Boron nitride

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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 therefore 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.

Because of excellent thermal and chemical stability, boron nitride ceramics are traditionally used as parts of high-temperature equipment. Boron nitride has potential use in nanotechnology. Nanotubes of BN can be produced that have a structure similar to that of carbon nanotubes, i.e. graphene (or BN) sheets rolled on themselves, but the properties are very different.

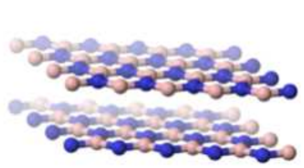
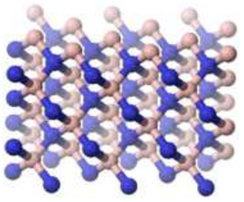
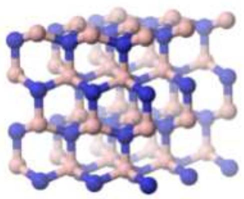
Boron nitride	
	
IUPAC name Boron nitride	
Identifiers	
CAS number	10043-11-5 ✓
PubChem	66227
ChemSpider	59612 ✓
EC number	233-136-6
MeSH	Elbor
ChEBI	CHEBI:50883 ✓
RTECS number	ED7800000
Gmelin Reference	216
Jmol-3D images	Image 1 (http://chemapps.stolaf.edu/jmol/jmol.php?model=B%23N)
SMILES	
InChI	
Properties	
Molecular formula	BN
Molar mass	24.82 g mol^{-1}
Appearance	Colorless crystals
Density	2.1 (hBN); 3.45 (cBN) g/cm^3
Melting point	2,973 °C (5,383 °F; 3,246 K) sublimates (cBN)
Solubility in water	insoluble
Electron mobility	200 cm^2/(V·s) (cBN)
Refractive index (n_D)	1.8 (hBN); 2.1 (cBN)
Structure	
Crystal structure	hexagonal, sphalerite, wurtzite
Thermochemistry	
Specific heat capacity *C*	19.7 J/K mol
Std molar entropy $S^\ominus_{298}$	14.77 J/K mol
Std enthalpy of formation $\Delta_f H^\ominus_{298}$	-250.91 kJ/mol
Gibbs free energy ΔG	-226.8 kJ/mol
Hazards	

Contents

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 BC_6N hybrids have been synthesized where carbon substitutes for some B and N atoms.[1]

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 (again like diamond). The cubic form has the sphalerite crystal structure, the same as that of diamond, and is also called β-BN or c-BN. The wurtzite BN form (w-BN) has the same structure as lonsdaleite, a 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.[2]

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

EU classification	Xi
R-phrases	R36/37
S-phrases	S26, S36
NFPA 704	0 0 0
Related compounds	
Related compounds	Boron arsenide Boron carbide Boron phosphide Boron trioxide
Except where noted otherwise, data are given for materials in their standard state (at 25 °C (77 °F), 100 kPa)	
✓ (verify) (what is: ✓/✗?)	
Infobox references	

Properties

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	9.5–10	~10[3]	1–2	10
Knoop hardness (GPa)	10		45	34		100
Bulk modulus (GPa)	100	36.5	400	400	34	440
Thermal conductivity (W/m.K)	3	600 ∥; 30 ⊥	740		200–2000 ∥; 2–800 ⊥	600–2000
Thermal expansion (10^{-6}/°C)		−2.7 ∥; 38 ⊥	1.2	2.7	−1.5 ∥; 25 ⊥	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)[4]		−0.48 ∥; -17.3 ⊥			−0.2..-2.7 ∥; -20..-28 ⊥	−1.6

Sources: amorphous BN,[5][6][7] *crystalline BN,*[8][9] *graphite,*[10] *diamond.*[9]

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 and isotropic.

Those materials are extremely hard, with the hardness of bulk c-BN being slightly smaller and w-BN even higher than that of diamond.[11] Polycrystalline c-BN with grain sizes on the order of 10 nm is also reported to have Vickers hardness comparable or higher than diamond.[12] Because of much better stability to heat and metals, c-BN surpasses diamond in mechanical applications.[13] 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.[8] 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 [14][15] or c-BN,[16] 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.[17][18]

Thermal stability

Hexagonal and cubic (and probably w-BN) BN show remarkable chemical and thermal stabilities. For example, h-BN is stable to decomposition at 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[8]

Solid	Ambient	Action	Threshold T (°C)
Mo	10^{-2} Pa vacuum	reaction	1360
Ni	10^{-2} Pa vacuum	wetting[19]	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
B		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:[8]

- 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.

Chemical stability

Boron nitride is insoluble in usual acids, but is soluble in alkaline molten salts and nitrides, such as LiOH, KOH, NaOH-Na_2CO_3, $NaNO_3$, Li_3N, Mg_3N_2, Sr_3N_2, Ba_3N_2 or Li_3BN_2, which are therefore used to etch BN.[8]

Thermal conductivity

The theoretical thermal conductivity of hexagonal Boron nitride nanoribbons (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 nanoribbons.[20][21] 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 nanoribbons at room temperature.[22]

Natural occurrence

In 2009 a naturally occurring boron nitride mineral (proposed name Qingsongite) was reported in Tibet. The substance was found in dispersed micrometer-sized inclusions of qingsongite (c-BN) in chromium-rich rocks in Tibet. In 2013, the International Minerological Association affirmed the mineral and the name.[23][24]

Synthesis

Preparation and reactivity of hexagonal BN

Boron nitride is produced synthetically. 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 a nitrogen atmosphere:[25]

$B_2O_3 + 2\ NH_3 \rightarrow 2\ BN + 3\ H_2O$ (T = 900 °C)

$B(OH)_3 + NH_3 \rightarrow BN + 3\ H_2O$ (T = 900 °C)

$B_2O_3 + CO(NH_2)_2 \rightarrow 2\ BN + CO_2 + 2\ H_2O$ (T > 1000 °C)

$B_2O_3 + 3\ CaB_6 + 10\ N_2 \rightarrow 20\ BN + 3\ CaO$ (T > 1500 °C)

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.[13][26]

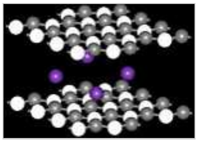
h-BN parts can be fabricated inexpensively by hot-pressing with subsequent machining. The parts are made from boron nitride powders adding boron oxide for better compressibility. Thin films of boron nitride can be obtained by chemical vapor deposition from boron trichloride and nitrogen precursors.[27] Combustion of boron powder in nitrogen plasma at 5500 °C yields ultrafine boron nitride used for lubricants and toners.[28]

Boron nitride reacts with iodine fluoride in trichlorofluoromethane at −30 °C to produce an extremely sensitive contact explosive, NI_3, in low yield.[29] Boron nitride reacts with nitrides of alkali metals and lanthanides to form nitridoborate compounds.[30] For example:

$Li_3N + BN \rightarrow Li_3BN_2$

Intercalation of hexagonal BN

Similar to graphite, various molecules, such as NH_3[31] or alkali metals,[32] 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.[33]



Structure of hexagonal boron nitride intercalated with potassium (B_4N_4K)

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.[34] 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.[35][36] 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 heterodiamond, a superhard compound of boron, carbon, and nitrogen.[37]

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 trifluoride is used for c-BN. Ion beam deposition, plasma-enhanced chemical vapor deposition, pulsed laser deposition, reactive sputtering, and other physical vapor deposition methods are used as well.[27]

Preparation of wurtzite BN

Wurtzite BN can be obtained via static high-pressure or dynamic shock methods.[38] 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 °C.[35]

Production statistics

Whereas the production and consumption figures for the raw materials used for BN synthesis, namely boric acid and boron trioxide, are well known (see boron), 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.[25]

Applications

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.[39]

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.[13]

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.[13] 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.[40]

Hexagonal BN is used in xerographic process and laser printers as a charge leakage barrier layer of the photo drum.[41] 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.[13]

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 550–850 °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.[42]

Cubic boron nitride

Cubic boron nitride (CBN or c-BN) is widely used as an abrasive.[43] 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.[39]

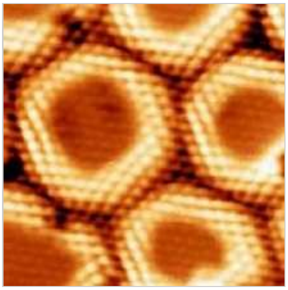
As cubic boron nitride consists of light atoms and is very robust chemically and mechanically, it is one of the popular materials for X-ray membranes: low mass results in small X-ray absorption, and good mechanical properties allow usage of thin membranes, thus further reducing the absorption.[44]

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 trichloroborazine 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.[45]

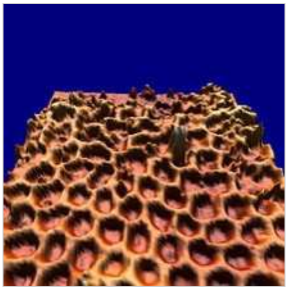
Other forms of boron nitride

Boron nitride nanomesh


BN nanomesh observed by scanning tunneling microscope. The center of each ring corresponds to the center of the pores

Boron nitride nanomesh is a nanostructured 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[46] or ruthenium[47] 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,[46] air [48] and some liquids,[49][50] but also up to temperatures of 800 °C.[46] In addition, it shows the extraordinary ability to trap molecules[49] and metallic clusters[47] which have similar sizes to the nanomesh pores, forming a well-ordered array. These characteristics promise interesting applications of the nanomesh in areas like catalysis, surface functionalisation, spintronics, quantum computing and data storage media like hard drives.[51]


Perspective view of nanomesh (structure ends at the back of the figure)

Boron nitride nanotubes

Boron nitride nanotubes were predicted in 1994[52] and experimentally discovered in 1995.[53] 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 nanotubes are very different: whereas carbon nanotubes can be metallic or semiconducting depending on the rolling direction and radius, a BN nanotube is an electrical insulator with a bandgap of ~5.5 eV, basically independent of tube chirality and morphology.[54] In addition, a layered BN structure is much more thermally and chemically stable than a graphitic carbon structure.[55][56]

All well-established techniques of carbon nanotube growth, such as arc-discharge,[53][57] laser ablation[58][59] and chemical vapor deposition,[60] are used to synthesize BN nanotubes. BN nanotubes 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.[61][62]

Electrical and field emission properties of such nanotubes can be tuned by doping with gold atoms via sputtering of gold on the nanotubes.[61][63] Doping rare-earth atoms of europium turns a BN nanotube into a phosphor material emitting visible light under electron excitation.[62] Quantum dots formed from 3-nanometer gold particles spaced across the nanotubes exhibit the properties of field-effect transistors at room temperature.[64]

Like BN fibers, boron nitride nanotubes show promise for aerospace applications where integration of boron and in particular the light isotope of boron (^{10}B) into structural materials improves their radiation-shielding properties; the improvement is due to strong neutron absorption by ^{10}B. Such ^{10}BN 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.[65]

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 include alumina and zirconia, borosilicate glasses, glass ceramics, enamels, and composite ceramics with titanium boride-boron nitride, titanium boride-aluminium nitride-boron nitride, and silicon carbide-boron nitride composition.[66]

Health issues

Boron nitride (along with Si_3N_4, NbN, and BNC) is reported to show weak fibrogenic activity and cause pneumoconiosis. The maximum concentration recommended for nitrides of nonmetals is 10 mg/m^3 for BN and 4 for AlN or ZrN.[8]

See also

- Beta carbon nitride
- Boron suboxide
- Superhard materials
- Wide bandgap semiconductors
- Graphene

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External links

- Synthesis and functionalization of BN nanotubes (http://www.nims.go.jp/synthesis/topics-e.html)
- National Pollutant Inventory: Boron and Compounds (http://www.npi.gov.au/resource/boron-and-compounds)
- Materials Safety Data Sheet (http://ptcl.chem.ox.ac.uk/MSDS/BO/boron_nitride.html) at University of Oxford

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