful when the electrical conductivity or chemical reactivity of graphite (alternative lubricant) would be problematic. Another advantage of h-BN over graphite is that its lubricity does not require water or gas molecules trapped between the layers. Therefore, h-BN lubricants can be used even in vacuum, e.g. in space applications. The lubricating properties of fine-grained h-BN are used in cosmetics, paints, dental cements, and pencil leads.



Ceramic BN crucible

Hexagonal BN was first used in cosmetics around 1940 in Japan. However, because of its high price, h-BN was soon abandoned for this application. Its use was revitalized in the late 1990s with the optimization h-BN production processes, and currently h-BN is used by nearly all leading producers of cosmetic products for foundations, make-up, eye shadows, blushers, kohl pencils, lipsticks and other skincare products.^[11]

Because of its excellent thermal and chemical stability, boron nitride ceramics are traditionally used as parts of high-temperature equipment. h-BN can be included in ceramics, alloys, resins, plastics, rubbers, and other materials, giving them self-lubricating properties. Such materials are suitable for construction of e.g. bearings and in steelmaking.^[11] Plastics filled with BN have less thermal expansion as well as higher thermal conductivity and electrical resistivity. Due to its excellent dielectric and thermal properties, BN is used in electronics e.g. as a substrate for semiconductors, microwave-transparent windows, and as a structural material for seals.

Hexagonal BN is used in xerographic process and laser printers as a charge leakage barrier layer of the photo drum . In the automotive industry, h-BN mixed with a binder (boron oxide) is used for sealing oxygen sensors, which provide feedback for adjusting fuel flow. The binder utilizes the unique temperature stability and insulating properties of h-BN.

Parts can be made of h-BN by hot pressing. Union Carbide Corporation produces three grades of BN. HBN, with boron oxide binder, usable to 550b - 850 °C in oxidizing atmosphere and up to 1600 °C in vacuum, but due to the boron oxide content is sensitive to water. HBR uses calcium borate binder and is usable at 1600 °C. HBC grade uses no binder and can be used to 3000 °C.

5 – 2 - Cubic boron nitride :

Cubic boron nitride (CBN or c-BN) is widely used as an abrasive. Its usefulness arises from its insolubility in iron, nickel, and related alloys at high temperatures, whereas diamond is soluble in these metals to give carbides. Polycrystalline c-BN (PCBN) abrasives are therefore used for machining steel, whereas diamond abrasives are preferred for aluminum alloys, ceramics, and stone. When in contact with oxygen at high temperatures, BN forms a passivation layer of boron oxide. Boron nitride binds well with metals, due to formation of interlayers of metal borides or nitrides. Materials with cubic boron nitride crystals are often used in the tool bits of cutting tools. For grinding applications, softer binders, e.g. resin, porous ceramics, and soft metals, are used. Ceramic binders can be used as well. Commercial products are known under names "Borazon" (by Diamond Innovations), and "Elbor" or "Cubonite" (by Russian vendors). Similar to diamond, the combination in c-BN of highest thermal conductivity and electrical resistivity is ideal for heat spreaders. Contrary to diamond, large c-BN pellets can be produced in a simple process (called sintering) of annealing c-BN powders in nitrogen flow at temperatures slightly below the BN decomposition temperature. This ability of c-BN and h-BN powders to fuse allows cheap production of large BN parts . As cubic boron nitride consists of light atoms and is very robust chemically and mechanically, it is one of the popular materials for X-ray membranes: low mass results in small X-ray absorption, and good mechanical properties allow usage of thin membranes, thus further reducing the absorption.
5 - 3 - Amorphous boron nitride :

Layers of amorphous boron nitride (a-BN) are used in some semiconductor devices, e.g. MISFETs. They can be prepared by chemical decomposition of tri chloro borazine with caesium, or by thermal chemical vapor deposition methods. Thermal CVD can be also used for deposition of h-BN layers, or at high temperatures, c-BN

6 - Other BN forms :

6 – 1 - Boron nitride fibers :

Hexagonal BN can be prepared in the form of fibers, structurally similar to carbon fibers, by thermal decomposition of extruded borazine $(B_3N_3H_6)$ fibers with addition of boron oxide in a nitrogen atmosphere at 1800 °C. An alternative method is thermal decomposition of cellulose fibers impregnated with boric acid or ammonium tetra borate in an atmosphere of ammonia and nitrogen above 1000 °C. Boron nitride fibers are used as reinforcement in composite materials, with the matrix materials ranging from organic resins to ceramics to metals (see Metal matrix composites).

6-2 - Boron nitride nano mesh :



Perspective view of nano mesh (structure ends at the back of the figure)

Boron nitride nano mesh is an inorganic nano structured two dimensional material. It consists of a single BN layer, which forms by self-assembly a highly regular mesh after high-temperature exposure of a clean rhodium or ruthenium surface to borazine under ultra-high vacuum. The nanomesh looks like an assembly of hexagonal pores. The distance between 2 pore centers is 3.2 nm and the pore diameter is ~ 2 nm.

The boron nitride nanomesh is not only stable to decomposition under vacuum, air and some liquids, but also up to temperatures of 800 °C. In addition, it shows the extraordinary ability to trap molecules and metallic clusters which have similar sizes to the nanomesh pores, forming a well- ordered array. These characteristics promise interesting applications of the nano mesh in areas like nano catalysis, surface functionalisation, spintronics, quantum computing and data storage media like hard drives.

6 – 2 - Boron nitride nano tubes :

Boron nitride nano tubes were theoretically predicted in 1994 and experimentally discovered in 1995. They can be imagined as a rolled up sheet of boron nitride. Structurally, it is a close analog of the carbon nanotube, namely a long cylinder with diameter of several to hundred nanometers and length of many micrometers, except carbon atoms are alternately substituted by nitrogen and boron atoms. However, the properties of BN nano tubes are very different: whereas carbon nano tubes can be metallic or semiconducting depending on the rolling direction and radius, a BN nano tube is an electrical insulator with a band gap of ~5.5 eV, basically independent of tube chirality and morphology. In addition, a layered BN structure is much more thermally and chemically stable than a graphitic carbon structure.

All well - established techniques of carbon nano tube growth, such as arc - discharge , laser ablation and chemical vapor deposition , are used to synthesize BN nano tubes. BN nano tubes can also be produced by ball milling of amorphous boron, mixed with a catalyst: iron powder, under NH_3 atmosphere. Subsequent annealing at ~1100 °C in nitrogen flow transforms most of the product into BN.

Electrical and field emission properties of the thus prepared nano tubes can be tuned by doping with gold atoms via sputtering of gold on the nano tubes. Doping rare - earth atoms of europium turns a BN nano tube into a phosphor material emitting visible light under electron excitation.

Like BN fibers, boron nitride nano tubes show promise for aerospace applications where integration of boron and in particular the light isotope of boron (¹⁰B) into structural materials improves their radiation-shielding properties; the improvement is due to strong neutron absorption by ¹⁰B. Such ¹⁰BN materials are of particular theoretical value as composite structural materials in future manned interplanetary spacecraft, where absorption - shielding from cosmic ray spallation neutrons is expected to be a particular asset in light construction materials.

6 – 4 - Composites containing BN :

Addition of boron nitride to silicon nitride ceramics improves the thermal shock resistance of the resulting material. For the same purpose, BN is added also to silicon nitride - alumina and titanium nitride-alumina ceramics. Other materials being reinforced with BN are, e.g., alumina and zirconia , borosilicate glasses, glass ceramics, enamels, and composite ceramics with titanium boride-boron nitride and titanium boride- aluminium nitride-boron nitride and silicon carbide-boron nitride composition .

7 - Health issues :

Boron nitride (along with $\rm Si_3N_4,~Nb~N$, and BNC) is reported to show weak fibrogenic activity and cause pneumoconiosis. The maximum concentration recommended for nitrides of nonmetals is 10 mg/m³ for BN and 4 for Al N or Zr N .

Boron Oxide

Boron oxide may refer to :

- I Boron Monoxide (B₂O)
- II Boron Sub Oxide (B₆O)
- III Boron Tri Oxide (B_2O_3) the most common form

I. Boron Monoxide

Boron monoxide (B_2O) is a chemical compound of boron and oxygen. Two experimental studies have proposed existence of diamond - like and graphite - like B_2O , as for boron nitride and carbon solids. How ever , a later , systematic , experimental study of boron oxide phase diagram suggests that B_2O is unstable . The instability of the graphite - like B_2O phase was also predicted theoretically.

IUPAC name : Boron (I) oxide			
Other names : Di- boron monoxide			
Molecular Formula	$B_2 O$		
Molar mass	38 g / mol		

II . Boron Sub Oxide

Boron Sub Oxide (chemical formula B_6O) is a solid compound of boron and oxygen. Its structure is built of eight icosahedra at the apexes of the rhombohedral unit cell (space group R3-m). Each icosahedron is composed of twelve boron atoms. Two oxygen atoms are located in the interstices along the [111] rhombohedral direction. Due to its short inter atomic bond lengths and strongly covalent character, B_6O displays a range of outstanding physical and chemical properties such as great hardness (close to that of diamond, rhenium diboride and boron nitride), low mass density, high thermal conductivity, high chemical inertness, and excellent wear resistance.^[3]

 B_6O can be synthesized by reducing B_2O_3 with boron or by oxidation of boron with zinc oxide or other oxidants. These boron sub oxide materials formed at or near ambient pressure are generally oxygen deficient (B_6O_x , x < 0.9) and have poor crystallinity and very small grain size (less than 5 µm). High pressure applied during the synthesis of B_6O can significantly increase the crystallinity, oxygen stoichiometry, and crystal size of the products. Mixtures of boron and B_2O_3 powders were usually used as starting materials in the reported methods for B_6O synthesis.

Oxygen - deficient boron sub oxide (B_6O_x , x <0.9) might form icosahedral particles, which are neither single crystals nor quasi crystals, but twinned groups of twenty tetrahedral crystals.

IUPAC name : Boron Sub Oxide			
Other names : Hexa boron monoxide			
Molecular Formula B ₆ O			
Molar mass	81 g / mol		
Appearance	Reddish icosahedral twinned crystals		
Density	$2.56 \text{ g} / \text{cm}^3$		
Melting point	2000 °C		

Boron trioxide

Contents

- 1 Introduction
- 2 Preparation
- 3 Hardness
- 4 Applications

1 – Introduction :

Boron trioxide (or **diboron trioxide**) is one of the oxides of boron. It is a white, glassy solid with the formula B_2O_3 . It is almost always found as the vitreous (amorphic) form ; however, it can be crystallized after extensive annealing. It is one of the most difficult compounds known to crystallize.

Glassy boron oxide $(g-B_2O_3)$ is thought to be composed of boroxol rings which are six- membere d rings composed of alternating 3-coordinate boron and 2 - coordinate oxygen. This view is controversial, however, because no model has ever been made of glassy boron oxide of the correct density containing a large number of six- membered rings. The rings are thought to make a few BO₃ triangles, but mostly link (polymerize) into ribbons and sheets. The crystalline form (α - B₂O₃) see structure in the infobox) is exclusively composed of BO₃ triangles. This trigonal , quartz - like network undergoes a coesite - like transformation to monoclinic β - B₂O₃ at several giga pascals and is 9.5 GPa.

Other names : boron oxide , diboron trioxide , boron			
sesqui oxide, boric oxide, boria, Boric acid anhydride			
Molecular Formula	$B_2 O_3$		
Molar Mass	69.6 g / mol		
Appearance	white, glassy solid		
	2.46 g/cm^3 , liquid ;		
Density	2.55 g/cm^3 , trigonal ;		
	$3.11 - 3.146 \text{ g/cm}^3$, onoclinic		

Melting Point	450 °C (trigonal) 510 °C (tetrahedral)
Boiling Point	1860 °C, sublimates at 1500 °C
Solubility in water	22 g / L
Solubility	partially soluble in methanol
Acidity (pK_a)	~ 4
LD ₅₀	3150 mg/kg (oral, rat)
Thermodynamic	Phase behaviour
data	Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

2 - Preparation :

Boron trioxide is produced by treating borax with sulfuric acid in a fusion furnace. At temperatures above 750 °C, the molten boron oxide layer separates out from sodium sulfate. It is then decanted, cooled and obtained in 96 – 97 % purity.

Another method is heating boric acid above ~300 °C. Boric acid will initially decompose into water steam and meta boric acid (HBO₂) at around 170 °C, and further heating above 300 °C will produce more steam and boron trioxide. The reactions are :

 $H_{3}BO_{3} \rightarrow HBO_{2} + H_{2}O$ $2 HBO_{2} \rightarrow B_{2}O_{3} + H_{2}O$

Boric acid goes to anhydrous microcrystalline B_2O_3 in a heated fluidized bed. Carefully controlled heating rate avoids gumming as water evolves. Molten boron oxide attacks silicates. Internally graphitized tubes via acetylene thermal decomposition are passivated.

Crystallization of molten α - B₂ O₃ at ambient pressure is strongly kinetically disfavored (compare liquid and crystal densities). Threshold conditions for crystallization of the amorphous solid are 10 k bar and ~ 200 °C.

3 - Hardness :

The bulk modulus of β - B_2O_3 is rather high (K = 180 GPa). The Vickers hardness of g- B_2O_3 is 1.5 GPa and of β - B_2O_3 is 16 GPa.

4 - Applications

- Fluxing agent for glass and enamels
- Starting material for synthesizing other boron compounds such as boron carbide
 - An additive used in glass fibers (optical fibres)
 - It is used in the production of borosilicate glass
- The inert capping layer in the LEC process for the production of gallium arsenide single crystal
 - As an acid catalyst in organic synthesis

Boron Phosphide

Contents

- 1 Introduction
- 2 History
- 3 Appearance
- 4 Chemical properties
- 5 Physical properties ^[4]

1 – Introduction :

Boron phosphide (BP) is a chemical compound of boron and phosphorus. It is a semiconductor .

Molecular Formula	BP
Molar Mass	42 g / mol
Appearance	maroon powder
Density	$2.90 \text{ g} / \text{cm}^3$
Melting point	1100 °C (decomposes)
Band gap	2 eV (indirect)
Electron mobility	5400 cm ² /(V*s) (300 K)
Thermal conductivity	4 W/(cm*K) (300 K)
Refractive index $(n_{\rm D})$	3.05 (0.63 µm)
Crystal structure	Zinc Blende
Coordination geometry	Tetrahedral

2 – History :

Crystals of boron phosphide have been synthesized by Henri Moissan as early as in 1891 .

3 - Appearance

Pure BP is almost transparent, n-type crystals are orange-red whereas p-type ones are dark red ^[4].

4 - Chemical properties :

BP is not attacked by acids or boiling aqueous alkali water solutions. It is only attacked by molten alkalis .

5 - Physical properties :

- coefficient of thermal expansion $\sim 3 \times 10^{-6} / ^{\circ} \text{K}$
- heat capacity $C_P \sim 0.8 \text{ J/(g*K)} (300 \text{ K})$
- Debye temperature = 1000 K
- relatively high micro hardness of 32 GPa (100 g load).
- electron and hole mobilities of few hundred $\mbox{cm}^2 \, / \, (V^*s)$ (up to 500)

Boron sulfide

1 – Introduction :

Boron sulfide is the chemical compound with the formula B_2S_3 . This polymeric material that has been of interest as a component of "high-tech" glasses and as a reagent for preparing organo sulfur compounds. Like the sulfides of silicon and phosphorus, B_2S_3 reacts with water, including atmospheric moisture to release H_2S . Thus, samples must be handled under anhydrous conditions.

Like the boron oxides, B_2S_3 readily forms glasses when blended with other sulfides such as P_4S_{10} . Such glasses absorb lower frequencies of Infra-red energy relative to conventional borosilicate glasses.

 B_2S_3 converts ketones into the corresponding thiones. For example, the conversion of benzophenone to its thione proceeds as follows:

$$B_2S_3 + 3 (C_6H_5)_2C = O \rightarrow B_2O_3 + 3 (C_6H_5)_2C = S$$

In practice, B_2S_3 would be used in excess.

IUPAC Name : Boron sulfide			
Other Names : Boron tri sulfide			
Molecular Formula	B_2S_3		
Molar Mass	118 g / mol		
Appearance	colorless crystals		
Density	1.55 g / cm^3 , solid		
Melting point	563 °C		
Boiling point	decomposes at high T		
Solubility in water	decomposes		
Crystal structure	monoclinic		

2 – Synthesis :

Besides other methods the boron sulfide can be obtained by the reaction of iron or manganese boride with hydrogen sulfide at temperatures of 300° C.

$$2 \text{ Fe } B + 4 \text{ H}_2 S \rightarrow B_2 S_3 + \text{Fe } S + 4 \text{ H}_2$$

The first synthesis was done by Jöns Jakob Berzelius in 1824 by direct reaction of amorphous boron with sulfur vapor.

$$2 B + 3 S \rightarrow B_2 S_3$$

Another synthesis was favoured by Friedrich Wöhler and Henri Etienne Sainte-Claire Deville first published in 1858, starting from boron and hydrogen sulfide.

$$2 B + 3 H_2 S \rightarrow B_2 S_3 + 3 H_2$$

Boron Tri Bromide

Contents

- 1 Introduction
- 2 Chemical properties
- 3 Synthesis
- 4 History
- 5 Applications

1 – Introduction :

Boron tri bromide, BBr₃, is a colorless, fuming liquid compound containing boron and bromine. It is usually made by heating boron trioxide with carbon in the presence of bromine: this generates free boron which reacts vigorously with the bromine. It is very volatile and fumes in air because it reacts vigorously with water to form boric acid and hydrogen bromide.

IUPAC name : Boron tri bromide			
Other names : Tri bromo borane			
Molecular Formula	B Br ₃		
Molar Mass	250.5 g/mol		
Appearance	colorless to amber liquid		
Density	$2.643 \text{ g} / \text{cm}^3$		
Melting point	−46.3 °C		
Boiling point	91.3 ° C		
Solubility in water	reacts violently		
Refractive index $(n_{\rm D})$	1.00207		
Specific heat capacity, C	0.2706 J/K		
GHS pictograms			
GHS signal word	DANGER		
Flash point	-18 °C		

2 - Chemical properties :

Boron tri bromide is commercially available and is a strong Lewis acid. It is an excellent demethylating or dealkylating agent for ethers, often in the production of pharmaceuticals. Additionally, it also finds applications in olefin polymerization and in Friedel - Crafts chemistry as a Lewis acid catalyst. The electronics industry uses boron tri bromide as a boron source in pre - deposition processes for doping in the manufacture of semi conductors.

3 - Synthesis :

The reaction of boron carbide with bromine at temperatures above 300 °C leads to the formation of boron tri bromide. The product can be purified by vacuum distillation.

4 – History :

The first synthesis was done by M. Poggiale in 1846 by reacting boron trioxide with carbon and bromine at high temperatures :

 $B_2O_3 + 3 C + 3 Br_2 \rightarrow 2 BBr_3 + 3 CO$

An improvement of this method was developed by F. Wöhler and Deville in 1857. By starting from amorphous boron the reaction temperatures are lower and no carbon monoxide is produced :

$$2 B + 3 Br_2 \rightarrow 2 BBr_3$$

5 - Applications :

Pharmaceutical Manufacturing Image Processing Semiconductor Doping Semiconductor Plasma Etching Photovoltaic Manufacturing Reagent for Various Chemical Processes.

Boron Tri Chloride



Contents

- 1 Introduction
- 2 Production and properties
- 3 Uses
- 4 Safety

1 – Introduction :

Boron tri chloride is a chemical compound with the formula BCl₃. This colorless gas is a valuable reagent in organic synthesis. It is also dangerously reactive.

2 - Production and properties :

Boron reacts with halogens to give the corresponding trihalides. Boron tri chloride is, however, produced industrially by direct chlorination of boron oxide and carbon at 500 °C.

 $B_2O_3 + 3 \text{ C} + 3 \text{ Cl}_2 \rightarrow 2 \text{ BCl}_3 + 3 \text{ CO}$

The synthesis is analogous to the Kroll process for the conversion of titanium dioxide to titanium tetrachloride. In the laboratory BF₃ reacted with AlCl₃ gives BCl₃ via halogen exchange. BCl₃ is a trigonal planar molecule like the other boron tri halides , and has a bond length of 175pm. It has a zero dipole moment because it is symmetric and therefore the dipole moments associated with the bonds cancel each other out. Boron tri chloride does not form dimers, although there is some evidence that may indicate dimerisation at very low temperatures (20°K). NMR studies of mixtures of boron trihalides shows the presence of mixed halides which may indicate a four centre intermediate e.g. a dimer. The absence of dimerisation

contrasts with the other tri halides of group 13 which contain 4 or 6 coordinate metal centers, for example see AlCl₃ and GaCl₃. A degree of π -bonding has been proposed to explain the short B – Cl distance although there is some debate as to its extent.

BCl₃ is a Lewis acid readily forming adducts with tertiary amines, phosphines, ethers, thioethers, and halide ions. For example, BCl₃S(CH₃)₂ (CAS# 5523-19-3) is often employed as a conveniently handled source of BCl₃ because this solid (m.p. 88-90 °C) releases BCl₃:

$$(CH_3)_2SBCl_3 \rightleftharpoons (CH_3)_2S + BCl_3$$

When boron tri chloride is passed at low pressure through devices delivering an electric discharge, diboron tetrachloride,^[5] Cl₂B-BCl₂, and tetra boron tetrachloride, formula B₄Cl₄, are formed. Colourless diboron tetrachloride (m.p. -93 °C) has a planar molecule in the solid, (similar to dinitrogen tetroxide, but in the gas phase the structure is staggered. It decomposes at room temperatures to give a series of mono chlorides having the general formula (BCl)_n, in which *n* may be 8, 9, 10, or 11; the compounds with formulas B₈Cl₈ and B₉Cl₉ are known to contain closed cages of boron atoms.

The mixed aryl and alkyl boron chlorides are also of interest. Phenyl boron dichloride is commercially available. Such species can be prepared by the reaction of BCl_3 with organotin reagents :

$$2 \text{ BCl}_3 + \text{R}_4\text{Sn} \rightarrow 2 \text{ RBCl}_2 + \text{R}_2\text{SnCl}_2$$

3 - Uses :

Boron tri chloride is a starting material for the production of elemental boron. It is also used in the refining of aluminium, magnesium, zinc, and copper alloys to remove nitrides, carbides, and oxides from molten metal. It has been used as a soldering flux for alloys of aluminium, iron, zinc, tungsten, and monel. Aluminum castings can be improved by treating the melt with boron tri chloride vapors. In the manufacture of electrical resistors, a uniform and lasting adhesive carbon film can be put over a ceramic base using BCl_3 . It has been used in the field of high energy fuels and rocket propellants as a source of boron to raise BTU value. BCl_3 is also used in plasma etching in semiconductor manufacturing. This gas etches metal oxides by formation of a volatile B O Cl_x compounds.

B Cl_3 is used as a reagent in the synthesis of organic compounds. Like the corresponding bromide, it cleaves C-O bonds in ethers.

4 - Safety

 BCl_3 is an aggressive reagent that releases hydrogen chloride upon exposure to moisture or alcohols. The dimethyl sulfide adduct is safer to use, when possible.

Boron Tri Fluoride



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1 – Introduction :

Boron tri fluoride is the chemical compound with the formula BF_3 . This pungent colourless toxic gas forms white fumes in moist air. It is a useful Lewis acid and a versatile building block for other boron compounds.

Molecular Formula	BF ₃
Molar mass	68 g / mol (anhydrous) 104 g / mol (dihydrate)
Appearance	colorless gas (anhydrous) colorless liquid (dihydrate)
Density	0.00276 g/cm^3 (anhydrous gas) 1.64 g/cm ³ (dihydrate)
Melting point	−126.8 °C
Boiling point	−100.3 °C
Solubility in water	very soluble
Solubility	soluble in benzene, toluene, hexane, chloroform and

	methylene chloride
Hazards	
GHS pictograms	Template:GHS04
GHS signal word	DANGER
EU classification	Very toxic (T +) Corrosive (C)
Flash point	non-flammable

2 - Structure and bonding :

The geometry of a molecule of BF_3 is trigonal planar. The D_{3h} symmetry conforms with the prediction of VSEPR theory. The molecule has no dipole moment by virtue of its high symmetry. The molecule is iso electronic with the carbonate anion, $CO_3^{2^-}$.

 BF_3 is commonly referred to as "electron deficient," a description that is reinforced by its exothermic reactivity toward Lewis bases.

In the boron tri halides, BX₃, the length of the B-F bonds (1.30 Å) is shorter than would be expected for single bonds,^[3] and this shortness may indicate stronger B-X π -bonding in the fluoride. A facile explanation invokes the symmetry-allowed overlap of a p orbital on the boron atom with the in-phase combination of the three similarly oriented p orbitals on fluorine atoms.

3 - Synthesis and handling :

 BF_3 is manufactured by the reaction of boron oxides with hydrogen fluoride:

 $B_2O_3 + 6 \ HF \rightarrow 2 \ BF_3 + 3 \ H_2O$

Typically the HF is produced *in situ* from sulfuric acid and fluorite (CaF₂). Approximately 2300 - 4500 tones of boron tri fluoride are produced every year.

On a laboratory scale, BF_3 is produced by the thermal decomposition of diazonium salts :

Ph N₂ B F₄ \rightarrow Ph F + BF₃ + N₂

Anhydrous boron tri fluoride has a normal boiling temperature of -100.3 C and a critical temperature of -12.3 C, so that it can be stored as a refrigerated liquid only between those temperatures. Storage or transport vessels should be designed to withstand internal pressure, since a refrigeration system failure could cause pressures to rise to the critical pressure of 49.85 bar (4.985 MPa).

Boron tri fluoride is corrosive. Suitable metals for equipment handling boron trifluoride include stainless steel, monel, and hastelloy. In presence of moisture it corrodes steel, including stainless steel. It reacts with polyamides. Poly tetra fluoro ethylene, poly chloro tri fluoro ethylene, poly vinylidene fluoride, and poly propylene show satisfactory resistance. The grease used in the equipment should be fluoro carbon based, as boron tri fluoride reacts with the hydrocarbon-based ones.

4 - Reactions :

Unlike the aluminium tri halides, the boron tri halides are all monomeric . They undergo rapid halide exchange reactions:

 $B \ F_3 + B \ Cl_3 \rightarrow B \ F_2 \ Cl + B \ Cl_2 \ F$

Because of the facility of this exchange process, the mixed halides cannot be obtained in pure form.

Boron tri fluoride is a versatile Lewis acid that forms adducts with such Lewis bases as fluoride and ethers :

Cs F + B F₃ \rightarrow Cs B F₄ O (C₂H₅)₂ + B F₃ \rightarrow B F₃O (C₂H₅)₂

Tetra fluoro borate salts are commonly employed as noncoordinating anions. The adduct with diethyl ether, **boron tri fluoride** **diethyl etherate** or just **boron tri fluoride etherate** $(BF_3 \cdot O(Et)_2)$ is a conveniently handled liquid and consequently is a widely encountered as a laboratory source of BF₃. It is stable as a solution in ether, but not stoichio metrically. Another common adduct is the adduct with dimethyl sulfide $(BF_3 \cdot S(Me)_2)$, which can be handled as a neat liquid.

4 – 1 - Comparative Lewis acidity :

All three lighter boron tri halides, BX_3 (X = F, Cl, Br) form stable adducts with common Lewis bases. Their relative Lewis acidities can be evaluated in terms of the relative exo thermicities of the adduct - forming reaction. Such measurements have revealed the following sequence for the Lewis acidity:

 $BF_3 < BCl_3 < BBr_3$ (strongest Lewis acid)

This trend is commonly attributed to the degree of π - bonding in the planar boron tri halide that would be lost upon pyramidalization of the BX₃ molecule. which follows this trend:

 $BF_3 > BCl_3 > BBr_3$ (most easily pyramidalized)

The criteria for evaluating the relative strength of π -bonding are not clear, however. One suggestion is that the F atom is small compared to the larger Cl and Br atoms, and the lone pair electron in p_z of F is readily and easily donated and overlapped to empty p_z orbital of boron. As a result, the pi donation of F is greater than that of Cl or Br.

In an alternative explanation, the low Lewis acidity for BF_3 is attributed to the relative weakness of the bond in the adducts F_3B -L.

4 – 2 – Hydrolysis :

Boron tri fluoride reacts with water to give boric acid and fluoro boric acid. The reaction commences with the formation of the aquo adduct, H_2O -BF₃, which then loses HF that gives fluoboric acid with boron tri fluoride.

 $4 \text{ BF}_3 + 3 \text{ H}_2\text{O} \rightarrow 3 \text{ HBF}_4 + "B(\text{OH})_3"$

The heavier tri halides do not undergo analogous reactions, possibly the lower stability of the tetrahedral ions BX_4^- (X = Cl, Br). Because of the high acidity of fluoro boric acid, the fluoro borate ion can be used to isolate particularly electrophilic cations, such as diazonium ions, that are otherwise difficult to isolate as solids.

5 – Uses :

Boron tri fluoride is most importantly used as a reagent in organic chemistry, typically as a Lewis acid. Examples :

• initiates polymerisation reactions of unsaturated compounds such as poly ethers

• as a catalyst in some isomerization, alkylation, esterification, condensation, Mukaiyama aldol addition, and other reactions

Other uses:

- applied as dopant in ion implantation
- p-type dopant for epitaxially grown silicon

• used in sensitive neutron detectors in ionization chambers and devices to monitor radiation levels in the Earth's atmosphere

- in fumigation
- as a flux for soldering magnesium
- to prepare diborane

6 – Discovery :

Boron tri fluoride was discovered in 1808 by Joseph Louis Gay-Lussac and Louis Jacques Thénard, who were trying to isolate "fluoric acid" (i.e. hydro fluoric acid) by combining calcium fluoride with vitrified boric acid; the resulting vapours failed to etch glass, so they named it *fluoboric gas*.

Boron Tri Iodide

- Introduction :

Boron tri iodide is a chemical compound of boron and iodine with chemical formula BI_3 . It has a trigonal planar molecular geometry. It is a crystalline solid. Its dielectric constant is 5.38 and its heat of vaporization is 40.5 kJ / mol.

For information on the three lighter boron tri halides (BF3 , BCl3 and $B\ Br3$) , see Boron _tri fluoride.

Molecular formula	BI ₃
Molar mass	391.5 g/mol
Appearance	crystalline solid
Density	$3.35 \text{ g} / \text{cm}^3 (50 ^\circ\text{C})$
Melting point	49.9 °C
Boiling point	210 °C,
Solubility in water	insoluble
Flash point	-18 °C

Boronic Acid



The general structure of a boronic acid, where R is a substituent.

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1 – Introduction :

A **boronic acid** is an alkyl or aryl substituted boric acid containing a carbon – boron bond belonging to the larger class of organo boranes. Boronic acids act as Lewis acids. Their unique feature is that they are capable of forming reversible covalent complexes with sugars, amino acids, hydroxamic acids, etc. (molecules with vicinal, (1,2) or occasionally (1,3) substituted Lewis base donors (alcohol, amine, carboxylate)). The pKa of a boronic acid is ~9, but they can form tetrahedral boronate complexes with pKa ~7. They are occasionally used in the area of molecular recognition to bind to saccharides for fluorescent detection or selective transport of saccharides across membranes.

Boronic acids are used extensively in organic chemistry as chemical building blocks and intermediates predominantly in the Suzuki coupling. A key concept in its chemistry is trans metallation of its organic residue to a transition metal.

The compound bortezomib with a boronic acid group is a drug used in chemotherapy. The boron atom in this molecule is a key substructure because through it certain proteasomes are blocked that would otherwise degrade proteins.

2 - Boronic acids :

Many air-stable boronic acids are commercially available. They are characterized by high melting points. Since boronic acids easily lose water to form the cyclic trimeric anhydride, commercial material oftentimes contains substantial quantities of this anhydride. This does not affect reactivity.



Methyl boronic acid Methyl
$$\overset{HO}{\overset{B}{\operatorname{CH}_3}} \overset{OH}{_{\operatorname{CH}_3}} 60$$
 91–94
cis- Propenyl boronic propene $\overset{HO}{\underset{B}{\operatorname{CH}_3}} \overset{HO}{_{\operatorname{B}}{\operatorname{OH}}} 86$ 65–70
Trans – Propenyl propene $\overset{HO}{\underset{H_3}{\operatorname{C}}} \overset{HO}{_{\operatorname{B}}{\operatorname{OH}}} 86$ 123–127

2 - 1 – Synthesis :

Boronic acids can be obtained via several methods. The most common way is reaction of organo metallic compounds based on lithium or magnesium (Grignards) with borate esters. For example phenyl boronic acid is produced from phenyl magnesium bromide and tri methyl borate followed by hydrolysis

> Ph Mg Br + B (OMe)₃ \rightarrow PhB (OMe)₂ + Me O Mg Br Ph B (OMe)₂ + H₂O \rightarrow Ph B (OH)₂ + Me OH

Another method is reaction of an arylsilane ($RSiR_3$) with boron tri bromide (BBr_3) in a trans metallation to $RBBr_2$ followed by acidic hydrolysis.

A third method is by palladium catalyzed reaction of aryl halides and tri flates with di boronyl esters in a coupling reaction. An alternative to esters in this method is the use of di boronic acid or tetra hydroxy di boron ($[B(OH_2)]_2$).

3 - Boronate esters

Boronate esters are esters formed between a boronic acid and an alcohol.



Comparison between boronic acids and boronate esters

The compounds can be obtained from borate esters by condensation with alcohols and diols. Phenyl boronic acid can be self condensed to the cyclic trimer called *tri phenyl anhydride* or *tri phenyl boroxin*.

Boronic ester	Diol	Structural formula	Molar mass	Boiling point (°C)
Allylboronic acid pinacol ester	pinacol	$\overset{H_3C}{\underset{H_2C}{\overset{O}{\longrightarrow}}}\overset{CH_3}{\underset{B}{\overset{O}{\longrightarrow}}}}_{CH_3}$	168	50 – 53 (5 mmHg)
Phenyl boronic acid tri methylene glycol ester	tri methylene glycol		162	106 (2 mmHg)
Di iso propoxy methyl borane	iso propanol	$\begin{array}{c} CH_3 CH_3 CH_3 \\ H_3C \stackrel{\textstyle \ }{\frown} O^{\stackrel{\scriptstyle \ }{B}} \circ \stackrel{\textstyle \ }{\frown} CH_3 \\ H_3C \stackrel{\scriptstyle \ }{\frown} O^{\stackrel{\scriptstyle \ }{C}} H_3 \end{array}$	144	105 -107

Compounds with 5- membered cyclic structures containing the C - O - B - O - C linkage are called **dioxa borolanes** and those with 6 - membered rings **dioxa borinanes**.

4 - Boronic acids in organic chemistry :

4 - 1 - Suzuki coupling reaction :

Boronic acids are used in organic chemistry in the Suzuki reaction. In this reaction the boron atom exchanges its aryl group with an alkoxy group from palladium.



4 - 2 - Chan - Lam coupling :

In the **Chan-Lam coupling** the alkyl, alkenyl or aryl boronic acid reacts with a N-H or O-H containing compound with Cu(II) such as copper(II) acetate and oxygen and a base such as pyridine forming a new carbon–nitrogen bond or carbon–oxygen bond for example in this reaction of 2-pyridone with *trans*-1-hexenylboronic acid:



The reaction mechanism sequence is deprotonation of the amine, coordination of the amine to the copper(II), trans metallation (transferring the alkyl boron group to copper and the copper acetate group to boron), oxidation of Cu (II) to Cu (III) by oxygen and finally reductive elimination of Cu (III) to Cu (I) with formation of the product. Direct reductive elimination of Cu (II) to Cu (I) to Cu (0) also takes place but is very slow. In catalytic systems oxygen also regenerates the Cu (II) catalyst.

4 - 3 - Liebeskind - Srogl coupling

In the Liebeskind - Srogl coupling a thiol ester is coupled with a boronic acid to produce a ketone.

4 - 4 - Conjugate addition

The boronic acid organic residue is a nucleophile in conjugate addition also in conjunction with a metal. In one study the pinacol ester of allyl boronic acid is reacted with dibenzylidene acetone in a such a conjugate addition :



The catalyst system in this reaction is tris(dibenzylidene acetone) di palladium (0) / tri cyclo hexyl phosphine .

Another conjugate addition is that of gramine with phenylboronic acid catalyzed by cyclo octadiene rhodium chloride dimer ^[13]:



4-5- Oxidation

Boronic esters are oxidized to the corresponding alcohols with base and hydrogen peroxide (for an example see: carbenoid)

4-6- Homologization

• In boronic ester homologization an alkyl group shifts from boron in a boronate to carbon :



Boronic ester homologization mechanism



Homologization application

In this reaction dichloro methyl lithium converts the boronic ester into a boronate. A lewis acid then induces a rearrangement of the alkyl group with displacement of the chlorine group. Finally an organo metallic reagent such as a Grignard reagent displaces the second chlorine atom effectively leading to insertion of an RCH₂ group into the C- B bond . Another reaction featuring a boronate alkyl migration is the Petasis reaction.

4 – 7 - Electrophilic allyl shifts

Allyl boronic esters engage in electrophilic allyl shifts very much like silicon pendant in the Sakurai reaction. In one study a diallylation reagent combines both :



4-8-Hydrolysis

Hydrolysis of boronic esters back to the boronic acid and the alcohol can be accomplished in certain systems with thionyl chloride and pyridine. Aryl Boronic acids or esters may be hydrolyzed to the corresponding phenols by reaction with hydroxylamine at room temperature.

4 – 8 - C - H coupling reactions

The diboron compound bis (pinacolato) diboron reacts with aromatic hetero cycles or simple arenes to an arylboronate ester with iridium catalyst $[IrCl(COD)]_2$ (a modification of Crabtree's catalyst) and base 4,4'-di-tert-butyl-2,2'-bipyridine in a C-H coupling reaction for example with benzene:



In one modification the arene reacts 1 on 1 (instead of a large excess) with cheaper pinacolborane $\$



Unlike in ordinary electrophilic aromatic substitution (EAS) where electronic effects dominate, the regioselectivity in this reaction type is solely determined by the steric bulk of the iridium complex. This is exploited in a meta - bromination of m - xylene which by standard AES would give the ortho product :



- 5 Boronic acids in supra molecular chemistry :
- 5 1 Saccharide recognition



An example of a diboronic acid based fluorescent sensor bound to a sugar acid, reported by James and coworkers in J. Am. Chem. Soc., 2004, 126(49), 16179-16186. The covalent pair-wise interaction between boronic acids and 1,2- or 1,3-diols in aqueous systems is rapid and reversible. As such the equilibrium established between boronic acids and the hydroxyl groups present on saccharides has been successfully employed to develop a range of sensors for saccharides . One of the key advantages with this dynamic covalent strategy lies in the ability of boronic acids to overcome the challenge of binding neutral species in aqueous media. If arranged correctly, the introduction of a tertiary amine within these supra molecular systems will permit binding to occur at physiological pH and allow signaling mechanisms such as photo induced electron transfer mediated fluorescence emission to report the binding event.

Potential applications for this research include systems to monitor diabetic blood glucose levels. As the sensors employ an optical response, monitoring could be achieved using minimally invasive methods, one such example is the investigation of a contact lens doped with boronic acid based sensors to monitor glucose levels within ocular fluid.

6 - Borinic acids and esters

Borinic acids and **borinate esters** have the general structure R_2BOR .



7 - Borate salts :

Borate salts are ate complexes and have the general structure $R_4B^-M^+$ for example potassium tetra phenyl borate (IUPAC name: potassium tetra phenyl boranuide).

Boro Phospho Silicate Glass

Boro phospho silicate glass, commonly known as **BPSG**, is a type of silicate glass that includes additives of both boron and phosphorus. Silicate glasses such as PSG and Boro phospho silicate glass are commonly used in semi conductor device fabrication for inter metal layers, i.e., insulating layers deposited between succeedingly higher metal or conducting layers.

BPSG has been implicated in increasing a device's susceptibility to soft errors since the Boron-10 isotope is good at capturing thermal neutrons from cosmic radiation. It then undergoes fission producing a gamma ray, an alpha particle, and a lithium ion. These products may then dump charge into nearby structures, causing data loss (bit flipping, or single event upset).

In critical designs, depleted boron consisting almost entirely of Boron-11 is used to avoid this effect as a radiation hardening measure. Boron-11 is a by-product of the nuclear industry.

Boro Silicate Glass



Boro silicate glassware (two beakers and a test tube).

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- 5 Usage
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1 – Introduction :

Borosilicate glass is a type of glass with the main glass-forming constituents silica and boron oxide. Boro silicate glasses are known for having very low coefficients of thermal expansion ($\sim 3 \times 10^{-6}$ / °C at 20°C), making them resistant to thermal shock, more so than any other common glass. Such glass is less subject to thermal stress and is commonly used for the construction of reagent bottles.

2 – History :

Boro silicate glass was first developed by German glassmaker Otto Schott in the late 19th century and sold under the brand name "Duran" in 1893. After Corning Glass Works introduced Pyrex in 1915, the name became a synonym for borosilicate glass in the English - speaking world.

The European manufacturer of Pyrex, Arc International, uses borosilicate glass in its Pyrex glass kitchen products ; how ever , the U.S. manufacturer of Pyrex kitchenware uses tempered soda - lime glass. Thus Pyrex can refer to either soda - lime glass or borosilicate glass when discussing kitchen glassware, while Pyrex, Bomex, Duran and Kimax all refer to borosilicate glass when discussing laboratory glass ware.

Most borosilicate glass is colorless. Colored borosilicate, for the studio glass trade, was first widely brought onto the market in 1986 when Paul Trautman founded North star Glass works . In 2000, former North star Glass works employee Henry Grimmett started Glass Alchemy and developed the first cadmium Crayon Colors and aventurine Sparkle colors in the borosilicate palette.

In addition to the quartz, sodium carbonate, and calcium carbonate traditionally used in glassmaking, boron is used in the manufacture of borosilicate glass. Typically, the resulting glass composition is about 70 % silica, 10 % boron oxide, 8 % sodium oxide, 8 % potassium oxide, and 1 % calcium oxide (lime). Though somewhat more difficult to make than traditional glass (Corning conducted a major revamp of their operations to make it), it is economical to produce; its superior durability, chemical and heat resistance finds excellent use in chemical laboratory equipment, cookware, lighting and, in certain cases, windows.

3 - Manufacturing process :

Boro silicate glass is created by adding boron to the traditional glass maker's frit of silicate sand, soda, and ground lime. Since boro silicate glass melts at a higher temperature than ordinary silicate glass, some new techniques were required for industrial production. Borrowing from the welding trade, burners combining oxygen with natural gas were required.
4 - Physical characteristics :

Borosilicate glass has a very low thermal expansion coefficient (3.3×10^{-6} /°K), about one-third that of ordinary glass. This reduces material stresses caused by temperature gradients which makes borosilicate the most suitable kind of glass for certain applications (see below).

The softening point (temperature at which viscosity is approximately $10^{7.6}$ poise) of type 7740 Pyrex is 820 °C .

Boro silicate glass is less dense than ordinary glass.

While more resistant to thermal shock than other types of glass, borosilicate glass can still crack or shatter when subject to rapid or uneven temperature variations. When broken, borosilicate glass tends to crack into large pieces rather than shattering (it will snap rather than splinter).

Optically, boro silicate glasses are crown glasses with low dispersion (Abbe numbers around 65) and relatively low refractive indices (1.51–1.54 across the visible range).

5 - Usage :

Virtually all modern laboratory glassware is borosilicate glass. It is so widely used in this application due to its chemical and thermal resistance and good optical clarity, but the glass can be reacted with sodium hydride to produce sodium boro hydride, a common laboratory reducing agent. Fused quartz is also found in some laboratory equipment when its higher melting point and transmission of UV are required (e.g. for tube furnace liners and UV cavettos), but the cost and difficulty of working with quartz make it excessive for the majority of laboratory equipment.

During the mid-twentieth century, borosilicate glass tubing was used to pipe coolants (often distilled water) through high power vacuum tube – based electronic equipment, such as commercial broadcast transmitters. Glass cook ware is another common usage. Boro silicate glass is used for measuring cups, featuring screen printed markings providing graduated measurements, which are widely used in American kitchens.

Aquarium heaters are some times made of borosilicate glass. Due to its high heat resistance, it can tolerate the significant temperature difference between the water and the nichrome heating element.

Many high - quality flashlights use borosilicate glass for the lens. This allows for a higher percentage of light transmittance through the lens compared to plastics and lower-quality glass.

Several types of High-Intensity Discharge (HID) lamps, such as mercury vapor and metal halide lamps, use borosilicate glass as the outer envelope material.

Specialty marijuana and tobacco pipes are made from borosilicate glass. The high heat resistance makes the pipes more durable.

Most pre manufactured glass guitar slides are also made of borosilicate glass.

New lamp working techniques led to artistic applications such as contemporary glass marbles. The modern studio glass movement has responded to color. "The availability of colors began to increase when companies such as Glass Alchemy introduced the Crayon Colors, which brought a whole new vivacity to the glass industry."^[6] Borosilicate is commonly used in the glass blowing form of lamp working and the artists create a range of products ranging from jewelry, kitchen ware, to sculpture as well as for artistic glass tobacco pipes.

Boro silicate glass is some times used for high-quality beverage glassware. Borosilicate glass lends kitchen- and glass ware increased durability along with microwave and dish washer compatibility. Most astronomical reflecting telescope glass mirror components are made of borosilicate glass because of its low coefficient of expansion with heat. This makes very precise optical surfaces possible that change very little with temperature, and matched glass mirror components that "track" across temperature changes and retain the optical system's characteristics.

The optical glass most often used for making instrument lenses is Schott BK-7 (or the equivalent from other makers), a very finely made borosilicate crown glass ⁻ It is also designated as 517642 glass after its 1.517 refractive index and 64.2 Abbe number. Other less costly borosilicate glasses, such as Schott B270 or the equivalent, are used to make "crown glass" eyeglass lenses. Ordinary lower-cost borosilicate glass, like that used to make kitchenware and even reflecting telescope mirrors, cannot be used for high-quality lenses because of the striations and inclusions common to lower grades of this type of glass. The maximum working temperature is 515 fahrenheit. While it transitions to a liquid starting at 550 degrees Fahrenheit (just before it turns red – hot), it is not workable until it reaches over 1000 fahrenheit. That means that in order to industrially produce this glass, oxygen/fuel torches must be used. Glassblowers borrowed technology and techniques from welders.

Boro silicate is also a material of choice for evacuated tube solar thermal technology, because of its high strength and heat resistance.

Borosilicate glasses also find application in the semiconductor industry in the development of micro electro mechanical systems (MEMS), as part of stacks of etched silica wafers bonded to the etched boro silicate glass.

The thermal insulation tiles on the Space Shuttle were coated with a borosilicate glass.

Lighting manufacturers use borosilicate glass in their refractors.

Additionally, borosilicate tubing is used as the feedstock for the production of parenteral drug packaging, such as vials and pre-filled syringes, and is also used for the production of ampoules and dental cartridges. The chemical resistance of borosilicate glass minimizes the migration of sodium ions from the glass matrix thus making it well suited for inject able drug applications. This type of glass is typically referred to as USP / EP JP Type I.

Borosilicate glasses are used for immobilization and disposal of radioactive wastes. In most countries high-level radioactive waste has been incorporated into alkali borosilicate or phosphate vitreous waste forms for many years and vitrification is an established technology.^[8] Vitrification is a particularly attractive immobilization route because of the high chemical durability of the vitrified glass product. This characteristic has been used by industry for centuries . The chemical resistance of glass can allow it to remain in a corrosive environment for many thousands and even millions of years.

6 – Boro silicate nano particles

It was initially thought that borosilicate glass could not be formed into nano particles, since an unstable boron oxide precursor prevented successful forming of these shapes. However, in 2008 a team of researchers from the Swiss Federal Institute of Technology at Lausanne were successful in forming borosilicate nano particles of 100 to 500 nanometers in diameter. The researchers formed a gel of tetra ethyl ortho silicate and tri methoxy boroxine. When this gel is exposed to water under proper conditions, a dynamic reaction ensues which results in the nano particles.

7 - In lamp working :

Boro silicate, or "boro" as it is often referred to, is used extensively in the glass blowing process lamp working, which involves using a burner torch to melt and form glass, using a variety of metal and graphite tools. Borosilicate is referred to as "hard glass" and has a higher melting point than "soft glass" which is used in glassblowing formed in large furnaces and large rods. Raw glass used in lampworking comes in glass rods for solid work and glass tubes for hollow work tubes and vessels / containers. Lamp working is used to make complex and custom scientific apparatus; most major universities have a lamp working shop to manufacture and repair their glass ware. For this kind of "scientific glass blowing", the specifications must be exact and the glass blower must be highly skilled and precise. Lamp working is also done as art and common items made include goblets, pipes, paper weights and pendants.

Pyrex



A Pyrex flask.

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1 – Introduction :

Pyrex is a brand name for glass ware , introduced by Corning Incorporated in 1915.

Originally, Pyrex was made from borosilicate glass. In the 1940s the composition was changed for some products to tempered soda - lime glass, which is the most common form of glass used in glass bake ware in the US and has higher mechanical strength so is less vulnerable to breakage when dropped (the leading cause of breakage in glass bake ware). In 1998, Corning divested its consumer products division which subsequently adopted the name World Kitchen.

In 1908, Eugene Sullivan, Director of Research at Corning Glass Works, developed Nonex, a boro silicate low- expansion glass, to reduce breakage in shock-resistant lantern globes and battery jars. (Borosilicate glass was originally developed at the Jena Glass works by Otto Schott, which Sullivan had learned about as a doctoral student in Leipzig, Germany.) Jesse Littleton of Corning discovered the cooking potential of boro silicate glass by giving his wife a casserole dish made from a cut-down Nonex battery jar. Corning removed the lead from Nonex, and developed Pyrex as a consumer product. Pyrex glass bake ware products are to be found in an estimated 80 % of American homes and approaching 400 million units have been sold since the divestiture in 1998 alone.

Pyrex kitchen glassware manufactured for sale in the United States is made at the World Kitchen facility in Charleroi, Pennsylvania. Pyrex products for the European Union are made at a factory in France.

2 - History of the Pyrex Brand :



Pyrex measuring cup, manufactured and sold in the U.S. (circa 1980) features graduations in both metric and U.S. Customary systems.

Borosilicate glass was first made by the German chemist and glass technologist Otto Schott, founder of Schott AG in 1893, 22 years before Corning produced the Pyrex brand. Schott AG sold the product under the name "Duran." In the English-speaking world, however, in the midst of World War I, Corning's Pyrex brand of borosilicate glass offered a non-German alternative. Ever since, the name Pyrex has been widely used as a genericized trademark for borosilicate glass in the English-speaking world.

Corning sold off its Consumer Products division in 1998 as World Kitchen but retained the Pyrex brand name, licensing it to World Kitchen and other companies that produce Pyrex-branded cookware (e.g. Newell Rubbermaid's Newell Cookware Europe). The brand in Europe, the Middle East and Africa is currently owned by Arc International who acquired the European business in early 2006 from Newell Rubbermaid, who had acquired it from Corning in the 1990s.

A Corning executive gave the following account of the etymology of the Pyrex brand name:

The word PYREX is probably a purely arbitrary word which was devised in 1915 as a trade-mark for products manufactured and sold by Corning Glass Works. While some people have thought that it was made up from the Greek pyr and the Latin rex we have always taken the position that no graduate of Harvard would be guilty of such a classical hybrid. Actually, we had a number of prior trade-marks ending in the letters ex. One of the first commercial products to be sold under the new mark was a pie plate and in the interests of euphonism the letter r was inserted between pie and ex and the whole thing condensed to PYREX.

Pyrex kitchen products in Europe made and sold by a subsidiary of Arc International tableware company are made from borosilicate glass.

3 – Design :

In 1958 an internal design department was started by John B. Ward. He redesigned the Pyrex ovenware and Flame ware. Over the years designers such as Penny Sparke, Betty Baugh, Smart Design, TEAMS Design, and others have contributed to the design of the line.

4 – Composition :

Older Pyrex (pre 1900s), European Pyrex, and Pyrex laboratory glass ware, is made of borosilicate glass. According to the National Institute of Standards and Technology, borosilicate Pyrex is composed of (as percentage of weight) : 14 % boron, 51 % oxygen, . 3 % sodium, 1 % aluminium, 38 % silicon, and less than 1 % potassium.

According to glass supplier Pulles and Hannique, borosilicate Pyrex is made of Corning 7740 glass, and is equivalent in formulation to Schott Glass 8830 glass sold under the "Duran" brand name. The composition of both Corning 7740 and Schott 8830 is given as 80.6% SiO_2 , 12.6 % B_2O_3 , 4.2 % Na_2O , 2.2 % Al_2O_3 , 0.04 % Fe_2O_3 , 0.1 % CaO, 0.05 % MgO, and 0.1 % Cl.

How ever, the Pyrex glass cookware made in Charleroi, Pennsylvania is made of tempered soda-lime glass.^[13]

5 - Use in laboratory ware :

Because Pyrex borosilicate glass has a high thermal resistance, it is often used in the manufacture of laboratory ware. In Europe, Scilabware Limited manufactures more than 800 items under the Pyrex brand name including beakers, bottles, flasks, dishes and test tubes.

6 - Problems With Pyrex :

Pyrex, when used as windows in plasma etchers in the semiconductor industry, tends to explode if hydrogen flame-polished to eliminate surface roughness in restoring the window properties, for this reason, quartz glass is preferred.

7 - Usage in telescopes :

Because of its low expansion characteristics, Pyrex is often the material of choice for reflective optics in astronomy applications. The California Institute of Technology's 200-inch (5.1 m) telescope mirror

at Palomar Observatory was cast by Corning during 1934 – 1936 out of boro silicate glass.

In 1932, George Ellery Hale approached Corning with the challenge of fabricating the required optic for his Palomar project. A previous effort to fabricate the optic from fused quartz had failed.

Corning's first attempt was a failure, the cast blank having voids. Using lessons learned, Corning was successful in the casting of the second blank. After a year of cooling, during which it was almost lost to a flood, in 1935 the blank was completed. The first blank now resides in Corning's Museum of Glass.

Sodium Per Borate



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- 2 Preparation and chemistry
- 3 Structure
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1 – Introduction :

Sodium per borate (**PBS**) is a white, odorless, water-soluble chemical compound with the chemical composition NaBO₃. It crystallizes as the mono hydrate, NaBO₃·H₂O, tri hydrate, NaBO₃·3H₂O and tetra hydrate, NaBO₃·4H₂O. The mono hydrate and tetra hydrate are the commercially important forms. The elementary structural unit of sodium per borates is a dimer anion $B_2O_4(OH)_4^{2-}$, in which two boron atoms are joined by two peroxo bridges in a chair-shaped 6 - membered ring, and the simplistic NaBO₃·nH₂O-type formulas are just a convenient way to express the average chemical composition.

Other names : PBS-1 (mono), PBS - 4 (tetra)	
UN number	1479
Molecular Formula	Na $BO_3 \cdot nH_2O$
Molar mass	<pre>100 g / mol (mono hydrate); 154 g / mol (tetra hydrate)</pre>
Appearance	white powders
Flash point	Non - flammable

2 - Preparation and chemistry :

Sodium per borate is manufactured by reaction of disodium tetra borate penta hydrate, hydrogen peroxide, and sodium hydroxide. The mono hydrate form dissolves better than the tetra hydrate and has higher heat stability; it is prepared by heating the tetra hydrate. Sodium per borate undergoes hydrolysis in contact with water, producing hydrogen peroxide and borate.

3 – Structure :

Unlike sodium per carbonate and per phosphate, the sodium per borate is not simply an adduct with hydrogen peroxide, and it does not contain individual and does not contain a BO_3^- ions. Rather, there is a cyclic dimer anion $B_2O_4(OH)_4^{2-}$, in which two boron atoms are joined by two peroxo bridges in a chair-shaped 6-membered ring . This makes the substance more stable, and safer for handling and storage. The formula of the sodium salt is thus $Na_2H_4B_2O_8$.

4 – Uses :

It serves as a source of active oxygen in many detergents, laundry detergents, cleaning products, and laundry bleaches . It is also present in some tooth bleaching formulas. It is used as a bleaching agent for internal bleaching of a non vital root treated tooth. The sodium per borate is placed inside the tooth and left in place for an extended period of time to allow it to diffuse into the tooth and bleach stains from the inside out. It has antiseptic properties and can act as a disinfectant. It is also used as a "disappearing" preservative in some brands of eye drops.

Sodium per borate is a less aggressive bleach than sodium hypochlorite, causing less degradation to dyes and textiles. Borates also have some non-oxidative bleaching properties.

Sodium per borate releases oxygen rapidly at temperatures over 60° C. To make it active at lower temperatures ($40 - 60^{\circ}$ C), it has to be mixed with a suitable activator, typically tetra acetyl ethylene diamine (TAED).