

CLASSIFICATION OF BORIDES

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Borides constitute a widely used class of refractory compounds, with applications in many branches of engineering. Among compounds known as interstitial phases they occupy a special position owing to the fact that, unlike carbon, nitrogen, hydrogen, and oxygen atoms, boron atoms are of a size enabling them to form in a lattice direct B-B bonds, whose presence brings borides close to the limit of applicability of Hagg's rule. As a result, a starting metallic lattice may, even in the case of lower borides, undergo appreciable changes.

The relationship between the composition, structure, and type of chemical linkage of borides is a complex one, and because of this no comprehensive system of classification has as yet been devised for these compounds. Kiessling [1] has attempted to classify borides according to type of crystal structure. Taking as a basis the formation by boron atoms of various structural elements, he has shown that boron atoms in borides either occupy isolated positions or form pairs or chains of varying degrees of complexity (straight, zigzag-shaped, and branched chains, bands, plane or corrugated grids, and two- and three-dimensional cells). In Fig. 1 are shown the possible structural elements formed from boron atoms in borides. A classification according to a key structure-determining factor - atomic size - does not seem to have a sufficiently broad basis. Nevertheless, it enables us to reveal to a first approximation the fundamental feature distinguishing borides from interstitial phases proper, viz., the formation in borides of direct B-B bonds.

The type of crystal structure of a compound is, of course, determined by the composition of the compound and the type of its chemical linkage. The composition of a compound in turn depends on the valence, electron concentration, and size of its atoms and also on certain structural characteristics. Examination of this complex set of factors provides information concerning the influence exerted by them on the formation of various types of chemical linkage in borides.

So far 80 boron-containing binary systems have been investigated, and it is known that compounds are formed, by metals of Groups Ia-VIIIa, crystallizing in more than 30 structural types, only in 60 of these systems; the elements of Groups Ib-IVb do not form compounds with boron.

Apart from this, it may be noted that the stability of borides of metals of the long periods decreases with increasing atomic number, so that no copper borides are formed. Cu-B, Au-B, and Ag-B are simple eutectic systems analogous to systems composed of carbon and a Group III or VIII metal. The greatest numbers of boride phases of different boron contents are formed by the rare-earth metals and the Groups III-VIII transition metals, for which various valence states linked with the overlapping of d, f, p, and s orbitals are possible.

Among the important factors on which the composition of boron compounds depends are the dimensional factor, allowing in the first place for the atomic size ratio r_B/r_{Me} , the electrochemical factor, linked with electronic transitions, and electron concentration, determined by the degree of localization and delocalization of electrons. All these factors are interrelated and depend on the positions of the elements involved in the Periodic System.

During the formation of borides, at the instant of reaction between atoms the states of all electrons, especially valence electrons, change; the electrons of atoms of the simple substances must pass from the s, d, and f states to the p states of boron (configuration $2s^2 2p^1$ of the outer electron shell of the boron atom) with the simultaneous formation of $s^x p^y$ configurations of high degree of stability. This may be effected both by single-electron $s \rightarrow p$ transitions ($s^2 p \rightarrow sp^2$) and by electron exchanges between boron atoms ($sp^2 + sp^2 \rightarrow sp^3 + sp$).

Thus, during the formation of a boride the outer electrons become redistributed and the sp^2 and sp^3 electron configurations characteristic of strong covalent bonds are formed. The role of the sp^2 and sp^3 electron states changes depending on the donor ability of atoms of the simple substances reacting with boron

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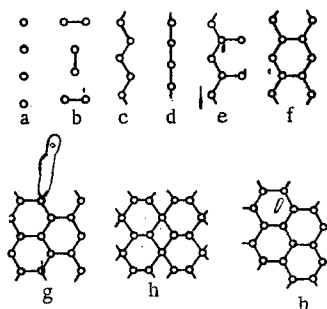


Fig. 1. Structural elements assembled from boron atoms in borides: a) isolated boron atoms; b) pairs of boron atoms; c) zigzag-shaped chains; d) straight chains; e) branched chains; f) double chains; g) chain construction; h) corrugated plane and stacked grids.

atoms to form boride phases. It is the various combinations of s^2p , sp , sp^2 , and sp^3 electron configurations that account for the multitude of structural types in which borides crystallize.

The differences in structure between the valence shells of isolated atoms of simple substances, which determine the possibility of stable electron configurations being formed by the localized part of valence electrons, constitutes the basis of a division of all chemical elements into three main classes of electronic analogs [7]. Accordingly, the compounds formed by the reactions of various elements with boron can be divided into three classes:

1. Boride phases formed by s elements having outer s electrons with completely filled or completely unfilled deeper electron shells.
2. Boride phases formed by ds and fds elements with atoms having incompletely filled d or f , d subshells.
3. Boride phases formed by sp elements having valence s , p electrons.

To the first class belong borides of alkali metals, beryllium, magnesium, and alkaline-earth metals. In alkali metals, whose isolated atoms are characterized by s^1 valence electron configurations, some stable s^2 configurations are formed whose energetic stability decreases with increasing principal quantum number. Because of this, the first ionization potentials monotonically fall from lithium to cesium, a further slight fall being recorded with francium (Table 1). The comparatively sharp fall in ionization potential observed on passing from sodium to potassium is linked with a partial transition of valence electrons to the completely vacant $3d$ states of potassium and following elements. Under these conditions, the s^2 configurations are disturbed and ionization of atoms is facilitated.

Thus, on passing from lithium to sodium and potassium the energetic possibility of d electrons participating in the setting up of bonds during a reaction with boron grows. Lithium has the least affinity for boron, and consequently with this metal compounds of lower symmetry can be expected to form compared with sodium and potassium, and particularly magnesium and aluminum, for which, in accordance with the diagonals rule, alkali metals have a good affinity [3]. The atomic radius of lithium is of the same order as that of magnesium. From spatial geometry considerations it follows that in the $Li-B$ system there should exist the diboride LiB_2 with the AlB_2 structure. Hofmann's study of the behavior of lithium boride of approximate composition $LiB_{2.15}$ has shown that lithium diboride is an extremely unstable compound which decomposes in air and dissolves in methanol [4].

As regards the existence of alkali metal hexaborides, opinions vary. According to Naslain [5], sodium and potassium form hexaborides with the CaB_6 structure in which borides of alkaline-earth and rare-earth metals crystallize; lithium, too, forms a hexaboride, but the structure of this compound is more complex than CaB_6 .

TABLE 1. Some Physical Characteristics of Alkali Metals, Aluminum, and Magnesium

Metal	Elec- tronic structure	Cova- lent radius, Å	Atom- ic radius, Å	Ionic radius, Å	Atom- ic vol. Å ³	1st (2nd) ionization potential, eV	Ioniz. energy, kcal/g- mole	Electro- negativ- ity	Melting point, °C	Boiling point, °C	Den- sity, g/ cm ³	Phases forming with boron
Li	s ² 2s ¹	1,34	1,57	0,68(+1)	13,1	5,39 (75,6)	124	0,98	186	1336	0,53	LiB ₂ , LiB ₆ (?), LiB ₁₀
Na	3s ¹	1,54	1,90	0,97(+1)	23,7	5,14 (47,3)	119	0,93	97,5	880	0,97	NaB ₆ (?), NaB ₁₅
K	4s ¹	1,96	2,35	1,33(+1)	45,3	4,34 (31,8)	100	0,82	62,3	760	0,86	KB ₆ (?)
Pb	5s ¹	2,11	1,49	1,48(+1)	55,9	4,18 (27,5)	—	0,82	38,5	700	1,53	Unknown
Cs	6s ¹	2,25	1,65	1,59(+1)	70,0	3,89 (25,1)	—	0,79	28,5	670	1,87	»
Fr	7s ¹	—	1,78	1,76(+1)	—	4,24	—	0,7	23,5	612	2,1	»
Mg	3s ²	1,30	1,60	0,65(+2)	14,0	7,63 (15,1)	176	1,2	650	1107	1,74	MgB ₂ , MgB ₄ , MgB ₆ , MgB ₁₂
Al	3s ² 3p ¹	1,18	1,43	0,50(+3)	10,0	5,94 (18,85)	138	1,5	660	2450	2,70	AlB ₂ , AlB ₁₀ , AlB ₁₂

Examination of the possibility of the existence of alkali metal hexaborides based on the principles of hexaboride formation formulated in [6] leads to the conclusion that these compounds cannot exist for the following reasons: Firstly, the second ionization potentials of alkali metals exceed the maximum allowable level of 11.5–12 eV; secondly, on the outer ns level of an alkali metal there is only one electron and not two, as in alkaline-earth and rare-earth metals; thirdly, the setting up of Me–B bonds should involve the participation of partially filled (n–1) d levels close to ns levels, and in alkali metals such levels do not exist.

Thus, it must be assumed that alkali metals and boron can only form compounds of low symmetry, in which a dominant role in the establishment of bonds is played by the electrons of boron atoms. Such compounds, e.g., LiB₁₀ and NaB₁₅, have been obtained.

Magnesium and alkaline-earth metals with an s² outer electron configuration of isolated atoms have many characteristics of the metals of their group and of nonmetals. This is a consequence of the s → p transition being allowed and of the s² configuration being able to change into the sp configuration characteristic of nonmetals.

A beryllium atom is characterized by a high probability of s → p transitions, the s² → sp equilibrium shifting to the right with rise in temperature because of the slightly greater energetic stability of sp configurations compared with s². The presence of sp configurations tending to become stabilized in the configurations of higher energetic order sp² and sp³ promotes the formation by beryllium atoms of complex structural elements in compounds whose atoms are electron donors. Apart from this, since s² configurations determine metallic properties and sp configurations nonmetallic properties, beryllium is both metallic and nonmetallic in character.

This characteristic feature of beryllium manifests itself also in its compounds with boron. Beryllium borides can be divided into two groups, one of which contains the borides Be₅B and Be₂B, whose melting points are low, and the other the compounds BeB₄, BeB₆, and BeB₉, whose melting points are close to those of refractory compounds. The first group of these borides has metallic conductivity, and the second, like pure boron, semiconducting conductivity. The two groups differ also in their chemical properties – oxidation and nitriding rates and ability to decompose hydrolytically. Be₅B and Be₂B and their eutectic alloys hydrolyze with the evolution of boron hydrides, the highest yield of the latter being obtained with Be₅B. With rise in boron concentration in these borides the yield of boron hydrides falls and the stability of the compounds in air grows, which is indicative of a strengthening of the B–B bonds. The beryllium borides BeB₂ and BeB₆ react with carbon, with the formation of borocarbides of composition BeC₂B₂(B₁₂). The higher borocarbide is similar in properties to boron carbide, while the lower borocarbide has the properties of a semimetal [8].

On passing to magnesium, the energetic stability of sp configurations diminishes and consequently the s² → sp equilibrium shifts to the left. Because of this, magnesium, while retaining some characteristics of nonmetals owing to the presence of atoms with sp configurations, possesses more pronounced metallic properties.

With calcium, strontium, and barium the electron transition equilibrium is $d \rightleftharpoons s^2 \rightleftharpoons sp$ owing to the presence in their isolated atoms of a completely empty 3d shell. In the direction from calcium to barium this equilibrium shifts toward $s \rightarrow d$ transitions, with a resultant enhancement of metallic properties.

In an examination of the electronic structure of beryllium, magnesium, and alkaline-earth metal atoms it should be borne in mind that with increasing principal quantum number stability and the degree of localization into p states decrease, while the degree of localization into d states increases. Thus, while for beryllium (and, to a smaller extent, for magnesium) $s^2 \rightarrow sp$ transitions are energetically favorable, for alkaline-earth metals in the direction from Ca to Ba $s^2 \rightarrow sd$ transitions become energetically more favorable.

Beryllium and magnesium on reacting with boron strongly resemble sp elements, even though they form compounds crystallizing in the AlB_2 structure, which is characteristic of transition metal borides, and the character of the variation of the physicochemical properties is similar to that observed with the homologous series of d transition metal borides.

Alkaline-earth metals form borides which crystallize in structures typical of d and f transition metal borides and are similar in properties to rare-earth metal borides.

The second class comprises borides of Groups IV-VIII transition metals, rare-earth metals, and actinides. Borides of transition metals with unfilled d electron subshells occupy in this class a special position owing to the fact that the valence electrons of isolated atoms of these metals become partially localized into d^0 , d^5 , and d^{10} configurations and partially remain unlocalized and are therefore capable of passing to p states.

Borides of d and f transition metals form homologous series of similar compounds, and are therefore particularly suitable for studies of general trends in the dependence of properties on the principal quantum number and the amount of valence electrons in atoms of boride-forming elements. In the series of borides ranging from Me_2B to MeB_{12} and then to MeB_{66-100} formed by d and f transition metals the diborides have received the most attention. In these diborides there arise mainly sp^2 configurations of boron atoms, resulting in a specific type of crystal structure similar to that of graphite, which too is based on sp^2 configurations and is characterized by the presence of plane grids (grid structures) joined together by collectivized electrons. The low donor capacity of molybdenum and tungsten, for which the high degree of stability of d^5 configurations is responsible, explains why under normal conditions there are no diborides of these metals and instead the borides Mo_2B_5 and W_2B_5 are formed.

It should be noted that with metals whose isolated atoms have more than five electrons in their d shells diboride formation is linked with the relative weights of d^5 and d^{10} configurations. Metals whose specific weights of atoms with the stable d^5 configurations is greater than their specific weights of atoms with d^{10} configurations form diborides (these metals are donors). Typical metals of this kind are ruthenium, osmium, and iridium. Iron, cobalt, nickel, platinum, and palladium form no diborides.

The formation of MeB_4 is mainly observed with metals tending to have the stable f^0 , f^7 , and f^{14} configurations. The donor capacity of lanthanide atoms is determined by their tendency to form these configurations with varying degrees of stability. The properties of hexaborides are also primarily linked with the electronic states of boron, while in the donor activity of rare-earth metals an important part is played by $f \rightarrow d$ transitions. The role of metallic states in the formation of the properties of borides diminishes on passing from di- to tetra- and dodecaborides. For the formation of stable dodecaborides localization of electronic states on the boron sublattice atoms is particularly important.

In the third class of borides are compounds formed by sp elements having valence s, p electrons. The formation and stability of these compounds are determined by the interaction of sp states and the possibility of the most stable states - sp^3 and s^2p^6 - arising in them. For example, in compounds of boron with nitrogen and phosphorus (BN and BP) the simplest modifications form in the case of boron atoms acquiring the valence electrons of nitrogen or phosphorus ($B - s^2p \rightarrow sp^2$, $N - s^2p^3 \rightarrow sp^4 \rightarrow sp^3 + p$, $B + N - sp^2 + sp^3 + p \rightarrow sp^3 + sp^3$), when both atoms of each compound assume sp^3 configurations. With boron nitride, strong B - B bonds are combined with -C - B - C- aleinic bonds acting on the diagonals of the elementary cell and imparting to the nitride semiconducting properties.

Thus, in the formation of borides the different types of interaction are linked with the tendency of each system to increase the degree of stability of electronic configurations of a given type.

There are no clearly defined boundaries between the above classes of borides. Furthermore, although on the basis of the electronic structures of metal and boron atoms all borides can be divided into three classes,

they can also be classified according to their crystallochemical properties into two groups.

The first group comprises metal-rich borides (phases of compositions Me_4B , Me_3B , Me_2B , Me_3B_2 , MeB , and Me_3B_4) and the second, boron-rich borides (phases of compositions MeB_2 , MeB_4 , MeB_6 , MeB_{12} , MeB_{41} , and MeB_{66-100}). The structures of borides of lower boron contents are determined by their metallic lattices, and the structures of higher borides by their boron atoms, which form strong sublattices with pronounced B-B bonds. In a boride of the first group electrons are transferred to the metal, the main role in electronic structure being played by metallic states and in interatomic bonds by Me-Me bonds. In a higher boride electrons are transferred to the boron sublattice, the main role in the electronic structure of the compound being now played by the sp states of boron and in interatomic bonds by B-B bonds. The first group of stable borides is made up of metals which, from the point of view of the configurational model of matter, are acceptors of electrons, and the second group, of metals which are donors of electrons. On transition from the first to the second group of borides the atomic configurations of boron become transformed and the lengths of the Me-Me and B-B bonds change, the latter growing shorter with increasing boron content in the borides, which in turn is indicative of an increase in the role played in them by the B-B bonds.

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