A Survey of Structural Types of Borates and Polyborates

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1 Introduction: Water-Containing Borates

In recent years, interesting new borate structures have been determined by X-ray diffraction. Therefore, it seems appropriate to survey this new development and to update a previous review [1].

The structures of hydrated borates and polyborates (Chapt. 1) are principially different from those of anhydrous species (Chapt. 2), although there are transitions between both the groups. These latter arise if the borates are not fully hydrated, or, for example, if the BO_3 group is associated with isolated OH groups (Chapt. 2.2.2), but also for boracites containing OH groups (Chapt. 2.8).

Silicoborates are not included in the present survey, since most of their structures are governed by the silicate moiety, e.g., axinites; only in a few cases is the structure determined by the borate group, e.g., in howlite.

In general, the crystal chemistry of borates is similar to that of silicates; differences arise from the fact that boron combines with oxygen not only in four-fold (tetrahedral) but also in three-fold (trigonal planar = triangular) coordination. As a result, silicate chemistry is considerably less complicated than borate chemistry.

In crystalline borates, in addition to the mononuclear anions BO_3^{3-} and BO_4^{5-} and their protonated or partially protonated equivalents, there exists an extensive series of polynuclear anions formed by corner-sharing of triangular and/or tetrahedral boron-oxygen moieties. The polyanions, in turn, may polymerize to from infinite chains, sheets or three-dimensional networks. It is not yet clearly understood which factors determine the coordination number of boron in a given boron-oxygen compound. For example, in the α-metaboric acid, α-HBO_2, all the boron atoms have triangular coordination, while both BO_3 and BO_4 groups exist in the monoclinic form of the β-metaboric acid, β-HBO_2; all boron atoms in another form of metaboric acid, γ-HBO_2, have coordination number four.

Several principles have been proposed for the classification of borates. The first one was suggested by C. L. Christ who organized the "crystal chemistry and systematic classification of hydrated borate minerals" in four rules [2]. Based on a more crystallographic point of view, Ch. Tennyson developed "a systematic of borates on crystallochemical basis", considering the analogy of borates with silicates and employing the terms nesoborates, soroborates, inoborates (chains), phylloborates (sheets) and tektoborates (networks) [3]. Edwards and Ross [4] formulated another classification on the basis of the rule that "the ratio of the charge of the tetrahedral boron to the total boron is equal to the ratio of the charge of the cation to the total boron". Unfortunately, this postulate fails for the hexaborates and for partially hydrated polyborates.

In 1970, Heller [1] suggested a classification of borates based on the number of boron atoms in the "fundamental building block". In 1971, J. R. Clark [5] added, in an article on "crystal chemistry of borates", a further principle as the fifth rule, namely that "the boric acid group, $B(OH)_3$, may exist in isolated form in the presence of more complex polyanions, or such insular groups may themselves polymerize and attach to side-chains of more complex polyanions", as first observed in the crystal structures of *veatchite* and *paraveatchite*. In 1977, Christ and Clark [6] reviewed the various principles and classifications in their article on "a crystal-chemical classification of borate structures with emphasis on hydrated borates". In addition to a sixth rule,

a shorthand notation using n and the symbols △ = triangle and T = tetrahedron was introduced, where n is the number of atoms characteristic of the fundamental building block. For n = 1, one can distinguish between the isolated[1] triangles 1:△ and isolated[1] tetrahedra 1:T. Each unit may be combined with others of its class to form pairs (dimers: 2:△ or 2:T), chains (∞), sheets (∞_2), or networks (∞_3). The true polyanions in which triangles and tetrahedra may exist together, begin with n = 3, i.e., the triborates.

The best examples for the short-hand notation are the known boric acids. Orthoboric acid H_3BO_3 = mineral *sassolite* crystallizes triclinic in $P\bar{1} = C_i^1$ [2]; it is named 1:△ [7], while metaboric acid crystallizes in three modifications: HBO_2-I = $B_3O_3(OH)_3$ orthorhombic (Pbnm = D_{2h}^{16}) must be formulated as $B_3O_3(OH)_3$ with the notation 3:3△, isolated [18]; HBO_2-II = $HB_3O_4(OH)_2$, monoclinic ($P2_1/a = C_{2h}^5$) is also a triborate with the short-hand notation $3\infty_2$:(2△ + T), chains [9]; and HBO_2-III = mineral *metaborite* is cubic ($P\bar{4}3n = T_d^4$) and consists of a three-dimensional network of tetrahedra, short-hand notation $1\infty_3$:T, network [10].

1.1 Monoborates Containing Tetra-Coordinate Boron

The ion $[B(OH)_4]^-$ with the notation 1:T, isolated (Fig. 1, 1a) has been found in the following species:
orthorhombic (space group Pbca = D_{2h}^{15}) $LiBO_2 \cdot 2\,H_2O = Li[B(OH)_4]$ [11,12]
hexagonal (P3 = C_3^1) $LiBO_2 \cdot 8\,H_2O = Li[B(OH)_4] \cdot 6\,H_2O$ [13,14]
triclinic $NaBO_2 \cdot 4\,H_2O = Na[B(OH)_4] \cdot 2\,H_2O$ [15]
tetragonal ($I\bar{4} = S_4^2$) $CsBO_2 \cdot 4\,H_2O = Cs[B(OH)_4] \cdot 2\,H_2O$ [16]
monoclinic ($P2/c = C_{2h}^4$) α-$CaB_2O_4 \cdot 4\,H_2O = Ca[B(OH)_4]_2$-I [17,18]
orthorhombic (Pban = D_{2h}^4) α'-$CaB_2O_4 \cdot 4\,H_2O = Ca[B(OH)_4]_2$-II [19]
triclinic β-$CaB_2O_4 \cdot 4\,H_2O = Ca[B(OH)_4]_2$-III = mineral *frolovite* [20], which is isotypic with β-$SrB_2O_4 \cdot 4\,H_2O = Sr[B(OH)_4]_2$-II [21]
monoclinic ($P2/c = C_{2h}^4$) α-$CaB_2O_4 \cdot 6\,H_2O = Ca[B(OH)_4]_2 \cdot 2\,H_2O$-I = mineral *hexahydroborite* [22,23]
monoclinic ($C2/c = C_{2h}^6$) β-$CaB_2O_4 \cdot 6\,H_2O = Ca[B(OH)_4]_2 \cdot 2\,H_2O$-II [24]
monoclinic ($P2_1/a = C_{2h}^5$) α-$SrB_2O_4 \cdot 4\,H_2O = Sr[B(OH)_4]_2$-I [25,26], which is isotypic with $BaB_2O_4 \cdot 4\,H_2O = Ba[B(OH)_4]_2$ [27] and also with the substitution product $Sr_{0.8}Ca_{0.2}B_2O_4 \cdot 4\,H_2O = Sr_{0.8}Ca_{0.2}[B(OH)_4]_2$ [28]
monoclinic ($P2_1/c = C_{2h}^5$) $BaB_2O_4 \cdot 5\,H_2O = Ba[B(OH)_4]_2 \cdot H_2O$ [29]
tetragonal (P4/nmm = D_{4h}^7) $Na_2Cl[B(OH)_4]$ = mineral *teepleite* [30,31]
tetragonal (P4/n = C_{4h}^3) $CuCl[B(OH)_4]$ = mineral *bandylithe* [32]
orthorhombic (Pnma = D_{2h}^{16}) $Mg_3(OH)_2(SO_4)[B(OH)_4]_2$ = mineral *sulfoborite* [33, 33A]
orthorhombic (Pbnm = D_{2h}^{16}) $Mn_3(OH)_2(PO_4)[B(OH)_4]$ = mineral *seamanite* [34]
tetragonal ($I\bar{4} = S_4^2$) $Ca_2(AsO_4)[B(OH)_4]$ = mineral *cahnite* [35,36] and
monoclinic ($P2_1/n = C_{2h}^6$) $MgCa_2(CO_3)[B(OH)_4]_2 \cdot 4\,H_2O$ = mineral *carboborite* [37].

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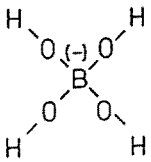
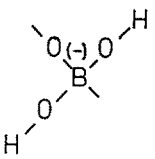
1 Isolated means that the unit is only connected by hydrogen bonds to the next unit, but not by oxygen bridges.

2 All triclinic crystals of borates belong to this space group; if there are doubts, this will be specifically mentioned.

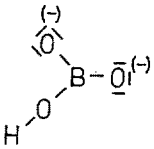
1. Monoborates:



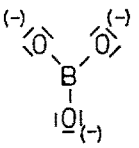
a 1: T, isolated
$[B(OH)_4]^-$



b 1∞: T, chains
$[B\,O(OH)_2]^-$

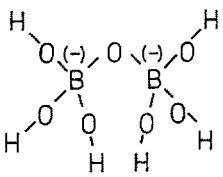


c 1: Δ, partially hydrated
$[B\,O_2(OH)]^{2-}$

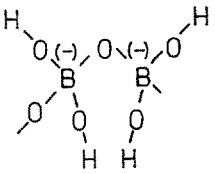


d 1: Δ, waterfree
$[B\,O_3]^{3-}$

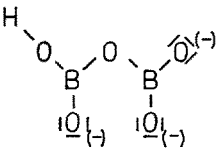
2. Diborates:



a 2: T, isolated
$[B_2\,O(OH)_6]^{2-}$

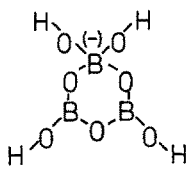


b 2∞: T, chains
$[B_2\,O_2(OH)_4]^{2-}$

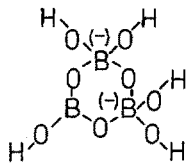


c 2: Δ, isolated, partially hydrated
$[B_2\,O_4(OH)]^{3-}$

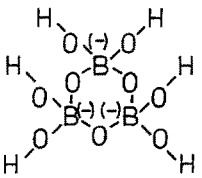
3. Triborates:



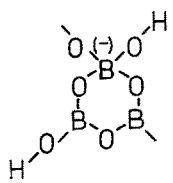
a 3: 2 Δ + T, isolated
$[B_3\,O_3(OH)_4]^-$



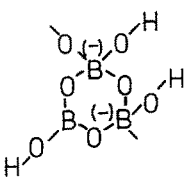
b 3: Δ + 2 T, isolated
$[B_3\,O_3(OH)_5]^{2-}$



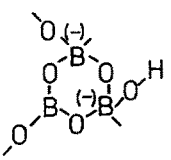
c 3: 3 T, isolated
$[B_3\,O_3(OH)_6]^{3-}$



d 3∞: 2 Δ + T, chains
$[B_3\,O_4(OH)_2]^-$



e 3∞: Δ + 2 T, chains
$[B_3\,O_4(OH)_3]^{2-}$

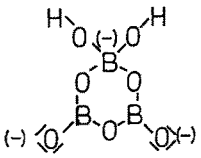


f $3\infty_2$: Δ + 2 T, sheets
$[B_3\,O_5(OH)]^{2-}$

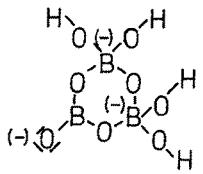
Fig. 1.

Fig. 1. (continued)

3. Triborates:

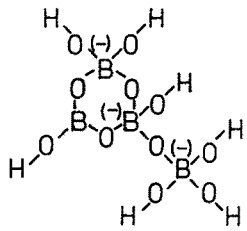


g 3 : (2 Δ + T), isolated, but not fully hydrated $[B_3O_5(OH)_2]^{3-}$

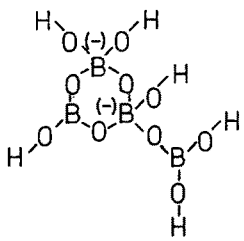


h 3: (Δ + 2 T), isolated, but not fully hydrated $[B_3O_4(OH)_4]^{3-}$

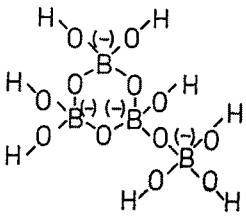
3. Triborates, modified:



i 3: (Δ + 2 T) + 1: T, modified $[B_4O_4(OH)_7]^{3-}$

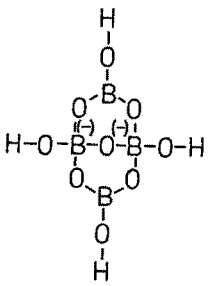


k 3: (Δ + 2 T) + 1: Δ, modified $[B_4O_4(OH)_6]^{2-}$

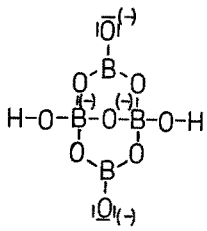


l 3: (3 T) + 1: T, modified $[B_4O_4(OH)_8]^{4-}$

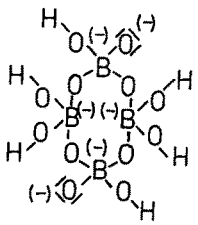
4. Tetraborates:



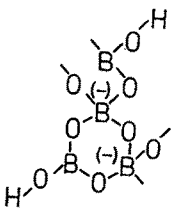
a 4−1: 2 Δ + 2 T, isolated $[B_4O_5(OH)_4]^{2-}$



b 4−1: 2 Δ + 2 T, isolated, but only partially hydrated $[B_4O_7(OH)_2]^{4-}$



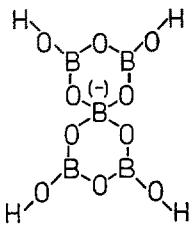
c 4−2: 4 T, isolated, but only partially hydrated $[B_4O_6(OH)_6]^{6-}$



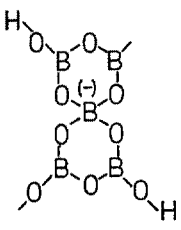
d 4∞: 2 Δ + 2 T, chains $[B_4O_6(OH)_2]^{2-}$

Fig. 1. (continued)

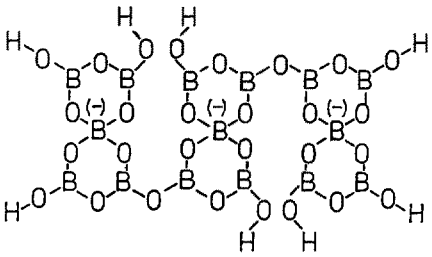
5. Pentaborates:



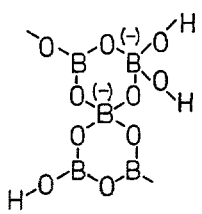
a 5 : 4 Δ + T,
isolated
$[B_5O_6(OH)_4]^-$



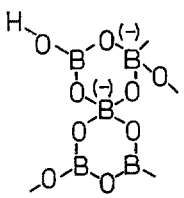
b $5\infty_2$: 4 Δ + T,
chains
$[B_5O_7(OH)_2]^-$



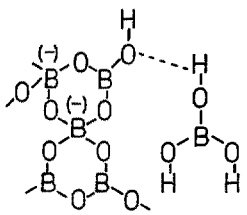
c 5: $(4\,\Delta + T)_3$, isolated, trimeric
$[B_{15}O_{20}(OH)_8]^{3-}$



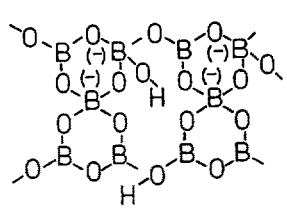
d $5\infty_2$: 3 Δ + 2 T,
chains A ≠ B
$[B_5O_7(OH)_3]^{2-}$



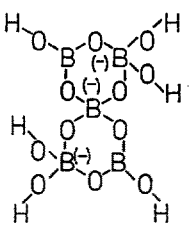
e $5\infty_3$: 3 Δ + 2 T,
sheets A ≠ B
$[B_5O_8(OH)]^{2-}$



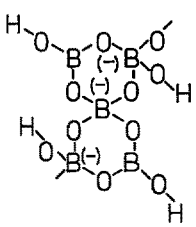
f $5\infty_3$: 3 Δ + 2 T, sheets,
modified + 1 Δ,
isolated B $(OH)_3$
$[B_6O_8(OH)_4]^{2-}$



g $5\infty_2$: 3 Δ + 2 T,
sheets, dimeric
$[B_{10}O_{16}(OH)_2]^{4-}$



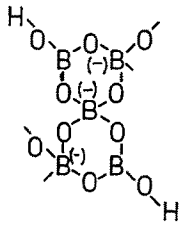
h 5: 2 Δ + 3 T,
A = B, isolated
$[B_5O_6(OH)_6]^{3-}$



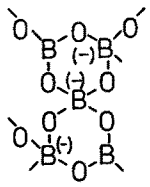
i 5∞: 2 Δ + 3 T,
A = B, chains
$[B_5O_7(OH)_4]^{3-}$

Fig. 1. (continued)

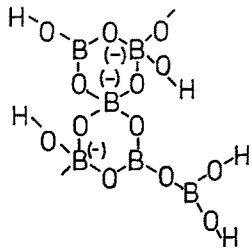
5. Pentaborates:



k $5\infty_2$: 2 Δ + 3 T, A=B, sheets $[B_5 O_8 (OH)_2]^{3-}$

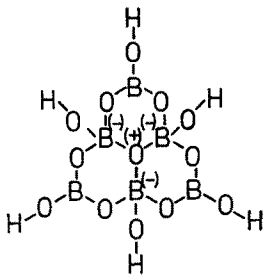


l $5\infty_3$: 2 Δ + 3 T, A=B, three-dimensional $[B_5 O_9]^{3-}$

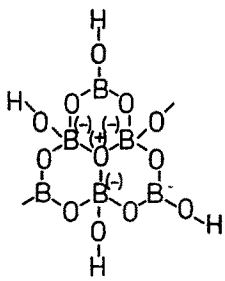


m 5∞: 2 Δ + 3 T, A=B, chains, + 1 Δ, modified $[B_6 O_8 (OH)_5]^{3-}$

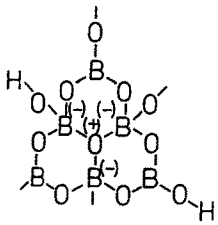
6. Hexaborates:



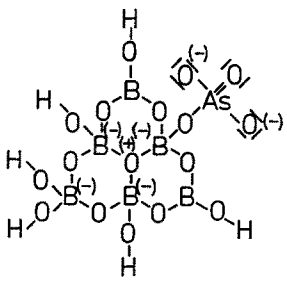
a 6: 3 Δ + 3 T, isolated $[B_6 O_7 (OH)_6]^{2-}$



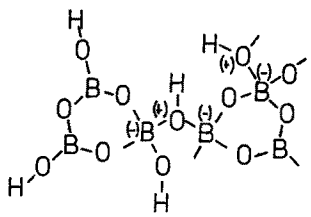
b 6∞: 3 Δ + 3 T, chains $[B_6 O_8 (OH)_4]^{2-}$



c $6\infty_2$: 3 Δ + 3 T, sheets $[B_6 O_9 (OH)_2]^{2-}$



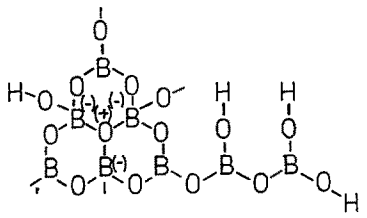
d 6: (2 Δ + 4 T) + As O_4, isolated, modified $[B_6 O_7 (OH)_6 \cdot O\,As\,O_3]^{5-}$



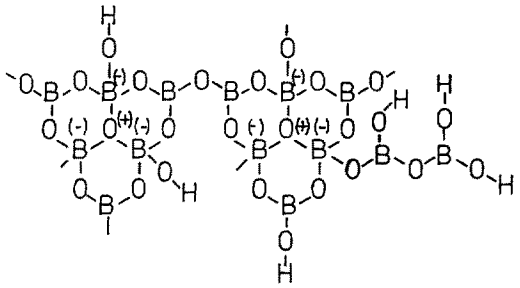
e $6\infty_2$: [(2 Δ + T) + (Δ + 2 T)], layers $[B_6 O_7 (OH)_5]^-$

Fig. 1. (continued)

6 Hexaborates:

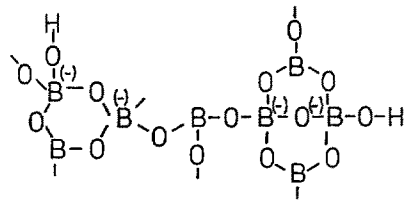


f $6\infty_2$: (3 Δ + 3 T) + 2 Δ, sheets, modified
$[B_8O_{11}(OH)_4]^{2-}$

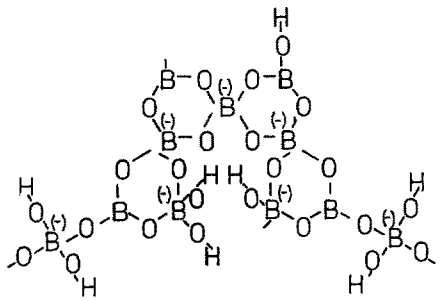


g $6\infty_2$: $(3\Delta + 3T)_2$ + 2 Δ, sheets, modified
$[B_{14}O_{20}(OH)_6]^{4-}$

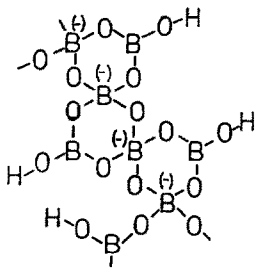
7. Higher Borates:



a $8\infty_3$: 3 (Δ + 2 T) + 1Δ + 4 (2 Δ + 2 T), network
$[B_8O_{13}(OH)_2]^{4-}$



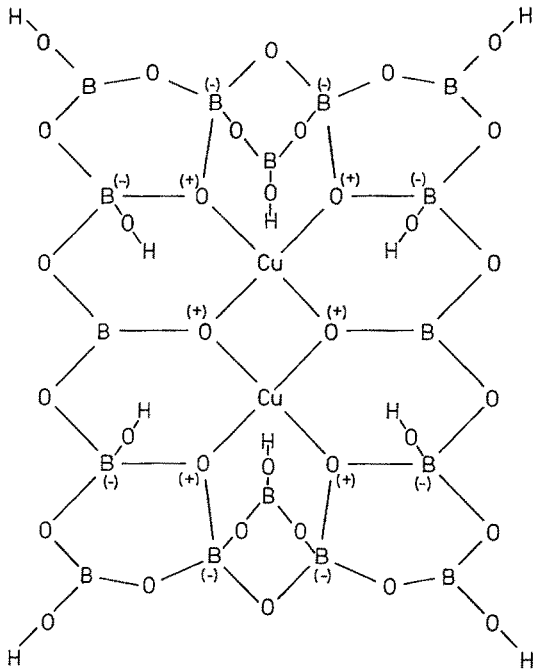
b $11\infty_2$: 9 (4 Δ + 5 T) + 2 T, sheets, modified
$[B_{11}O_{16}(OH)_8]^{7-}$



c $8\infty_2$: (4 Δ + 4 T),chains
$[B_8O_{12}(OH)_4]^{4-}$

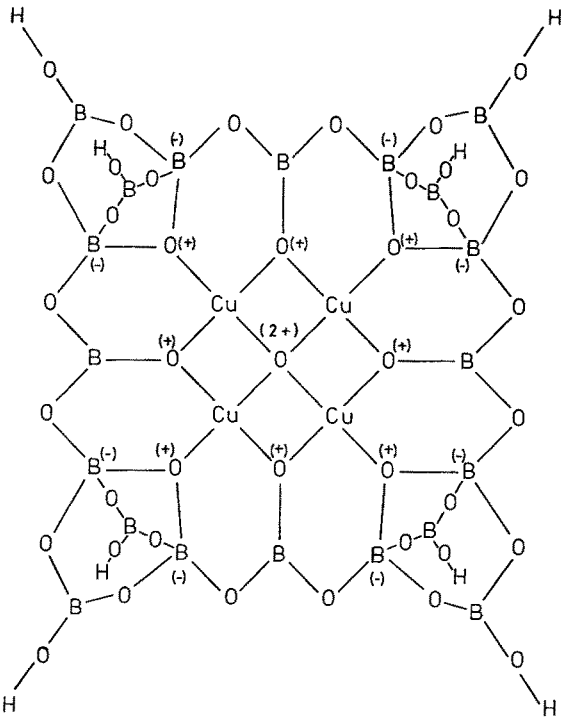
Fig. 1. (continued)

7. Higher Borates:



d

Complex
$\{Cu_2\,O_6\,[B_{16}\,O_{18}\,(OH)_{10}]\}^{6-}$



e

Complex
$\{Cu_4\,O\,[B_{20}\,O_{32}\,(OH)_8]\}^{6-}$

A substituted $[B(OH)_4]^-$ ion is present in the orthorhombic (Pbca = D_{2h}^{15}) $Na[B(OCH_3)_4] \cdot CH_3OH \cdot 1.5\ H_2O$ [38] and in the orthorhombic (Pnma = D_{2h}^{16}) $[C_5H_{12}N][B(OCH_3)_4]$ [39], another one in the hexagonal ($P6_3 = C_6^6$) $Na[B(OH)F_3]$ containing distorted tetrahedrally coordinated boron [40].

1.2 Polymeric Monoborates Containing Three-Coordinate Boron

Partially hydrated monomer anions containing three-coordinate boron (type 1::△, partially hydrated) (Fig. 1, 1c) have been found in the orthorhombic (Pnma = D_{2h}^{16}) $Na_4[B_2O_5] \cdot H_2O = Na_2[BO_2(OH)]$ [41]

1.2.1 Monoborates Containing Three-Coordinate Boron and Other Ions

The isolated $[BO_3]^{3-}$ ion (type 1:△) (Fig. 1, 1d) containing OH groups and other ions has been observed in the
orthorhombic (Pbca = D_{2h}^{15}) $Be_4[B_2O_7] \cdot H_2O = Be_2(OH,F)[BO_3]$ = mineral *hambergite* [42]
trigonal (P321 = D_3^2) $Be_4[B_2O_7] \cdot 3\ H_2O = Be_2(OH,F)[BO_3] \cdot H_2O$ = mineral *berborite* [43,44]
hexagonal ($P6_3/m = C_{6h}^2$) $Mg_3(OH,F)_3[BO_3]$ = *fluoborite* type [45]
monoclinic ($I2/m = C_{2h}^3$) $Mg_{10}[B_2O_{13}] \cdot 9\ H_2O = Mg_5[O(OH)_5(BO_3)] \cdot 2\ H_2O$ = mineral *wightmanite*, a 3 Å wallpaper structure with large, open channels [46], mentioned also as triclinic $Mg_9[(OH)_6(BO_3)]_2 \cdot 2\ H_2O$ [47]
monoclinic $Mg_5[(Cl,OH)_2(OH)_5(BO_3)] \cdot 5\ H_2O$ = mineral *shabynite*, similar to *wightmanite*, but from which it differs in X-ray powder reflections and chemical composition [48]
orthorhombic ($P2_12_12_1 = D_2^4$) $Mg_7[(Cl,OH)_5(BO_3)_3]$ = mineral *karlite* [49]
hexagonal ($P6_3/m = C_{6h}^2$) $Al_{12}[B_{10}O_{33}] \cdot 3\ H_2O = Al_6[(OH)_3(BO_3)_5]$ = mineral *jeremejevite* with a polymeric structure, similar to *fluoborite* and *painite*, with edge-connected BO_3 triangles [50,51] and
cubic ($Fd3 = T_h^4$) $Cd_4[B_2O_7] \cdot H_2O = Cd_4[(OH)_2(BO_3)_2]$ [52].

1.3 Diborates

If two $[B(OH)_4]^-$ ions are condensed, the fully hydrated 2:T, isolated (Fig. 1, 2a) diborate ion $[B_2O(OH)_6]^{2-}$ is formed which exists in
tetragonal ($P4_2 = C_4^3$) $Mg[B_2O_4] \cdot 3\ H_2O = Mg[B_2O(OH)_6]$ = mineral *pinnoite* [53,54] and in
triclinic $Ca[B_2O_4] \cdot 5\ H_2O = Ca[B_2O(OH)_6] \cdot 2\ H_2O$ = mineral *pentahydroborite* [55,56].
Further condensation of this ion leads to the chain 2∞:T, chains (Fig. 1, 1b or 2b), diborate ion $[B_2O_2(OH)_4]^{2-}$ which has been found in
monoclinic ($C2/c = C_{2h}^6$) $Ca[B_2O_4] \cdot 2\ H_2O$-II $= Ca[B_2O_2(OH)_4]$ = mineral *vimsite* [57].
2:△, isolated, but not fully hydrated (Fig. 1, 2c) is the ion $[B_2O_4(OH)]^{3-}$ consisting of one BO_3^{3-} and a $BO_2(OH)$ group which has been found in the monoclinic ($P2_1/a = C_{2h}^5$) members of the szaibelyite group:

$Mg_2[B_2O_5] \cdot H_2O = Mg_2(OH)[B_2O_4(OH)] =$ mineral *szaibelyite* (former *ascharite*) [58, 59]

$Mg_2[B_{2-x}H_{3x}O_5] \cdot H_2O$ ($x \approx 0.18$) = mineral *hydroxyascharite* [60] and
$Mn_2[B_2O_5] \cdot H_2O = Mn_2(OH)(B_2O_4(OH)] =$ mineral *sussexite* [59, 61].

1.4 Triborates

3:2△ + T, isolated (Fig. 1, 3a): The anion $[B_3O_3(OH)_4]^-$ occurs in the monoclinic ($C2/c = C_{2h}^6$) $Na[B_3O_5] \cdot 2\,H_2O = Na[B_3O_3(OH)_4]$ = mineral *ameghinite* [62].

3:△ + 2T, isolated (Fig. 1, 3b): The ion $[B_3O_3(OH)_5]^{2-}$ has been found in
monoclinic ($P2_1/a = C_{2h}^5$) $Mg_2[B_6O_{11}] \cdot 15\,H_2O$-I $= Mg[B_3O_3(OH)_5] \cdot 5\,H_2O$-I = mineral *inderite* [63]
triclinic $Mg_2[B_6O_{11}] \cdot 15\,H_2O$-II $= Mg[B_3O_3(OH)_5] \cdot 5\,H_2O$-II = mineral *kurnakovite* [64]
triclinic $Ca_2[B_6O_{11}] \cdot 7\,H_2O = Ca[B_3O_3(OH)_5] \cdot H_2O$ = mineral *meyerhofferite* [65, 66]
triclinic $Ca_2[B_6O_{11}] \cdot 9\,H_2O = Ca[B_3O_3(OH)_5] \cdot 2\,H_2O$ [66, 67]
monoclinic ($P2_1/a = C_{2h}^5$) $Ca_2[B_6O_{11}] \cdot 13\,H_2O = Ca[B_3O_3(OH)_5] \cdot 4\,H_2O$ = mineral *inyoite* [66, 68]
monoclinic ($C_{2/c} = C_{2h}^6$) $MgCa[B_6O_{11}] \cdot 11\,H_2O = MgCa[B_3O_3(OH)_5]_2 \cdot 6\,H_2O$ = mineral *inderborite* [69, 70]
orthorhombic ($Pnma = D_{2h}^{16}$) $Zn_2[B_6O_{11}] \cdot 7\,H_2O = Zn[B_3O_3(OH)_5] \cdot H_2O$ [71].

A partially fluoridized $[B_3O_3(OH)_5]^{2-}$ ion occurs in orthorhombic $K_2[B_3O_3(OH)F_4]$ [72].

3:3T, isolated (Fig. 1, 3c): This ion $[B_3O_3(OH)_6]^{3-}$ is contained in monoclinic

$(B2/b = C_{2h}^6)\, Ca[B_2O_4] \cdot \frac{8}{3} H_2O = Ca_3[B_3O_3(OH)_6]_2 \cdot 2\,H_2O =$ mineral *nifontovite* [73].

3∞:(2△ + T), chains (Fig. 1, 3d): The ion $[B_3O_4(OH)_2]^-$ has been found in

orthorhombic ($Pnma = D_{2h}^{16}$) $Tl[B_3O_5] \cdot \frac{3}{2} H_2O = Tl[B_3O_4(OH)_2] \cdot \frac{1}{2} H_2O$ [74].

3∞:(△ + 2T), chains (Fig. 1, 3e): The anion $[B_3O_4(OH)_3]^{2-}$ has been found in monoclinic ($P2_1/a = C_{2h}^5$) high-temperature $Ca_2[B_6O_{11}] \cdot 5\,H_2O$-I $= Ca[B_3O_4(OH)_3] \cdot H_2O$-I = mineral *colemanite* [66, 75, 76]
the monoclinic ($P2_1 = C_2^2$) low-temperature synthetic $Ca_2[B_6O_{11}] \cdot 5\,H_2O$-II $= Ca[B_3O_4(OH)_3] \cdot H_2O$-II [77]
monoclinic ($P2/c = C_{2h}^4$) $MgCa[B_6O_{11}] \cdot 6\,H_2O = MgCa[B_3O_4(OH)_3]_2 \cdot 3\,H_2O$ = mineral *hydroboracite* [78, 79]; and perhaps in $Sr_2[B_6O_{11}] \cdot 5\,H_2O$ [76A].

$3\infty_2$:(△ + 2T), sheets (Fig. 1, 3f): The anion $[B_3O_5(OH)]^{2-}$ has been found in synthetic orthorhombic ($Pbn2_1 = C_{2v}^9$) $Ca_2[B_6O_{11}] \cdot H_2O$-I $= Ca[B_3O_5(OH)]$-I [66, 80, 81], and in
monoclinic ($P2_1/a = C_{2h}^5$) $Ca_2[B_6O_{11}] \cdot H_2O$-II $= Ca[B_3O_5(OH)]$-II = mineral *fabianite* [81, 82].

3:(△ + 2T), isolated, but not fully hydrated (Fig. 1, 3h): The ion $[B_3O_4(OH)_4]^{3-}$ occurs in the

isotypic orthorhombic ($Pna2_1 = C_{2v}^9$) triborates $KBO_2 \cdot \frac{4}{3} H_2O = K_3[B_3O_4(OH)_4] \cdot 2\ H_2O$ [6,83–85] and

$RbBO_2 \cdot \frac{4}{3} H_2O = Rb_3[B_3O_4(OH)_4] \cdot 2\ H_2O$ [86], and in the

monoclinic ($P2_1/b = C_{2h}^5$) $Ca_2Cl[B_3O_4(OH)_4]$ = mineral *solongoite* [87].

3:(2△ + T), isolated, but only partially hydrated (Fig. 1, 3g) is the ion $[B_3O_5(OH)_2]^{3-}$, found in the orthorhombic (Pnma = D_{2h}^{16}) $NaBO_2 \cdot \frac{1}{3} H_2O = Na_3[B_3O_5(OH)_2]$ [88,89].

3:(△ + 2T) + 1T, modified (Fig. 1, 3i): The ion $(B_4O_4(OH)_7]^{3-}$ has been found in monoclinic (I2/a = C_{2h}^4) $Ca[B_8O_{15}]Cl_2 \cdot 21\ H_2O = Ca_2[B_3O_3(OH)_4 \cdot OB(OH)_3]Cl \cdot 7\ H_2O$ = mineral *hydrochlorborite* [90].

3:(3T) + 1T, modified (Fig. 1, 3l): The ion $[B_4O_4(OH)_8]^{4-}$ is better formulated as $[B_3O_3(OH)_5 \cdot OB(OH)_3]^{4-}$ and is found in monoclinic ($P2_1/n = C_{2h}^5$) $Ca[B_2O_4] \cdot 2\ H_2O$-I = $Ca_2[B_3O_3(OH)_5 \cdot OB(OH)_3]$ = mineral *uralborite* [91,92].

3:(△ + 2T) + 1△, modified (Fig. 1, 3k): The ion $[B_4O_4(OH)_6]^{2-}$ should exist in monoclinic ($P2_1/a = C_{2h}^5$) $Mg[B_4O_7] \cdot 9\ H_2O$-I = $Mg[B_3O_3(OH)_4 \cdot OB(OH)_2] \cdot 6\ H_2O$ [93].

1.5 Tetraborates

4-1:(2△ + 2T), isolated (Fig. 1, 4a): The anion $[B_4O_5(OH)_4]^{2-}$ has been found in
trigonal (R32 = D_3^7) $Na_2[B_4O_7] \cdot 5\ H_2O = Na_2[B_4O_5(OH)_4] \cdot 3\ H_2O$ = mineral *tincalconite* [94]
monoclinic (C2/c = C_{2h}^6) $Na_2[B_4O_7] \cdot 10\ H_2O = Na_2[B_4O_5(OH)_4] \cdot 8\ H_2O$ = mineral *borax* [95,96]
orthorhombic ($P2_12_12_1 = D_2^4$) $K_2[B_4O_7] \cdot 4\ H_2O = K_2[B_4O_5(OH)_4] \cdot 2\ H_2O$ [97]
monoclinic ($P2_1 = C_2^2$) $(NH_4)_2[B_4O_7 \cdot 4\ H_2O = (NH_4)_2[B_4O_5(OH)_4] \cdot 2\ H_2O$ [98]
monoclinic (B2/b or C2/c = C_{2h}^6) $[NH_3CH_2CH_2NH_3][B_4O_5(OH)_4]$ [99,100]
triclinic $Mg[B_4O_7] \cdot 9\ H_2O$-II = $Mg(H_2O)_5[B_4O_5(OH)_4] \cdot 2\ H_2O$ = mineral *hungchaoite* [101,102]. The isotypic synthetical orthorhombic ($P2_12_12_1 = D_2^4$) "octaborates" of the $Rb_2Sr[B_4O_5(OH)_4]_2 \cdot 8\ H_2O$ type:
$K_2Ca[B_8O_{14}] \cdot 12\ H_2O = K_2Ca[B_4O_5(OH)_4]_2 \cdot 8\ H_2O$ [103,106]
$Rb_2Ca[B_4O_5(OH)_4]_2 \cdot 8\ H_2O$ [107]
$Cs_2Ca[B_4O_5(OH)_4]_2 \cdot 8\ H_2O$ [107]
$(NH_4)_2Ca[B_4O_5(OH)_4]_2 \cdot 8\ H_2O$ [108]
$K_2Sr[B_4O_5(OH)_4]_2 \cdot 8\ H_2O$ [103]
$Rb_2Sr[B_4O_5(OH)_4]_2 \cdot 8\ H_2O$ [109]
$Cs_2Sr[B_4O_5(OH)_4]_2 \cdot 8\ H_2O$ [107]
$K_2Ba[B_4O_4(OH)_4]_2 \cdot 8\ H_2O$ [103] and
$Rb_2Ba[B_4O_5(OH)_4]_2 \cdot 8\ H_2O$ [110];
triclinic $Mn[B_4O_7] \cdot 9\ H_2O = Mn[B_4O_5(OH)_4] \cdot 7\ H_2O$ [111].

4-1:(2△ + 2T) (Fig. 1, 4b), isolated (but only partially hydrated): The anion

$[B_4O_7(OH)_2]^{4-}$ occurs in orthorhombic (Pmcb = D_{2h}^9) $Ca(Mn,Mg)[B_2O_5] \cdot 1.5\ H_2O = Ca_2(Mn,Mg)_2(OH)_4[B_4O_7(OH)_2]$ = mineral *roweite* [112,113].

4:∞(2△ + 2T), chains (Fig. 1, 4d): The anion $[B_4O_6(OH)_2]^{2-}$ is built not just by polymerization as in the triborate case, but also by breaking of a B—O bond in each polyanion entering the chain (5, 6). It has been found in
monoclinic ($P2_1/c = C_{2h}^5$) $Na_2[B_4O_7] \cdot 4\ H_2O = Na_2[B_4O_6(OH)_2] \cdot 3\ H_2O$ = mineral *kernite* [114–116]
orthorhombic (Pbca = D_{2h}^{15}) $Na_2[B_4O_7] \cdot H_2O = Na_2[B_4O_6(OH)_2]$ [117,118]
orthorhombic ($P2_12_12_1 = D_2^4$) $Tl_2[B_4O_7] \cdot 3\ H_2O = Tl_2[B_4O_6(OH)_2] \cdot 2\ H_2O$ [119]
and perhaps
triclinic $Tl_2[B_4O_7] \cdot 1.5\ H_2O = Tl_2[B_4O_6(OH)_6] \cdot \frac{1}{2} H_2O$
which is formulated by the authors as $Tl_4[B_8O_{12}(OH)_{12}] \cdot H_2O$ with the short-hand formulation 7:(3△ + 4T) + △ [120,120A]; [4]

4-2:(4T), isolated (Fig. 1, 4c), but only partially hydrated: The tetraborate ion $[B_4O_6(OH)_6]^{6-}$ has been reported in monoclinic (A2/m = C_2^3) $Ca_4Mg(CO_3)_2[B_4O_9] \cdot 3\ H_2O = Ca_4Mg(CO_3)_2[B_4O_6(OH)_6]$ = mineral *borcarite* [121].

1.6 Pentaborates

5:4△ + T, isolated (Fig. 1, 5a): The ion $[B_5O_6(OH)_4]^-$ has been found in
monoclinic ($P2_1/c = C_{2h}^5$) $Na[B_5O_8] \cdot 2\ H_2O = Na[B_5O_6(OH)_4]$ [122]
monoclinic ($C2/c = C_{2h}^6$) $Na[B_5O_8] \cdot 5\ H_2O = Na[B_5O_6(OH)_4] \cdot 3\ H_2O$ = mineral *sborgite* [123]
orthorhombic (Aba2 = C_{2v}^{17}) $K[B_5O_8] \cdot 4\ H_2O = K[B_5O_6(OH)_4] \cdot 2\ H_2O$ = mineral *santite* [124,126]
isotypic[3] $NH_4[B_5O_8] \cdot 4\ H_2O$-I = α-$NH_4[B_5O_6(OH)_4] \cdot 2\ H_2O$ [125,127,128]
monoclinic (Pn = C_s^1) $NH_4[B_5O_8] \cdot 4\ H_2O$-II = β-$NH_4[B_5O_6(OH)_4] \cdot 2\ H_2O$ [128–130], probably in
orthorhombic $(n\text{-}C_3H_7)_4N[B_5O_6(OH)_4]$ [131]
monoclinic ($P2_1/a = C_{2h}^5$) $Cs[B_5O_6(OH)_4] \cdot 2DMSO$ [132] and
monoclinic ($P2_1 = C_2^2$ or $P2_1/m = C_{2h}^2$ [133], better $P2_1/c = C_{2h}^5$ [134]) $Tl[B_5O_8] \cdot 4\ H_2O = Tl[B_5O_6(OH)_4] \cdot 2\ H_2O$.

5∞$_2$:(4△ + T), chains (Fig. 1, 5b): The ion $[B_5O_7(OH)_2]^-$ occurs in monoclinic ($P2_1/c = C_{2h}^5$) $NH_4[B_5O_8] \cdot 2\ H_2O = NH_4[B_5O_7(OH)_2] \cdot H_2O$ = mineral *larderellite* [135].

5:∞$_2$(3△ + 2T), chains (Fig. 1, 5d): The ion $[B_5O_7(OH)_3]^{2-}$ has been found in triclinic $Na_4[B_{10}O_{17}] \cdot 7\ H_2O = Na_2[B_5O_7(OH)_3] \cdot 2\ H_2O$ = mineral *ezcurrite* [136, 137].

5:∞$_3$(3△ + 2T), sheets (Fig. 1, 5e): The ion $[B_5O_8(OH)]^{2-}$ occurs in
orthorhombic (Pna2$_1$ = C_{2v}^9) $Na_4[B_{10}O_{17}] \cdot 5\ H_2O = Na_2[B_5O_8(OH)] \cdot 2\ H_2O$ = mineral *nasinite* [117,138] and the
isostructural $K_4[B_{10}O_{17}] \cdot 5\ H_2O = K_2[B_5O_8(OH)] \cdot 2\ H_2O$ [139].

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3 $Rb[B_5O_8] \cdot 4\ H_2O = Rb[B_5O_6(OH)_4] \cdot 2\ H_2O$ [126A] and
4 +△ should be reserved for side chains

5:∞_3(3△ + 2T), sheets, modified with $B(OH)_3$ (Fig. 1, 5f): The ion $[B_5O_8(OH) \cdot B(OH)_3]^{2-}$ exists in
monoclinic ($P2_1/a = C_{2h}^5$) $Ca[B_6O_{10}] \cdot 5\,H_2O = Ca[B_5O_8(OH) \cdot B(OH)_3] \cdot 3\,H_2O$ = mineral *gowerite* [140]
monoclinic ($Aa = C_S^4$) $Sr_4[B_{22}O_{37}] \cdot 7\,H_2O$-I = $Sr_2\{[B_5O_8(OH)]_2 \cdot B(OH)_3\} \cdot H_2O$-I = mineral *veatchite* [141,142] and
monoclinic ($P2_1 = C_2^2$) $Sr_4[B_{22}O_{37}] \cdot 7\,H_2O$-II = $Sr_2\{[B_5O_8(OH)]_2 \cdot B(OH)_3\} \cdot H_2O$-II = mineral *paraveatchite* [143].

5:(2△ + 3T), A = B, isolated (Fig. 1, 5h): The ion $[B_5O_6(OH)_6]^{3-}$ has been found in triclinic $NaCa[B_5O_9] \cdot 8\,H_2O = NaCa[B_5O_6(OH)_6] \cdot 5\,H_2O$ = mineral *ulexite* [144].

5:∞(2△ + 3T), A = B, chains (Fig. 1, 5i): The ion $[B_5O_7(OH)_4]^{3-}$ occurs in monoclinic ($P2_1/c = C_{2h}^5$) $NaCa[B_5O_9] \cdot 5\,H_2O = NaCa[B_5O_7(OH)_4] \cdot 3\,H_2O$ = mineral *probertite* [145–147].

5:∞_2(2△ + 3T), A = B, sheets (Fig. 1, 5k): The ion $[B_5O_8(OH)_2]^{3-}$ exists in
tetragonal ($P4_12_12_1 = D_4^4$) $Li_3[B_5O_9] \cdot H_2O$-I = $Li_3[B_5O_8(OH)_2]$-I [148,149]
orthorhombic ($Pn2b = C_{2v}^6$) $Li_3[B_5O_9] \cdot H_2O$-II = $Li_3[B_5O_8(OH)_2]$-II [150]
orthorhombic ($Pbca = D_{2h}^{15}$) $Na_3[B_5O_9] \cdot 2\,H_2O = Na_3(H_2O)[B_5O_8(OH)_2]$ [117,151] and
monoclinic ($C2/c = C_{2h}^6$) $Na_2Ca_3(SO_4)_2Cl[B_5O_9] \cdot H_2O = Na_2Ca_3(SO_4)_2Cl[B_5O_8(OH)_2]$ = mineral *heidornite* [152].

5:∞_3(2△ + 3T), A = B, network (Fig. 1, 5l): The ion $[B_5O_9]^{3-}$ has been found in
orthorhombic ($Pca2_1 = C_{2v}^5$) $Na_3[B_5O_9] \cdot H_2O$ [153]
monoclinic ($Aa = C_S^4$) $Ca_2[B_5O_9]Cl \cdot H_2O$-I = mineral *hilgardite* [154]
triclinic ($Pl = C_1^1$) $Ca_2[B_5O_9]Cl \cdot H_2O$-II = $[Ca_2(B_5O_9)Cl \cdot H_2O]_3$ = mineral *parahilgardite* [155,156] and in the
probably isostructural species $(Ca,Sr)_2[B_5O_9](OH,Cl) \cdot H_2O$-III = minerals *strontiohilgardite*, *tyretskite* or *chlortyretskite* (they are a structural pair, depending on the content of Sr or/and OH/Cl) [157–159].

5:∞(2△ + 3T), A = B, chains, modified + △ (Fig. 1, 5m): The ion $[B_5O_7(OH)_3 \cdot OB(OH)_2]^{3-}$ has been found in monoclinic ($C2/c = C_{2h}^6$) $K_2Mg_4[B_{24}O_{41}] \cdot 19\,H_2O = KMg_2H[B_5O_7(OH)_3 \cdot OB(OH)_2]_2 \cdot 4\,H_2O$ = mineral *kaliborite* [160].

5:∞_2(3△ + 2T), sheets, modified (Fig. 1, 5g): The ion $[B_5O_8(OH) \cdot OB_5O_7(OH)]^{4-}$ occurs in monoclinic ($P2_1/c = C_{2h}^5$) $Na_4[B_{10}O_{17}] \cdot 3\,H_2O = Na_4[B_{10}O_{16}(OH)_2] \cdot 2\,H_2O = Na_4(H_2O)_2[(HO)B_5O_8 \cdot OB_5O_7(OH)]$ = mineral *biringuccite* [161].

5:(4△ + T)$_3$, isolated, trimeric (Fig. 1, 5c): The ion $[B_5O_6(OH)_3 \cdot OB_5O_6(OH)_2 OB_5O_6(OH)_3]^{3-}$ exists in monoclinic ($C2/c = C_{2h}^6$) $NH_4[B_5O_8] \cdot 2\frac{2}{3}H_2O = (NH_4)_3[B_{15}O_{20}(OH)_8] \cdot 4\,H_2O = (NH_4)_3[B_5O_6(OH)_3 \cdot OB_5O_6(OH)_2 \cdot OB_5O_6(OH)_3] \cdot 4\,H_2O$ = mineral *ammonioborite* [162].

1.7 Hexaborates

6:3△ + 3T, isolated (Fig. 1, 6a): The ion $[B_6O_7(OH)_6]^{2-}$ has been found in
orthorhombic ($Pbca = D_{2h}^{15}$) $Mg[B_6O_{10}] \cdot 5\,H_2O = Mg[B_6O_7(OH)_6] \cdot 2\,H_2O$ = mineral *aksaite* [163,164]

monoclinic ($P2_1/c = C_{2h}^5$) $Mg[B_6O_{10}] \cdot 6\ H_2O = Mg[B_6O_7(OH)_6] \cdot 3\ H_2O = Mg(H_2O)_6\{Mg[B_6O_7(OH)_6]_2\}$ [165,166]
monoclinic ($P2_1/c = C_{2h}^5$) $Mg[B_6O_{10}] \cdot 7\ H_2O = Mg[B_6O_7(OH)_6] \cdot 4\ H_2O$ $Mg(H_2O)_6\{Mg[B_6O_7(OH)_6]_2\} \cdot 2\ H_2O$ = mineral *admontite* [167,168]
trigonal ($R\bar{3}c = D_3^6$) $Mg[B_6O_{10}] \cdot 7\frac{1}{2}\ H_2O$ $Mg(B_6O_7(OH)_6] \cdot 4\frac{1}{2}\ H_2O = Mg(H_2O)_6\{Mg[B_6O_7(OH)_6]_2\} \cdot 3\ H_2O$ = mineral *macallisterite* [169,170]
monoclinic ($P2_1/c = C_{2h}^5$) $Na_6Mg[B_{24}O_{40}] \cdot 22\ H_2O = Na_6Mg(H_2O)_8[B_6O_7(OH)_6] \cdot 2\ H_2O$ = mineral *rivadavite* [171]
monoclinic ($P2_1/b = C_{2h}^5$) $Co[B_6O_{10}] \cdot 10\ H_2O = Co(H_2O)_3[B_6O_7(OH)_6] \cdot 4\ H_2O$ [172,173] and the
isostructural $Ni[B_6O_{10}] \cdot 10\ H_2O = Ni[B_6O_7(OH)_6] \cdot 7\ H_2O$ [172,173]
triclinic $Ni[B_6O_{10}] \cdot 8\ H_2O = Ni(H_2O)_4[B_6O_7(OH)_6] \cdot H_2O$ [174]
monoclinic ($P2_1/c = C_{2h}^5$) $Co[B_6O_{10}] \cdot 7\ H_2O = Co(H_2O)_6\{Co[B_6O_7(OH)_6]_2\} \cdot 2\ H_2O$ [175]
monoclinic ($P2_1/b = C_{2h}^5$) $Ni(H_2O)_3[B_6O_7(OH)_6] \cdot 3\ H_2O \cdot \frac{1}{2}(CH_3)_2CO$ [176]
monoclinic ($P2_1/b = C_{2h}^5$) $Ni(H_2O)_3[B_6O_7(OH)_6] \cdot \frac{3}{2}\ H_2O \cdot C_2H_5OH$ [177] and
isostructural $Co(H_2O)_3[B_6O_7(OH)_6] \cdot \frac{3}{2}\ H_2O \cdot C_2H_5OH$ [173,178]
triclinic $K_2Co[B_{12}O_{20}] \cdot 10\ H_2O = K_2(H_2O)_2\{Co[B_6O_7(OH)_6]_2\} \cdot 2\ H_2O$ [179]
monoclinic ($P2_1/c = C_{2h}^5$) $Ni_{0.8}Mn_{0.2}(H_2O)_3[B_6O_7(OH)_6] \cdot C_2H_5OH \cdot 0.42\ H_2O$ [180]
triclinic $Na_6Co_3[B_6O_{10}]_6 \cdot 44\ H_2O = Na_6Co_3[B_6O_7(OH)_6]_6 \cdot 26\ H_2O$ [181] and
triclinic $(NH_4)_2Zn(H_2O)_4[B_6O_7(OH)_6]_2$ and the isotypic $K_2Cd(H_2O)_4[B_6O_7(OH)_6]_2$ [182].

6:∞(3△ + 3T), chains (Fig. 1, 6b): The ion $[B_6O_8(OH)_4]^{2-}$ has been found in
monoclinic ($P2_1/a = C_{2h}^5$) $Na_2Mg[B_{12}O_{20}] \cdot 8\ H_2O = Na_2Mg[B_6O_8(OH)_4]_2 \cdot 4\ H_2O$ = mineral *aristarainite* [183,184].

6:∞_2(3△ + 3T), sheets (Fig. 1, 6c): The ion $[B_6O_9(OH)_2]^{2-}$ occurs in
monoclinic ($P2_1/a = C_{2h}^5$) $Sr[B_6O_{10}] \cdot 4\ H_2O = Sr[B_6O_9(OH)_2] \cdot 3\ H_2O$ = mineral *tunellite* [185] and the
isotypic $Ca[B_6O_{10}] \cdot 4\ H_2O = Ca[B_6O_9(OH)_2] \cdot 3\ H_2O$ = mineral *nobleite* [185,186].

6:∞_2(3△ + 3T) + 2△, sheets, modified (Fig. 1, 6f): The ion $[B_6O_9(OH) \cdot OB(OH) \cdot OB(OH)_2]^{2-}$ occurs in
monoclinic ($P2_1 = C_2^2$) $Sr[B_8O_{13}] \cdot 2\ H_2O = Sr[B_8O_{11}(OH)_4] = Sr[B_6O_9(OH) \cdot OB(OH) \cdot OB(OH)_2]$ = mineral *strontioborite* [187]
isotypic $Ca[B_8O_{13}] \cdot 2\ H_2O = Ca[B_8O_{11}(OH)_4] = Ca[B_6O_9(OH) \cdot OB(OH) \cdot OB(OH)_2$ [188].

6:∞_2[(3△ + 3T)$_2$ + 2△], sheets, modified (Fig. 1, 6g): The ion $[B_6O_9(OH)_2 \cdot OB_6O_8(OH) \cdot OB(OH) \cdot OB(OH)_2]^{4-}$ has been found in
monoclinic ($P2_1/a = C_{2h}^5$) $(Sr,Ca)_2[B_{14}O_{23}] \cdot 8\ H_2O = (Sr,Ca)_2[B_{14}O_{20}(OH)_6] \cdot 5\ H_2O = (Sr,Ca)_2[B_6O_9(OH)_2 \cdot OB_6O_8(OH) \cdot OB(OH) \cdot OB(OH)_2] \cdot 5\ H_2O$ = mineral *volkovite* [189]
the isotypic compounds $Ca_2[B_{14}O_{23}] \cdot 8\ H_2O = Ca_2[B_{14}O_{20}(OH)_6] \cdot 5\ H_2O = Ca_2[B_6O_9(OH)_2 \cdot OB_6O_8(OH) \cdot OB(OH) \cdot OB(OH)_2] \cdot 5\ H_2O$ = mineral *ginorite* [189,190]

$Sr_2[B_{14}O_{20}(OH)_6] \cdot 5\ H_2O = Sr_2[B_6O_9(OH)_2 \cdot OB_6O_8(OH) \cdot OB(OH) \cdot OB(OH)_2] \cdot 5\ H_2O$ = mineral *strontioginorite* [189].

6:∞_2[(2△ + T) + (△ + 2T)], layers (Fig. 1, 6e): The ion $[B_6O_7(OH)_5]^-$ has been found in monoclinic ($P2_1/c = C_{2h}^5$) $Mg[B_{12}O_{19}] \cdot 5\ H_2O = Mg[B_6O_7(OH)_5]_2$ [191].

6:(2△ + 4T), isolated, modified + AsO_4 (Fig. 1, 6d): The ion $[B_6O_7(OH)_6 \cdot OAsO_3]^{5-}$ has been found in monoclinic ($P2_1/a = C_{2h}^5$) $Ca_4Mg[B_{12}O_{20}](AsO_4)_2 \cdot 20\ H_2O = Ca_4Mg[(B_6O_7(OH)_6) \cdot OAsO_3]_2 \cdot 14\ H_2O$ = mineral *teruggite* [192].

1.8 Higher Borates

8:∞_3[3(△ + 2T) + △ + 4(2△ + 2T)], network (Fig. 1, 7a): The ion $[B_8O_{13}(OH)_2]^{4-}$ has been found in triclinic $Ca[B_4O_7] \cdot \frac{1}{2} H_2O = Ca[B_8O_{13}(OH)_2]$ [193, 194].

8:∞_2[4(2△ + 2T) + 4(2△ + 2T)], chains (Fig. 1, 7c): The ion $[B_8O_{12}(OH)_4]^{4-}$ occurs in $Tl_2[B_4O_7] \cdot \frac{3}{2} H_2O = Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$; see tetraborates [120, 120A].

6:∞_2[(3△ + 3T) + 2△], sheets: The ion $[B_8O_{11}(OH)_4]^{2-}$ has been found in $Ca[B_8O_{13}] \cdot 2\ H_2O$ and $Sr[B_8O_{13}] \cdot 2\ H_2O$ = mineral *strontioborite*; see hexaborates [187, 188].

5:∞_2(3△ + 2T)$_2$, sheets: The ion $[B_{10}O_{16}(OH)_2]^{4-}$ exists in $Na_4[B_{10}O_{17}] \cdot 3\ H_2O$ = mineral *biringuccite*; see pentaborates [161].

11:∞_2[9(4∞ + 5T) + 2T], sheets, modified (Fig. 1, 7b): The ion $[B_{11}O_{16}(OH)_8]^{7-}$ has been found in orthorhombic (Pbcn = D_{2h}^{14}) $Mg_6[B_{22}O_{39}] \cdot 9\ H_2O = Mg_3[B_{11}O_{15}(OH)_9] = HMg_3[B_{11}O_{16}(OH)_8] = HMg_3\{B_9O_{12}(OH)_4 \cdot [O_2B(OH)_2]_2\}$ = mineral *preobratschenskite* [6, 195, 196, 197].

5:∞_2[(2△ + 3T, A = B) + △], chains, modified: The ion $[B_{12}O_{16}(OH)_{10}]^{6-}$ is better formulated as $[B_5O_7(OH)_3 \cdot OB(OH)_2]^{3-}$ and exists in the compound $K_2Mg_4[B_{24}O_{41}] \cdot 19\ H_2O = HKMg_2(H_2O)_4[B_5O_7(OH)_3 \cdot OB(OH)_2]_2$ = mineral *kaliborite* (*paternoite*); see pentaborates [6, 160, 196, 197].

12:(6△ + 6T), isolated: The ion $[B_{12}O_{20}(OH)_4]^{8-}$ exists in monoclinic ($P2_1/c = C_{2h}^5$) $Na_4[B_6O_{11}] \cdot H_2O = Na_8[B_{12}O_{20}(OH)_4]$ [198].

6:∞_2[(3△ + 3T) + 2△], sheets:

The ion $[B_{14}O_{20}(OH)_6]^{4-}$ has been found in $(Sr,Ca)_2[B_{14}O_{23}] \cdot 8\ H_2O$ = mineral *volkovite* [189]

in $Ca_2[B_{14}O_{23}] \cdot 8\ H_2O$ = mineral *ginorite* [190] and in

$Sr_2[B_{14}O_{23}] \cdot 8\ H_2O$ = mineral *strontioginorite* [189, 190]; see hexaborates.

5:(4△ + T)$_3$, isolated, trimeric: The ion $[B_{15}O_{20}(OH)_8]^{3-}$ occurs in $NH_4[B_5O_8] \cdot 2\frac{2}{3} H_2O = (NH_4)_3[B_{15}O_{20}(OH)_8] \cdot 4\ H_2O$ = mineral *ammonioborite*; see pentaborates [162].

16:(8 Δ + 8T), complex: The im $[B_{16}O_{24}(OH)_8]^{8-}$ exists in the monoclinic complex $K_6\{UO_2[B_{16}O_{24}(OH)_8]\} \cdot 12\ H_2O$ [201].

16:(6△ + 10T), complex: The ion $[B_{16}O_{24}(OH)_{10}]^{10-}$ exists in the triclinic complex $8\ B_2O_3 \cdot 2\ CuO \cdot 3\ Na_2O \cdot 17\ H_2O = Na_6\{Cu_2[B_{16}O_{24}(OH)_{10}]\} \cdot 12\ H_2O$ [199]; Fig. 1, 7d.

20:(12△ + 8T), complex: The ion $[B_{20}O_{32}(OH)_8]^{12-}$ has been found in tetragonal (I4 = S_4^2) $Na_5H\{Cu_4O[B_{20}O_{32}(OH)_8]\} \cdot 32\ H_2O$; and in triclinic $HK_5\{Cu_4O[B_{20}O_{32}(OH)_8]\} \cdot 32\ H_2O$ [200]; Fig. 1, 7e.

1.9 Peroxoborates

Known are the structures of
triclinic $NaBO_3 \cdot 4\ H_2O = Na_2[B_2(O_2)_2(OH)_4] \cdot 6\ H_2O$ [202]
triclinic $NaBO_3 \cdot 3\ H_2O = Na_2[B_2(O_2)_2(OH)_4] \cdot 4\ H_2O$ [202A]
monoclinic ($P2_1/c = C_{2h}^5$) $LiBO_3 \cdot H_2O = Li_2[B_2(O_2)_2(OH)_4]$ [203]. In all three compounds, there exists the ion $[B_2(O_2)_2(OH)_4]^{2-}$ (see Fig. 2).

Unknown are the structures of the triclinic $NaBO_3 \cdot 3\ H_2O$ [204,205]; orthorhombic $Na_2B_2O_5 \cdot 4\ H_2O$ [206]; orthorhombic $KBO_3 \cdot H_2O$ [207,209]; and triclinic $KBO_3 \cdot H_2O_2$ [208,209]; X-ray powder data have been reported for all compounds.

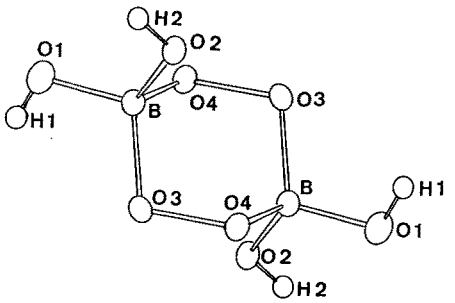


Fig. 2

1.10 Incompletely Characterized Hydrated Borates

The structures of the following hydrated borates and polyborates are unknown but X-ray powder data on the species have been reported:

Trigonal ($C3 = C_3^4$) $B_2O_3 \cdot Li_2O \cdot H_2O = LiBO_2 \cdot \frac{1}{2} H_2O$ and $2\ B_2O_3 \cdot Li_2O \cdot 2\ H_2O$ [210]
$2\ B_2O_3 \cdot Li_2O \cdot 5\ H_2O = Li_2[B_4O_7] \cdot 5\ H_2O = Li_2[B_4O_5(OH)_4] \cdot 3\ H_2O$ (?) [211]
$B_2O_3 \cdot Na_2O \cdot 4\ H_2O = Na[B(OH)_4]$ (?) [212]
triclinic $B_2O_3 \cdot Tl_2O \cdot H_2O = TlBO_2 \cdot \frac{1}{2} H_2O$ and
orthorhombic (Pbam = D_{2h}^9 or Pba2 = C_{2v}^8) $B_2O_3 \cdot Tl_2O \cdot 2\ H_2O = TlBO_2 \cdot H_2O$ [213];
monoclinic ($P2/c = C_{2h}^4$ or $Pc = C_s^2$) $Mg[B_4O_7] \cdot 3\ H_2O = Mg[B_4O_5(OH)_4] \cdot H_2O$ (?) = mineral *halurgite* [214]
monoclinic $P2/m = C_{2h}^1$ (?) $B_2O_3 \cdot 2\ MgO \cdot 2\ MgCO_3 \cdot H_2O = Mg_4[B_2O_5](CO_3)_2 \cdot H_2O$ = mineral *canavesite* [215]
monoclinic ($C2 = C_2^3$, or $Cm = C_3^3$, or $C2/m = C_{2h}^3$) $B_2O_3 \cdot 3\ MgO \cdot P_2O_5 \cdot 8\ H_2O = Mg_3[B_2O(OH)_4](PO_4)_2 \cdot 6\ H_2O$ (?) = mineral *lüneburgite* [216,217]
$12\ B_2O_3 \cdot MgO \cdot 5\ CaO \cdot 30\ H_2O = Ca_5Mg[B_{24}O_{42}] \cdot 30\ H_2O = Ca_5Mg[B_4O_5(OH)_4]_6 \cdot 18\ H_2O$ (?) = hexagonal (?) mineral *wardsmithite* [218]

cubic ($F4_132 = O^4$) $B_2O_3 \cdot MgO \cdot 2\,CaO \cdot CaCO_3 \cdot 0.36\,H_2O = Ca_3Mg[(BO_3)_2(CO_3)] \cdot 0.36\,H_2O$ = mineral *sakhaite* [219,220]
orthorhombic ($Pbca = D_{2h}^{15}$) $B_2O_3 \cdot MgO \cdot CaCl_2 \cdot 7\,H_2O = CaMg[B_2O_4]\,Cl_2 \cdot 7\,H_2O$ = mineral *chelkarite* [221]
$B_2O_3 \cdot xMgO \cdot yCaO \cdot zCaCl_2 \cdot 2n\,H_2O = (Ca,Mg)_2(BO_3)Cl \cdot n\,H_2O$ = mineral *aldzhanite* [221,222]
monoclinic $B_2O_3 \cdot MgCO_3 \cdot 2\,CaO \cdot 10\,H_2O = MgCa_2[B_2O_3(OH)_4](CO_3) \cdot 8\,H_2O$ (?) = mineral *carboborite* [223]
$B_2O_3 \cdot CaO \cdot H_2O = Ca[B_2O_4] \cdot H_2O$ = mineral *korzhinskiite* [90]
monoclinic ($P2_1/m = C_{2h}^2$ or $P2_1 = C_2^2$) $B_2O_3 \cdot 2\,CaO \cdot H_2O = Ca_2[B_2O_5] \cdot H_2O$-I $= Ca[B_2O_4(OH)_2]$-I (?) [224]
orthorhombic $B_2O_3 \cdot 2\,CaO \cdot H_2O = Ca_2[B_2O_5] \cdot H_2O$-II = mineral *sibirskite* [225]
$5\,B_2O_3 \cdot 4\,CaO \cdot 7\,H_2O = Ca_4[B_{10}O_{14}] \cdot 7\,H_2O = Ca_2[B_5O_6(OH)_7]$ or $Ca_2[B_5O_7(OH)_5] \cdot H_2O$ = mineral *priceite* (*pandermite*) [226]
monoclinic $5\,B_2O_3 \cdot 4\,CaO \cdot 20\,H_2O = Ca_4[B_{10}O_{14}] \cdot 20\,H_2O = Ca_4[B_5O_7(OH)_5] \cdot 15\,H_2O$ (?) = mineral *tertschite* [227]
monoclinic or triclinic $2\,B_2O_3 \cdot 3\,CaO \cdot 9\,H_2O = Ca_3[B_4O_9] \cdot 9\,H_2O = Ca_3[B(OH)_4]_4(OH)_2$ (?) = mineral *olshanskyite* [228]
$2\,B_2O_3 \cdot 2\,(Ca,Sr)O \cdot H_2O = (Ca,Sr)_2[B_4O_7(OH)_2]$ (?) = mineral *kurgantaite* [158]
$3\,B_2O_3 \cdot (Ca,Sr)O \cdot 3\,H_2O = (Ca,Sr)[B_6O_{10}] \cdot 3\,H_2O = Ca[B_3O_4(OH)_2] \cdot H_2O$ (?) = mineral *volkovskite* [229,230]
hexagonal $2\,B_2O_3 \cdot CaO \cdot CaCl_2 \cdot 3\,H_2O = Ca_2[B_4O_7](Cl, OH)_2$ = mineral *ekaterinite* [231]
monoclinic ($P2/m = C_{2h}^1$ or $P2 = C_2^1$ or $Pm = C_s^1$) $B_2O_3 \cdot xCaO \cdot yCaCl_2 \cdot n\,H_2O$ = mineral *ivanovite* [232]
tetragonal (?) chloride-containing $(Ca,Mg,Mn)_4[B_2O_7] \cdot 2\,H_2O = (Ca,Mg,Mn)_4[B_2O_5(OH,Cl)_4]$ (?) = mineral *wiserite* [61,225,233]
monoclinic ($P2_1/c = C_{2h}^5$) $B_2O_3 \cdot BaO \cdot H_2O = Ba[B_2O_4] \cdot H_2O$ [234]
cubic ($P43m = T_d^1$) $11\,B_2O_3 \cdot 4\,Al_2O_3 \cdot 8\,BeO \cdot (Cs,K,Rb)_2O \cdot 2\,H_2O = (Cs,K,Rb)\{Be_4Al_4[B_{11}O_{26}(OH)_2]\}$ = mineral *rhodicite* [235,236]
orthorhombic ($Pbca = D_{2h}^{15}$) $6\,B_2O_3 \cdot 4\,Al_2O_3 \cdot 4\,NaCl \cdot 2\,KCl \cdot 26\,H_2O = KNa_2Al_4[B_6O_{15}]Cl_3 \cdot 13\,H_2O = KNa_2\{Al_4[B_2O(OH)_6]_3(OH)_6Cl_3\} \cdot H_2O$ (?) = mineral *satimolite* [221,237,238]
hexagonal $11\,B_2O_3 \cdot 7\,(Na_2O,CaO) \cdot RE_2O_3 \cdot 7\,H_2O = (Ca,Na_2)_7(RE)_2[B_{22}O_{43}] \cdot 7\,H_2O$ or, more probably, $12\,B_2O_3 \cdot 6\,(Na_2O, CaO) \cdot RE_2O_3 \cdot 6\,H_2O = (Ca,Na_2)_6(RE)_2[B_{24}O_{45}] \cdot 6\,H_2O$ = mineral *braitschite* [239].

1.11 Hydrated Boropolytungstates

The following boron-containing heteropolytungstates have not yet been completely characterized:
hexagonal ($P6_222 = D_6^4$ or $P6_422 = D_6^5$) $K_5[BW_{12}O_{40}] \cdot 18\,H_2O$

cubic ($F\bar{4}3m = T_d^2$ or $Fm3m = O_h^5$) $K_9[BW_{11}O_{39}] \cdot 14\,H_2O$
and tetragonal compounds $K_7[BMn^{2+}W_{11}O_{40}H_2] \cdot 16\,H_2O$ and $Ba_3[BMn^{3+}W_{11}O_{40}H_2] \cdot 26\,H_2O$ [240].

The latter may be isostructural with tetragonal (P4/mnc = D_{4h}^6) $Ba_3[BCo^{3+}(H_2O)W_{11}O_{39}] \cdot 26\ H_2O$, which has been studied recently [240A].

2 Crystal Chemistry of Anhydrous Borates

The main principles of anhydrous borate systemics are that

a) every boron atom is linked to three or four oxygen atoms;

b) a single structure may contain either triangular or tetrahedral coordination or both;

c) polymerization or formation of chains, layers or framework is brought about by linking the tops of the triangles and tetrahedra;

d) in framework and layered polyanions the triangles and tetrahedra tend to form compact clusters with small negative charge of the type of diborate (2△ + 2T), triborate (2△ + 1T), pentaborate (4△ + 1T), boroxinic (3△), ditriborate (1△ + 2T), dipentaborate (3△ + 2T), and other single and double ring boron-oxygen anions and radicals;

e) complex polyanions tend to "twinning";

f) in the majority of complex polyanions each oxygen atom is bound to two boron atoms; for compounds with the general formula $mB_2O_3 \cdot n\ M_xO_y$ and $m > 1$, the relationship $n = n_\Delta/n_T = m - 1$ is true;

g) a frequent exception for polyanions, including layered and framework structures, is a coordination number of one or three (in cubic boracites and hydrated complex higher polyborates even four) for some oxygen atoms;

h) no triangles and tetrahedra are encountered in anhydrous borates either in isolated forms nor in island polyanions;

i) an increase in the factor $N(B_2O_3)/N(M_xO_y)$ as well as in the cation size leads to a rise in the degree of polymerization of the anion and the number N, while an increased charge causes the opposite [241].

A classification is proposed for the anhydrous borates, which is based on the composition of anion-forming components, valence of cations, type and size of cations and on the ratio of total numbers of cations to number of boron atoms N. Borates, borosilicates, boroaluminates, boroberyllates, borocarbonates, boromolybdates and borotungstates are arranged into groups where $N = >1$, $N = 1$, $N = 1$ to 0.5, $N = 0.5$ to 0.33, and $N = <0.33$. Based on the nature of univalent elements, orthoborates, fluoroborates, metaborates, and polyborates have been recognized [242].

The structure of several alkali metal borate crystals has been studied as an aid for interpreting the "boron oxide anomaly". Five kinds of BO_3 units such as $B^\Delta(3\ B_3)$, $B^\Delta(2\ B_3, B_4)$, $B^\Delta(B_3, 2\ B_4)$, $B^\Delta(3\ B_4)$ and B^R, and two kinds of RBO_4 units such as $B^T(4\ B_3)$ and $B^T(3\ B_3, B_4)$ are the basic constituents of the crystals $B_2O_3 \cdot xR_2O$ ($0 \leqq x \leqq 1.0$). The variation of the fractions of those units with x shows two trends. The number of B_4 units to which a B_3 or a B_4 unit is bonded, increases gradually with x. The fraction of each kind of B^Δ or B^T unit becomes maximal in one of the crystals, in which the unit is the single B_4 or B_3 unit. These tendencies suggest that four kinds of B_4 units bonded with > 1 B_4 units appear in the range $0.5 < x \leqq 1.0$, if the fraction of the B^T units is assumed to increase linearly with x in this range. A relation of the relative stability between the real and hypothetical units is derived from the viewpoint

of the energy of the units, defined as, for example, a sum of the bond energies. The B—O bond energies of the RBO_4 units in some crystals have been calculated and were found to vary from 130 to 135 kcal/mol [243].

Based on previous classifications, G. K. Gode [244] and S. García-Blanco [245] have reviewed the crystal chemistry of borates, the latter for hydrated and anhydrous borates.

2.1 Orthoborates Containing the Anion BO_3^{3-}

2.1.1 Orthoborates With M^{3+} Cations, MBO_3

The compounds MBO_3 containing three-coordinate boron are all similar to known types of $CaCO_3$.

2.1.1.1 Orthoborates with Calcite Structure

Trigonal ($R\bar{3}c = D_{3d}^6$) compounds MBO_3 are of the $CaCO_3$-I type with hexagonal dense packing of O atoms and planar BO_3^{3-} groups. To this type belong the high-pressure phases α-$AlBO_3$ [51,246,248]; α-$GaBO_3$ [51,248,249]; α-$InBO_3$ [250–252]; α-$TlBO_3$ [248]; $BiBO_3$ [251,253]; α-$ScBO_3$ [251,254,255]; the high-temperature phase β-YBO_3-I [249,257]; the high-temperature/high-pressure phase γ-$YbBO_3$-III [257]; the low-temperature phase β-$LuBO_3$-II [248,256,258]; furthermore, $TiBO_3$ [259]; VBO_3 [259,260]; $CrBO_3$ [259–261]; $FeBO_3$ [262]; $Fe_{0.9}Ga_{0.1}BO_3$ [263]; $Fe_{1-x}Sc_xBO_3$ [264]; $Fe_{1-x}Lu_xBO_3$ [264]; $Fe_{0.9}Ti_{0.1}BO_3$ [263]; $Fe_{0.8}Cr_{0.2}BO_3$ [263]; $RhBO_3$ [248]; and $AmBO_3$ [265].

2.1.1.2 Orthoborates with Vaterite Structure

2.1.1.2.1 Orthoborates with Pseudo-Vaterite Structure. Hexagonal ($P\bar{6}c2 = D_{3h}^2$) compounds MBO_3 with pseudo-*vaterite* structure are of $CaCO_3$-II type. Such compounds exhibiting distorted packing and non-planar BO_3^{3-} groups are called the $YbBO_3$-II type. To this type belong the low-temperature phase α-$YbBO_3$-II [268,269]; and the high-temperature phase μ-$LuBO_3$-I [268]. Orthoborates similar to the $YbBO_3$-II type (hexagonal, perhaps $P\bar{6}c2 = D_{3h}^2$) are: γ-$CeBO_3$-IV [268]; γ-$PrBO_3$ [268]; and γ-$NdBO_3$ [268].

2.1.1.2.2 Orthoborates with High-Vaterite Structure. Hexagonal ($P6_322 = D_6^6$) compounds MBO_3 of the $CaCO_3$-II′ structure belong to the $GdBO_3$-II type. These are: the high-temperature phases $GdBO_3$-II [270]; $TbBO_3$-II [270]; $DyBO_3$-II [270]; $HoBO_3$-II [270]; $ErBO_3$-II [270]; $TmBO_3$-II [270]; $YbBO_3$-I [270]; and $LuBO_3$-III [270].

2.1.1.2.3 Orthoborates with "Vaterite" Structure. Hexagonal ($P6_3/mmc = D_{6h}^4$) compounds MBO_3 contain BO_4 tetrahedra; these structures are named the YBO_3-II type. To this type belong the low-temperature/low-pressure phases β-$TlBO_3$ [266]; α-YBO_3-II [250,266,267]; α-$SmBO_3$-II [250,267–269]; $EuBO_3$-II [250,267,268]; $GdBO_3$-III [250,267,268]; $TbBO_3$-III [268]; $DyBO_3$-III [250,267,268]; $HoBO_3$-I [250,267,268]; $ErBO_3$-I [250,267,268]; $TmBO_3$-I [250,267,268]; and in older literature α-$YbBO_3$-II [250,267] as well as the high-temperature phase μ-$LuBO_3$-I [250,267].

2.1.1.3 Orthoborates with Aragonite Structure

Orthoborates MBO_3 with *aragonite* = $CaCO_3$-III structure are orthorhombic (Pmcn = D_{2h}^{16}) with dolomite-like packing and planar BO_3^{3-} groups; they are called the $LaBO_3$-II type. To this type belong the low-temperature phases α-$LaBO_3$-II [250, 271-273]; α-$CeBO_3$-III [274, 275]; $Ce_{1-x}Tb_xBO_3$ [275]; α-$PrBO_3$-III [276]; α-$NdBO_3$-III [250, 273]; $PmBO_3$ [277]; and the high-pressure phases λ-$SmBO_3$-III [276] and λ-$EuBO_3$-III [276].

2.1.1.4 Orthoborates of the $LaBO_3$-I Type

Orthoborates of the $LaBO_3$-I type are monoclinic ($P2_1/m = C_{2h}^2$); to this type belong the high-temperature/high-pressure phases β-$LaBO_3$-I [272] and β-$CeBO_3$-II [272].

2.1.1.5 Orthoborates of the High-$NdBO_3$-I Type

The following orthoborates MBO_3 of the high-temperature $NdBO_3$-I type are triclinic ($P1 = C_1^1$) with isolated BO_3^{3-} groups of nonequilateral triangles:
the high-temperature phases ν-$CeBO_3$-I [272]; ν-$PrBO_3$-I [278]; ν-$NdBO_3$-I [250, 278]; ν-$SmBO_3$-I [278, 279]; and the
high-pressure phases ν-$EuBO_3$-I [278]; ν-$GdBO_3$-I [278]; ν-$TbBO_3$-I [278] and ν-$DyBO_3$-I [278].

2.1.2 Orthoborates With M^{2+} Cations, $M_3(BO_3)_2$

2.1.2.1 Orthoborates with Kotoite Structure

The following orthoborates $M_3(BO_3)_2$ are of orthorhombic (Pnmn = D_{2h}^{12}) $Mg_3(BO_3)_2$ = *kotoite* type with hexagonal dense packing of the O atoms and isolated BO_3^{3-} groups containing non-equilateral B—O bonds: $Mg_3(BO_3)_2$ = mineral *kotoite* [280, 281]; $Mn_3(BO_3)_2$ = mineral *jimboite* [282, 283]; $Co_3(BO_3)_2$ [281, 284]; and $Ni_3(BO_3)_2$ [285, 286].

2.1.2.2 Orthoborates with $Ca_3(BO_3)_2$ Structure

To the trigonal ($R\bar{3}c = D_{3d}^6$) $Ca_3(BO_3)_2$ type with distorted packing of O atoms, Ca columns and not exactly planar BO_3^{3-} groups belong $Ca_3(BO_3)_2$ [287, 288]; $Sr_3(BO_3)_2$ [289]; $Hg_3(BO_3)_2$ [290]; and $Eu_3(BO_3)_2$ [291].

2.1.2.3 Orthoborates with $Zn_3(BO_3)_2$ Structure

The monoclinic (Bb = C_s^4 or C2/c = C_{2h}^6) $Zn_3(BO_3)_2$ type is so far represented only by $Zn_3(BO_3)_2$ [292, 293], containing four-coordinate boron.

2.1.3 Orthoborates With M^+ Cations, M_3BO_3

α-Li_3BO_3-II is monoclinic ($P2_1/c = C_{2h}^5$) with nearly planar BO_3^{3-} groups [294], but not isotypic with monoclinic ($P2_1/c = C_{2h}^5$) Na_3BO_3 [295].

Ag_3BO_3-I is trigonal with R32 = D_3^7 [296], Ag_3BO_3-II with $R\bar{3}c = D_{3d}^6$ [297]; Tl_3BO_3 is hexagonal ($P6_3/m = C_{6h}^2$) [298].

β-Li_3BO_3-I is perhaps monoclinic and γ-Li_3BO_3-III perhaps cubic with a = 614.6 pm [294].

2.1.4 Orthoborates $M^{1+}M^{2+}[BO_3]$

To the monoclinic ($C2/c = C_{2h}^6$) $LiZn[BO_3]$-II type belong $LiZn[BO_3]$-II [299,300] and $LiMn[BO_3]$ [299,300]; hexagonal ($P\bar{6} = C_{3h}^1$) is $LiCd[BO_3]$-I [301,302]; triclinic ($I\bar{1} = C_i^1$) is $LiCd[BO_3]$-II [301,304,305]. Other hexagonal types are $LiMg[BO_3]$ and $LiZn[BO_3]$-I [306].

2.1.5 Orthoborates $M_3^{1+}M^{3+}[BO_3]_2$

To the monoclinic ($P2_1/c = C_{2h}^5$) $Na_3Nd[BO_3]_2$ type with isolated BO_3^{3-} triangles in a complex structure belong $Na_3La[BO_3]_2$ [307] and $Na_3Nd[BO_3]_2$ [307,308].

2.1.6 Orthoborates $M_2^{2+}M'^{2+}[BO_3]_2$

Tetragonal $Ca_2Mg[BO_3]_2$ is isomorphous with $Na_2Ca[CO_3]_2$; hexagonal $Ba_2Mg[BO_3]_2$ is isomorphous with the mineral *buetschliite*. $(Na,K)_2(Ca,Mg)[CO_3]_2$ [309].

2.1.7 Orthoborates $M^{3+}M'^{3+}[BO_3]_2$

Isomorphous with the mineral *dolomite*, $CaMg[CO_3]_2$, are the trigonal ($R\bar{3} = C_{3i}^2$) compounds with partial cation disorder: $YCr[BO_3]_2$ [310]; $DyCr[BO_3]_2$ [310]; $ErCr[BO_3]_2$ [310]; $YbCr[BO_3]_2$ [310]; $LuCr[BO_3]_2$ [310]; $YFe[BO_3]_2$ [264]; $DyFe[BO_3]_2$ [264]; $HoFe[BO_3]_2$ [264]; $ErFe[BO_3]_2$ [264]; $TmFe[BO_3]_2$ [264]; $YbFe[BO_3]_2$ [264]; and $LuFe[BO_3]_2$ [264].

2.1.8 Orthoborates $M^{2+}M^{4+}[BO_3]_2$

Also isomorphous with *dolomite* are the following trigonal ($R\bar{3} = C_{3i}^2$) compounds with weak rotation at the BO_3^{3-} groups as compared to the ideal position: $MgSn[BO_3]_2$ [311,312]; $CaSn[BO_3]_2$ = mineral *nordenskjöldine* [311–314]; $SrSn[BO_3]_2$ [311–313]; $SrSn_{1-x}Ti_x[BO_3]_2$ [311]; $BaSn[BO_3]_2$ [311–313]; $BaSn_{1-x}Ti_x[BO_3]_2$ [311]; $MnSn[BO_3]_2$ = mineral *tusionite* [314,315]; $FeSn[BO_3]_2$ [314]; $CoSn[BO_3]_2$ [314]; $NiSn[BO_3]_2$ [314]; $CdSn[BO_3]_2$ [314]; $Sr_{1-x}Ba_xTi[BO_3]_2$ [311]; $BaTi[BO_3]_2$ [311,312]; $CaZr[BO_3]_2$ [312,315]; $SrZr[BO_3]_2$ [312,313]; $BaZr[BO_3]_2$ [312,313]; $PbZr[BO_3]_2$ [316]; $CdZr[BO_3]_2$ [312,313]; $CaHf[BO_3]_2$ [313]; $SrHf[BO_3]_2$ [313]; and $BaHf[BO_3]_2$ [313].

2.1.9 Orthoborates $M^{1+}M^{5+}[BO_3]_2$

In monoclinic ($Pn = C_s^2$) $RbNb[BO_3]_2$, octahedra chains of NbO_6 are tilted in the *a*-direction (100); the true formula is $\{RbNb[BO_3]_2\}_5$ [317]. Isotypic are $RbTa[BO_3]_2$ and $TlTa[BO_3]_2$ [317]; orthorhombic ($Pna2_1 = C_{2v}^9$) $TlNb[BO_3]_2$ has a similar, but different structure [303].

2.1.10. Orthoborates $M_3^{1+}M_2^{3+}[BO_3]_3$

Isomorphous with the mineral *shortite*, $Na_2Ca_2[CO_3]_3$, are the orthorhombic ($Amm2 = C_{2v}^{14}$) compounds $Na_3[La_2(BO_3)_3]$ and $Na_3[Nd_2(BO_3)_3]$ [307,308]; while $Li_3[In_2(BO_3)_3]$ belongs to another orthorhombic space group [318]. To the monoclinic ($P2_1/n = C_{2h}^5$) $Li_3[Nd_2(BO_3)_3]$ type belong $Li_3[La_2(BO_3)_3]$ [319], $Li_3[Nd_2(BO_3)_3]$ [247,308,319]; $Li_3[Pr_2(BO_3)_3]$ [320]; and $Li_3[Eu_2(BO_3)_3]$ [321].

2.1.11 Orthoborates $M_6^{1+}M^{3+}[BO_3]_3$

Members of the monoclinic ($P2_1/b = C_{2h}^5$) $Li_6[Yb(BO_3)_3]$ type are: $Li_6[Nd(BO_3)_3]$ [308]; $Li_6[Gd(BO_3)_3]$ [308]; $Li_6[Ho(BO_3)_3]$ [322]; and $Li_6[Yb(BO_3)_3]$ [323].

2.1.12 Orthoborates $M_6^{1+}M_2^{3+}[BO_3]_4$

In the following compounds of the triclinic $Li_3[Ga(BO_3)_2]$ type, $\{M_2(BO_3)_4\}_\infty^{6\infty-}$ chains with two different BO_3^{3-} groups have been found: $Li_6[Al_2(BO_3)_4]$ [324] and $Li_6[Ga_2(BO_3)_4]$ [325].

2.1.13 Orthoborates $M_3^{2+}M_2^{3+}[BO_3]_4$

In the following compounds of the orthorhombic ($Pc2_1n = C_{2v}^9$) $Sr_3La_2B_4O_{12}$ type, four different isolated planar BO_3^{3-} groups and chains of distorted La—O and Sr—O polyhedra are found:

$Ca_3[Y_2(BO_3)_4]$ [326,327]; $Ca_3[La_2(BO_3)_4]$ [327]; $Ca_3(Pr_2(BO_3)_4]$ [327];
$Ca_3[Nd_2(BO_3)_4]$ [327]; $Ca_3[Sm_2(BO_3)_4]$ [327]; $Ca_3[Gd_2(BO_3)_4]$ [327];
$Ca_3[Tb_2(BO_3)_4]$ [327]; $Ca_3[Dy_2(BO_3)_4]$ [327]; $Ca_3[Ho_2(BO_3)_4]$ [327];
$Ca_3[Er_2(BO_3)_4]$ [327]; $Ca_3[Tm_2(BO_3)_4$ [327]; $Ca_3[Yb_2(BO_3)_4]$ [326];
$Ca_3[Lu_2(BO_3)_4]$ [327]; $Sr_3[La_2(BO_3)_4]$ [327–331]; $Sr_3[Pr_2(BO_3)_4]$ [328,329,331,332,333];
$Sr_3[Nd_2(BO_3)_4]$ [328,329,334,335]; $Sr_3[Sm_2(BO_3)_4]$ [328,329]; $Sr_3[Eu_2(BO_3)_4]$ [328];
$Sr_3[Gd_2(BO_3)_4]$ [327–329,331,333] $Sr_3[Tb_2(BO_3)_4]$ [328,329]; $Sr_3[Dy_2(BO_3)_4]$ [328,329];
$Sr_3[Ho_2(BO_3)_4]$ [328,329]; $Sr_3[Er_2(BO_3)_4]$ [328,329,336]; $Sr_3[Tm_2(BO_3)_4]$ [328];
$Sr_3[Yb_2(BO_3)_4$ [327–329]; $Sr_3[Lu_2(BO_3)_4$ [328]; $Ba_3[La_2(BO_3)_4]$ [327,331,333];
$Ba_3[Gd_2(BO_3)_4]$ [327]; $Eu_3[Eu_2(BO_3)_4]$ [337]; and $Co_3[Ho_2(BO_3)_4]$ [284].

2.1.14 Orthoborates $M^{3+}M_3'^{3+}[BO_3]_4$

Isomorphous with the mineral *huntite*, $CaMg_3[CO_3]_4$, are the trigonal ($R32 = D_3^7$) compounds of the $Y[Al_3(BO_3)_4]$ type with two different isolated BO_3^{3-} groups and Al—O helices:

$Y[Al_3(BO_3)_4]$ [338–342]; $Y_{1-x}Nd_x[Al_3(BO_3)_4]$ [343,344]; $Pr[Al_3(BO_3)_4]$ [340];
$Nd[Al_3(BO_3)_4]$-I [339,340,345]; $Sm[Al_3(BO_3)_4]$ [339,340,346]; $Eu[Al_3(BO_3)_4]$ [339,340];
$Gd[Al_3(BO_3)_4]$ [339,340]; $Tb[Al_3(BO_3)_4]$ [339,340] $Dy[Al_3(BO_3)_4]$ [339,340];
$Ho[Al_3(BO_3)_4]$ [339,340]; $Er[Al_3(BO_3)_4]$ [338,339,340]; $Y_{1-x}Er_x[Al_3(BO_3)_4]$ [338];
$Tm[Al_3(BO_3)_4]$ [340]; $Yb[Al_3(BO_3)_4]$ [339]; $Lu[Al_3(BO_3)_4]$ [340];
$Gd_{1-x}Lu_x[Al_3(BO_3)_4]$ [347]; $Y[Ga_3(BO_3)_4]$ [340,348–350]; $La[Ga_3(BO_3)_4]$ [340,349,350];
$Pr[Ga_3(BO_3)_4]$ [340,349]; $Nd[Ga_3(BO_3)_4]$ [340,349,350,354]; $Sm[Ga_3(BO_3)_4]$ [340,348–350];
$Eu[Ga_3(BO_3)_4]$ [340,348–350]; $Gd[Ga_3(BO_3)_4]$ [340,348–351]; $Tb[Ga_3(BO_3)_4]$ [340,348–350];

$Dy[Ga_3(BO_3)_4]$ [348-350]; $Ho[Ga_3(BO_3)_4]$ [349]; $Er[Ga_3(BO_3)_4]$ [340,349,350];
$Yb[Ga_3(BO_3)_4]$ [340,349,350]; $Sm[Cr_3(BO_3)_4]$ [339]; $Gd[Cr_3(BO_3)_4]$ [339];
$Sc[Fe_3(BO_3)_4]$ [353]; $In[Fe_3(BO_3)_4]$ [353]; $Y[Fe_3(BO_3)_4]$ [340,350-353];
$La[Fe_3(BO_3)_4]$ [340,350,351]; $Pr[Fe_3(BO_3)_4]$ [340,350,353]; $Nd[Fe_3(BO_3)_4]$ [340,350-353];
$(Nd_{0.5}Bi_{0.5})[Fe_3(BO_3)_4]$ [353,355]; $Er[Fe_3(BO_3)_4]$ [353]; $Sm[Fe_3(BO_3)_4]$ [340,350-353];
$Eu[Fe_3(BO_3)_4]$ [340,350,351,353]; $Gd[Fe_3(BO_3)_4]$ [340,350-353]; $Tb[Fe_3(BO_3)_4]$ [340,350,351];
$Dy[Fe_3(BO_3)_4]$ [340,350-352]; $Ho[Fe_3(BO_3)_4]$ [340,351,352]; $Er[Fe_3(BO_3)_4]$ [340,350,353];
$Tm[Fe_3(BO_3)_4]$ [340]; $Yb[Fe_3(BO_3)_4]$ [340,350]; $Bi[(Fe_{1.35}Al_{1.65})(BO_3)_4]$ [353].

Isomorphous with the mineral *xanthite* crystallizes the monoclinic ($C2/c = C_{2h}^6$) high-temperature phase $Nd[Al_3(BO_3)_4]$ containing two different isolated BO_3^{3-} groups [356,358]; the monoclinic high-temperature phase $Gd[Al_3(BO_3)_4]$ crystallizes in $C2 = C_2^3$ or $C2/m = C_{2h}^3$ or $Cm = C_s^3$ [357].

2.1.15 Orthoborates $M_3^{2+}M_3^{3+}(BO_3)_5$

The hexagonal ($P6_3mc = C_{6v}^4$ or $P\bar{6}2c = D_{3h}^2$ or $P6_3/mmc = D_{6h}^4$) $Ca_3[La_3(BO_3)_5]$ [359] crystallizes isomorphous with the mineral *burbankite*.

2.2 BO_3^{3-} Groups Besides Other Ions

2.2.1 BO_3^{3-} Groups Besides O^{2-} Ions

2.2.1.1 Warwickite-Type, $M^{2+}M^{3+}[O(BO_3)]$

The following compounds $M^{2+}M^{3+}[BO_4]$ belong to the orthorhombic ($Pnma = D_{2h}^{16}$) $(Mg,Fe)_3Ti[O(BO_3)]_2$ = mineral *warwickite* type: $Mg(Mg_{0.5}Ti_{0.5})[O(BO_3)]$ = mineral *warwickite* [46];

$MgGa[O(BO_3)]$ [360]; $MgTi^{3+}[O(BO_3)]$ [361]; $MgV^{3+}[O(BO_3)]$ [361];
$MgCr^{3+}[O(BO_3)]$ [360]; $MgFe^{3+}[O(BO_3)]$ [362,363]; $CaIn[O(BO_3)]$ [360,362];
$CaSc[O(BO_3)]$ [364]; $CaY[O(BO_3)]$ [270]; $CaGd[O(BO_3)]$ [270];
$CaTb[O(BO_3)]$ [270]; $CaDy[O(BO_3)]$ [270]; $CaHo[O(BO_3)]$ [270]
$CaEr[O(BO_3)]$ [270]; $CaTm[O(BO_3)]$ [270]; $CaYb[O(BO_3)]$ [270];
$CaLu[O(BO_3)]$ [364]; $Mn^{2+}Fe^{3+}[O(BO_3)]$ [360]; $Fe^{2+}Fe^{3+}[O(BO_3)]$ [362];
$CoGa[O(BO_3)]$ [360]; $CoSc[O(BO_3)]$ [360]; $CoCr^{3+}[O(BO_3)]$ [360];
$CoFe^{3+}[O(BO_3)]$ [362,365]; $NiCr^{3+}[O(BO_3)]$ [366]; the low-pressure $NiFe^{3+}[O(BO_3)]$-I [362];
$CdIn[O(BO_3)]$ [360]; $CdSc[O(BO_3)]$ [360].

2.2.1.2 Vonsenite-Ludwigite Type, $M_2^{2+}M^{3+}[O_2(BO_3)]$

The following compounds belong to the orthorhombic ($Pbam = D_{2h}^9$) vonsenite-ludwigite series:

$(Mg,Fe^{2+})_2(Fe^{3+},Al)[O_2(BO_3)]$ = mineral *ludwigite* [362,367,368]
$Mg_2(Fe, Ti, Mg)[O_2(BO_3)]$ = mineral *azoproite* [369]
$Fe_2^{2+}Fe^{3+}[O_2(BO_3)]$ = mineral *vonsenite* [362,367,370-372]
$Co_2Fe^{3+}[O_2(BO_3)]$ [362]

$Ni_2Fe^{3+}[O_2(BO_3)]$ [367, 372]
$Cu_2Fe^{3+}[O_2(BO_3)]$ [362]
$Fe_2^{2+}V^{3+}[O_2(BO_3)]$ [361], $Co_2V^{3+}[O_2(BO_3)]$ [361]
$Ni_2Al[O_2(BO_3)]$ [373] and
$Co_2^{2+}Co^{3+}[O_2(BO_3)]$ [374].

2.2.1.3 Hulsite Type, $M_2^{2+}M^{3+}[O_2(BO_3)]$

To the hulsite type belongs only the monoclinic (P2/m = C_{2h}^1) solid series (Fe^{2+},Mg, Fe^{3+},Sn^{4+})$[BO_5]$, for example $Mg_{0.7}Fe_{1.5}^{2+}Fe_{0.6}^{3+}Sn_{0.2}^{4+}[O_2(BO_3)]$ = mineral *hulsite* [375, 376].

2.2.1.4 Pinakiolite Type, $M_2^{2+}M^{3+}[O_2(BO_3)]$

To the pinakiolite type belongs only the monoclinic (C2/m = C_{2h}^3) solid series $(Mg,Mn^{2+})_2Mn^{3+}[BO_5]$, for example $(Mg,Mn)_{1.77}(Mn,Fe,Al)_{1.11}[O_2(BO_3)]$ = mineral *pinakiolite* [46]; or $Mg_{1.9}(Mn,Al,Fe)_{1.0}[O_2(BO_3)]$ = also *pinakiolite* [377].

2.2.1.5 Takéuchite Type, $M_2^{2+}M^{3+}[O_2(BO_3)]$

The orthorhombic (Pnnm = D_{2h}^{12}) takéuchite type is represented by the solid series $(Mg,Mn^{2+})_2(Mn^{3+},Fe^{3+},Ti^{4+})[BO_5]$, for example, $Mg_{1.59}Mn_{0.42}^{2+}Mn_{0.78}^{3+}Fe_{0.19}^{3+}Ti_{0.01}^{4+}$-$[O_2(BO_3)]$ = mineral *takéuchite* [378]; and $(Mg,Mn^{2+},Mn^{3+})_{2.95}[O_2(BO_3)]$ = mineral *orthopinakiolite* [377].

2.2.1.6 Borates $M_5^{2+}M^{4+}[O_2(BO_3)]_2$

The orthorhombic (Pbam = D_{2h}^9) borates $Ni_5Ti[B_2O_{10}] = Ni_5Ti[O_2(BO_3)]_2$ and $Co_5Ti[B_2O_{10}] = Co_5Ti[O_2(BO_3)]_2$ are similar to the ludwigite type [379].

2.2.1.7 Borates $M^{2+}M_2^{3+}[O(BO_3)_2]$

While α-$CaAl_2[B_2O_7]$ = α-$CaAl_2[O(BO_3)_2]$-II is hexagonal ($P6_322$ = D_6^6) [380], β-$CaAl_2[O(BO_3)_2]$-I is monoclinic [380]; $BaAl_2[O(BO_3)_2]$ is also monoclinic (P2/c = C_{2h}^4 or Pc = C_2^2) [381].

2.2.1.8 Borates $M_4^{3+}[O_3(BO_3)_2]$

$Bi_4[B_2O_9]$ = $Bi_4[O_3(BO_3)_2]$ crystallizes monoclinic ($P2_1/c$ = C_{2h}^5) with isolated BO_3^{3-} groups [382].

2.2.1.9 Borates $M_3^{2+}M_2^{3+}[O_3(BO_3)_2]$

The $Ca_3Gd_2[B_2O_9] = Ca_3Gd_2[O_3(BO_3)_2]$ type (C2/m = C_{2h}^3 or C2 = C_2^3 or Cm = C_S^3) is represented by $Ca_3La_2[O_3(BO_3)_2]$ [270]; $Ca_3Gd_2[O_3(BO_3)_2]$ [270]; and $Ca_3Yb_2[O_3(BO_3)_2]$ [270].

2.2.1.10 Borates $M_3^+M_3^{5+}[O_6(BO_3)_2]$

The trigonal (P31m = C_{3v}^2) $K_3Nb_3[B_2O_{12}] = K_3Nb_3[O_6(BO_3)_2]$ and the hexagonal ($P\bar{6}2m$ = D_{3h}^3) $K_3Ta_3[B_2O_{12}] = K_3Ta_3[O_6(BO_3)_2]$ have two nonequivalent non-symmetrical BO_3^{2-} groups with a pentagonal channel-structure like $K_6Nb_6[Si_4O_{26}]$ [383, 384].

2.2.1.11 Borates $M^{3+}M^{6+}[O_3(BO_3)]$

The monoclinic ($P2_1 = C_2^2$) $LaMo[BO_6] = La_2Mo_2[O_3(BO_3)]_2$ type with endless B—O chains of distorted BO_3^{3-} triangles is represented by $La_2Mo_2[O_3(BO_3)]_2$ [385] and $La_2W_2[O_3(BO_3)]_2$ [385], and perhaps also by $CeMo[BO_6]$ [386]. $PrMo[BO_6]$ and $NdMo[BO_6]$ [386] seem to have other structures; considering the B—O distances in the Mo compound (123, 129, and 155 pm), one can classify these compounds to the metaborates $LaBO_2[OMoO_3]$.

2.2.1.12 Borates $M_5^{3+}[O_6(BO_3)]$

The orthorhombic ($Cmc2_1 = C_{2v}^{12}$) $Al_5[BO_9] = Al_5[O_6(BO_3)]$ type is found in the compound $B_2O_3 \cdot 5\,Al_2O_3$ [387] or in $2\,B_2O_3 \cdot 9\,Al_2O_3 = Al_{20-(4/11)}[B_{4+(4/11)}O_{36}]$ [388].

2.2.1.13 Borates $M_{13}^{3+}[O_{12}(BO_3)_5]$

The monoclinic ($P2_1/c = C_{2h}^5$) compound $La_{13}[B_5O_{27}]$ is better formulated as $La_{13}[O_{12}(BO_3)_5]$ [389].

2.2.1.14 Borates $M^{2+}M_9^{3+}M^{4+}[O_{15}(BO_3)]$

The hexagonal ($P6_3 = C_6^6$) $CaAl_9Zr[BO_{18}] = CaZrB[Al_9O_{18}] = CaZrAl_9[O_{15}(BO_3)]$ has been found in the mineral *painite* with BO_3^{3-} triangles in a rigid dense $[Al_9O_{18}]$ octahedral framework topologically identical to those found in *jeremejevite* and *fluoborite* [390].

2.2.1.15 Other Not Completely Characterized Orthoborates with Oxygen Ions

The monoclinic ($P2/m = C_{2h}^1$) $Ba_3Al_4[O_3(BO_3)_4]$ [381] and the monoclinic ($P2 = C_2^1$ or $Pm = C_S^1$) $NaMg_3Mn_3[O_5(BO_3)_2]$ [391] are not yet completely characterized by X-ray structural analysis.

The borates of the type $M_2^{3+}M^{6+}[B_2O_9]$ with M^{6+} = Mo or W and M^{3+} = Pr, Nd, Sm, Eu, Gd, and Tb belong to one type, those with M^{6+} = W and M^{3+} = Sm, Eu, Gd, Tb, and Dy to another [385, 386, 392, 393], while the compounds $M_4^{3+}M^{6+}[B_2O_{12}]$ with M^{6+} = W, M^{3+} = La to Ho [393] and $M_6^{3+}M_3^{6+}[B_4O_{24}]$ with M^{6+} = Mo, M^{3+} = Pr or Nd are isostructural, as based on X-ray diffraction results [386].

2.2.2 BO_3^{3-} Groups besides Halide Ions

2.2.2.1 $Be_2[(BO_3)F]$ Type

The monoclinic ($C2 = C_2^3$) $Be_2[(BO_3)F]$ type is represented only by $B_2O_3 \cdot 3\,BeO \cdot Be(F,OH)_2$ = mineral *hambergite* [42, 394].

2.2.2.2 $KBe_2[(BO_3)F_2]$ Type

The monoclinic ($C2 = C_2^3$) $KBe_2[(BO_3)F_2]$ type is related to the hambergite type; it is found in $B_2O_3 \cdot K_2O \cdot 2\,BeO \cdot 2\,BeF_2 = KBe_2[(BO_3)\,F_2]$ [395]; $RbBe_2[(BO_3)\,F_2]$; $CsBe_2[(BO_3)F_2]$; and probably also $NaBe_2[(BO_3)F_2]$ [396].

2.2.2.3 $Mg_2[(BO_3)F]$-I Type

To this orthorhombic ($Pnma = D_{2h}^{16}$) warwickite type belong the high-temperature phases β-$Mg_2[(BO_3)F]$-I [397] and $Mn_2[(BO_3)F]$ [360].

2.2.2.4 $Mg_2[(BO_3)F]$-II Type

To this orthorhombic ($Pna2_1 = C_{2v}^9$) olivine type belong the low-temperature phase α-$Mg_2[(BO_3)F]$-II and the solid series $Mg_2[(BO_3)F_{1-x}(OH)_x]$ and $Mg_2[(BO_3)_{1-y}F_{1-3y}]$ [398].

2.2.2.5 Fluoborite Type

The hexagonal ($P6_3/m = C_{6h}^2$) type with BO_3^{3-} groups orientated vertical to the trigonal axes, is represented by γ-$Mg_3[(BO_3)F_3]$ or by $Mg_3[(BO_3)(F,OH)_3]$ = mineral *fluoborite* [45, 390, 397].

2.2.2.6 $Mg_5[(BO_3)_3F]$ Type

The orthorhombic ($Pna2_1 = C_{2v}^9$) type is represented only by $Mg_5[(BO_3)_3F]$ [399]; it has a hexagonal dense structure like the olivine-chondrodite group.

2.2.2.7 $Ca_2[(BO_3)Cl]$ Type

This monoclinic ($P2_1/c = C_{2h}^5$) type is represented only by the synthetic compound $Ca_2[(BO_3)Cl]$ [400].

2.2.2.8 $Eu_2[(BO_3)Cl]$ Type

To this hexagonal ($P6_3mc = C_{6v}^4$) type belong $Eu_2[(BO_3)Cl]$ and $Eu_2[(BO_3)Br]$ [401].

2.2.2.9 $Mg_7[(BO_3)_3Cl_5]$ Type

This orthorhombic ($P2_12_12_1 = D_2^4$) type is only represented by $Mg_7[(BO_3)_3(Cl,OH)_5]$ = mineral *karlite* [49].

2.2.2.10 $Pb_6[(BO_3)_3OCl]$ Type

This type with nearly planar BO_3^{3-} groups has only one member, the synthetic orthorhombic ($Pcmb = D_{2h}^{11}$) $Pb_6[(BO_3)_3OCl] = Pb_4O[Pb_2(BO_3)_3Cl]$ [402].

2.2.2.11 $Al_6[(BO_3)_5F_3]$ or Jeremejevite Type

This hexagonal ($P6_3/m = C_{6h}^2$) type is represented by $Al_6[(BO_3)_5(F,OH)_3]$ = mineral *jeremejevite*; of the two different BO_3^{3-} groups, one is strictly planar whereas the other one deviates significantly from planarity [50, 51, 392, 403, 404].

2.2.3 BO_3^{3-} Groups besides CO_3^{2-} or SO_4^{2-} and/or O^{2-} Ions

The cubic ($F4_132 = O^4$) compound $Ca_3Mg[(BO_3)_2(CO_3)]$ contains $\frac{1}{3}$ mol H_2O as the mineral *sakhaite*, and is therefore mentioned already in chapter 1 [219, 220].

Hexagonal ($P6_3 = C_6^6$) $Ca_4Mn_3^{3+}[O_3(BO_3)_3(CO_3)]$ = mineral *gaudefroyite* contains isolated BO_3^{3-} groups [405].

The synthetic orthorhombic ($Pnma = D_{2h}^{16}$) compound $B_2O_3 \cdot 5\,PbO \cdot PbSO_4 = Pb_6[O_2(BO_3)_2(SO_4)]$ also contains isolated distorted BO_3^{3-} groups [406].

2.3 Monoborates Containing Four-Coordinate Boron Only

2.3.1 The Ion BO_4^{5-}

2.3.1.1 Chrysoberyll Type, $M^{2+}M^{3+}[BO_4]$

To the orthorhombic (Pnma = D_{2h}^{16}) $BeAl_2O_4$ = chrysoberyll type with slightly distorted tetrahedral boron belong the following borates: $MgAl[BO_4]$ = mineral *sinhalite* [408]; $Mg_{0.95}Fe^{2+}_{0.05}Al[BO_4]$ [409]; $MgGa[BO_4]$ [366]; $NiCr^{3+}[BO_4]$ [366]; and the high-pressure phase $NiFe^{3+}[BO_4]$-II [407,408].

2.3.1.2 CaAl[BO_4] Type

Only orthorhombic (Ccc2 = C_{2v}^{13}) $CaAl[BO_4]$ represents this type [380,410].

2.3.1.3 SrAl[BO_4] Type

Only orthorhombic (Pccn = D_{2h}^{10}) $SrAl[BO_4]$ represents this type [411].

2.3.1.4 BaMg[SiO_4] Type

To the hexagonal $BaMg[SiO_4]$ type belong $CaLa[BO_4]$ and $SrLa[BO_4]$; $CaY[BO_4]$ is not isomorphous [412].

2.3.1.5 LiGe[BO_4] Type

This orthorhombic (Fmm2 = C_{2v}^{18}) type is represented by $Li_2O \cdot B_2O_3 \cdot 2\,GeO_2$ = $LiGe[BO_4]$ [413].

2.3.1.6 Ta_t BO_4] Type

To this tetragonal ($I4_1/amd$ = D_{4h}^{19}) zirkone type belong $Nb[BO_4)$ [414]; $Ta[BO_4]$ [414]; and $(Nb,Ta)[BO_4]$ = mineral *behierite* [415].

2.3.2 The Ion BO_4^{5-} Besides O^{2-} Ions

2.3.2.1 Norbergite Type, $M_3^{3+}[BO_6]$

To the orthorhombic (Pnma = D_{2h}^{16}) *norbergite* = $Mg_2SiO_4 \cdot Mg(OH,F)_2$ type with the anion $[O_2(BO_4)]^{9-}$ belong $Al_3[BO_6]$ = $Al_3[O_2(BO_4)]$ [51] and $Fe_3[BO_6]$ = $Fe_3[O_2(BO_4)]$ [416].

2.3.2.2 Gd_3[BO_6] Type

To the monoclinic (C2/m = C_2^3 or C2 = C_2^3 or Cm = C_S^3) $Gd_3[O_2(BO_4)]$ type belong $Y_3[BO_6]$; the high-temperature phase $Sm_3[BO_6]$-I; $Eu_3[BO_6]$; $Gd_3[BO_6]$; $Tb_3[BO_6]$; $Dy_3[BO_6]$; $Ho_3[BO_6]$; $Er_3[BO_6]$; $Tm_3[BO_6]$; the low-temperature phase $Yb_3[BO_6]$-II [270]; perhaps also $La_3[BO_6]$ [417].

2.3.2.3 Lu_3[BO_6] Type

To the monoclinic (C2/m = C_2^3 or C2 = C_2^3 or Cm = C_S^3) $Lu_3[O_2(BO_4)]$ type belong the high-temperature phase $Yb_3[BO_6]$-I and $Lu_3[BO_6]$ [270].

2.3.2.4 $Ni_2Nb[BO_6]$ Type, $M_2^{2+}M^{5+}[BO_6]$

This orthorhombic (Pnma = D_{2h}^{16}) type is represented by $Ni_2Nb[BO_6] = Ni_2Nb[O_2BO_4]$ [418].

2.3.2.5 Chondrodite Type, $M^{2+}M_4^{3+}[B_2O_{10}]$

To the monoclinic ($P2_1/c = C_{2h}^5$) $Mg_5[(OH,F)_2(SiO_4)_2]$ = mineral *chondrodite* type belongs $B_2O_3 \cdot CoO \cdot 2\,Al_2O_3 = Al_4Co[O_2(BO_4)_2]$ with BO_4 tetrahedra, connecting chains of Al octahedra [419].

2.3.3 The Ion $[B_3O_7]^{5-}$

All the B atoms are tetrahedral in the ion $[B_3O_7]^{5-}$, found in the orthorhombic (Cmma = D_{2h}^{21}) $CaAl[B_3O_7]$ = mineral *johachidolite* [420,421]; see also triborates (Chapt. 2.6.2).

2.3.4 Tetracoordinate Boron Besides Halide or Germanate

2.3.4.1 Baryte Type

To the orthorhombic (Pnma = D_{2h}^{16}) baryte = $BaSO_4$-II type belongs the borate $Ba_2[(BO_3)F]$ [422,423].

2.3.4.2 Sulphohalite Type

The cubic ($F\bar{4}3m = T_d^2$) compound $Ca_3Er_3Ge_2[BO_{13}] = Ca_3Er_3[O(BO_4)(GeO_4)_2]$ is of a *sulphohalite* = $Na_6[ClF(SO_4)_2]$ related type [424].

2.3.5 BO_4^{5-} Ions Besides PO_4^{3-} or AsO_4^{3-}

$Ca[BPO_5]$, $Sr[BPO_5]$, $Ca[BAsO_5]$, and $Sr[BAsO_5]$ are hexagonal (P6cc = C_{6v}^2 or P6/mcc = D_{6h}^2) with tetrahedral boron [425]; $Ba[BPO_5]$ is isomorphous [426].

$Pb[BPO_5]$ and $Pb[AsBO_5]$ are also hexagonal in the stillwellite = $RE[BSiO_5]$ type with tetrahedral boron [427].

α-$Mg_3[BPO_7]$ and α-$Zn_3[BPO_7]$ crystallize in the orthorhombic space group Imm2 = C_{2v}^{20}; β-$Zn_3[BPO_7]$ is hexagonal in $P\bar{6}m2 = D_{3h}^1$ or $P\bar{6}2m = D_{3h}^3$ [428].

2.3.6 The High-Pressure B_2O_3

The orthorhombic ($Ccm2_1 = C_{2v}^{12}$) high-temperature/high-pressure phase B_2O_3-II contains boroxine rings with distorted tetrahedral boron [429]; the structure of the hexagonal ($P3_1 = C_3^2$) low-pressure B_2O_3 is still unknown [430].

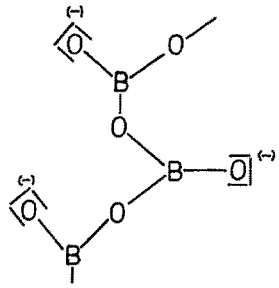
2.4 Metaborates, BO_2^-

2.4.1 Metaborates With M^+ Cations, MBO_2

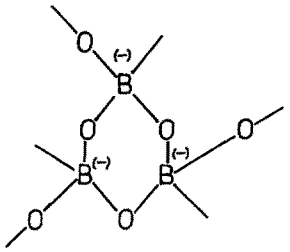
2.4.1.1 $LiBO_2$-I Type

The $LiBO_2$-I type is represented only by monoclinic ($P2_1/c = C_{2h}^5$) α-$LiBO_2$-I with the short-hand notation $1:\infty(\triangle)$, chains (Fig. 3a) [13,431].

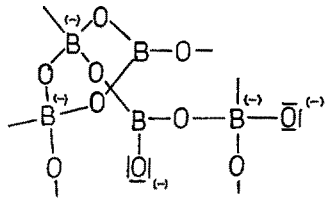
Metaborates:



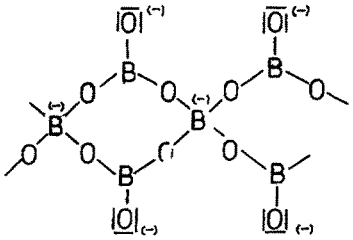
a α-Li B O_2
1 : ∞ (1 Δ), chains



b γ-Li B O_2
3 : ∞_3 (3 T), network

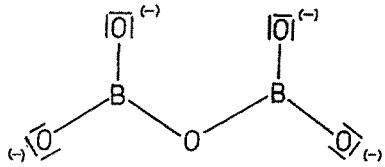


c $B_5 O_{10}^{5-}$
5 : ∞_2 (2 Δ + 3 T), layers



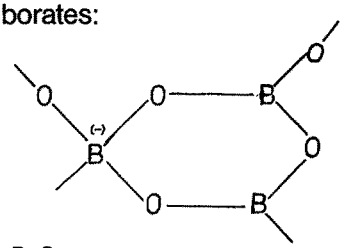
d $B_6 O_{12}^{6-}$
6 : ∞ (4 Δ + 2 T), chains

Diborates:



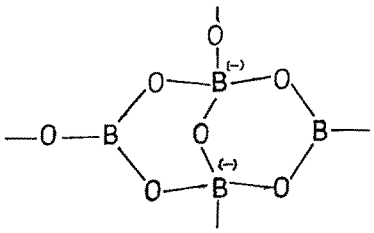
e $B_2 O_5^{4-}$
2 : 2 Δ, isolated

Triborates:

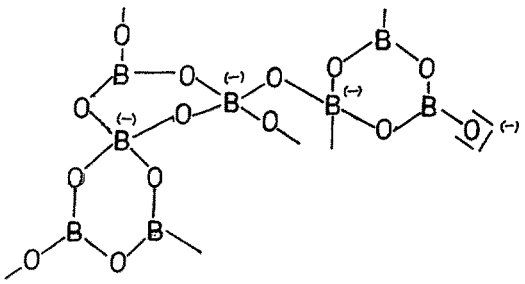


f $B_3 O_5^-$
3 : ∞ (2 Δ + T), chains

Tetraborates:



g $B_4 O_7^{2-}$
4 : ∞_3 (2 Δ + 2 T), network

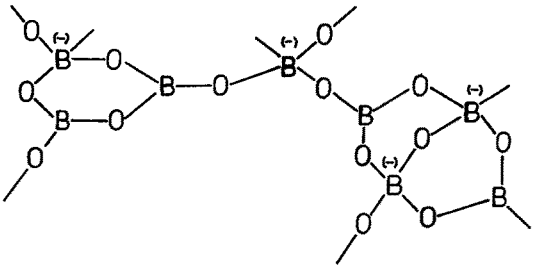


h $Na_4 B_8 O_{14}$
8 : ∞_3 (5 : 3 Δ + 2 T, 3 : 2 Δ + T), network

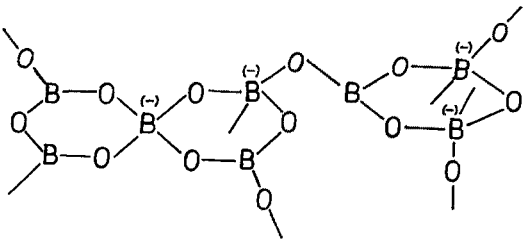
Fig. 3.

Fig. 3. (continued)

Tetraborates:

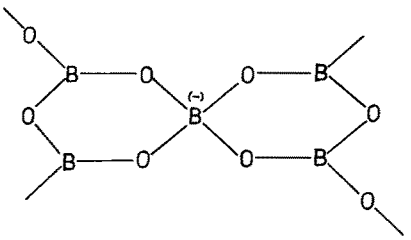


i $Ca_2B_8O_{14}$
$8:\infty_3$ (3:2 Δ + T, 1 T), 4:2 Δ + 2 T)
network



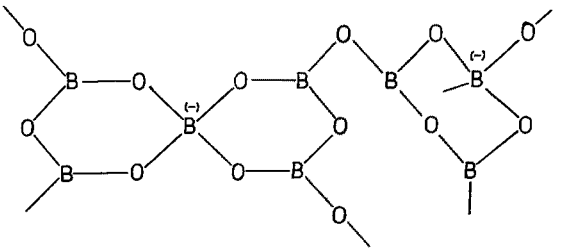
k $Ba_2B_8O_{14}$
$8:\infty_3$ (5:3 Δ + 2 T, 3:Δ + 2 T),
network

Pentaborates:



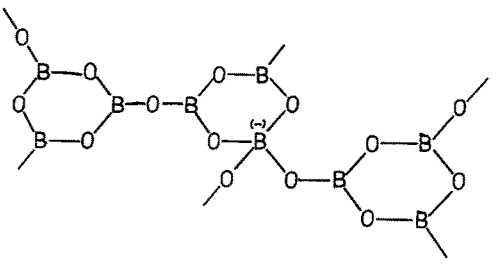
l $B_5O_8^-$
5:4 Δ + T,
isolated

Octaborates:



m $B_8O_{13}^{2-}$
$8:\infty_2$ (3:2 Δ + T, 5:4 Δ + T),
layers

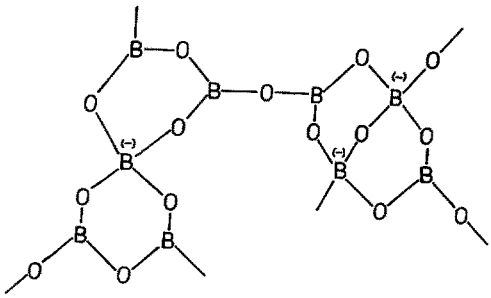
Nonaborates:



n $B_9O_{14}^-$
$9:\infty_3$ (2x3:3 Δ, 3:2 Δ + T),
network

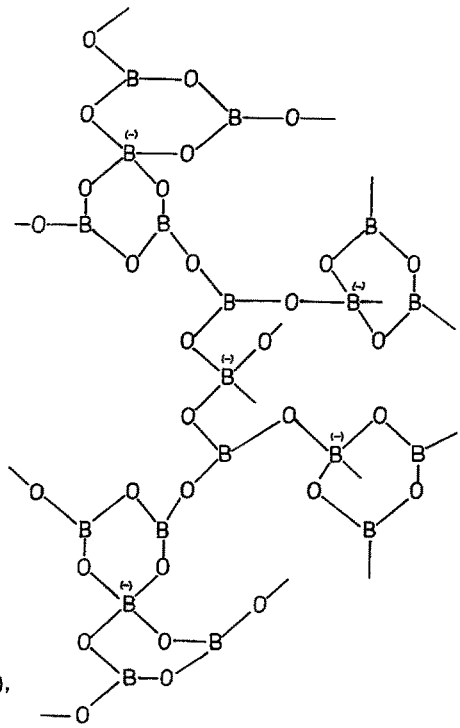
Fig. 3. (continued)

Nonaborates:



o $B_9O_{15}^{3-}$
9: ∞_3 (5:4 Δ + T, 4:2 Δ + 2 T), network

Higher Borates:



p $B_{19}O_{31}^{5-}$
19: ∞_3 (2x5:4 Δ + T, 2x3:2 Δ + T, 2 Δ, 1 T), network

2.4.1.2 $LiBO_2$-II Type

The tetragonal ($1\bar{4}2d = D_{2d}^{12}$) γ-$LiBO_2$-II has the notation 3: ∞_3(3T), network with tetrahedral boron (Fig. 3b) [432,433].

2.4.1.3 $LiBO_2$-III Type

The monoclinic β-$LiBO_2$-III has the notation 2: ∞(△ + T); chains containing trigonal and tetrahedral boron [433,434].

2.4.1.4 $NaBO_2$ Type

To the trigonal ($R\bar{3}c = D_{3d}^6$) $NaBO_2$ type with $B_3O_6^{3-}$ (boroxine) rings belong α-$Na_3[BO_2]_3$ [435,436]; α-$K_3[BO_2]_3$ [437]; α-$Rb_3[BO_2]_3$ [437]; and α-$Cs_3[BO_2]_3$ [437].

2.4.1.5 $AgBO_2$ Type

The $AgBO_2$ type is represented only by orthorhombic (Pbcn = D_{2h}^{14}) $AgBO_2$ with the notation $2:\infty(\triangle + T)$ and containing a BO_2^- isopolyanion where boron is coordinated in equal parts tetrahedrally and trigonal-planar by oxygen [438].

2.4.1.6 $TlBO_2$ Type

The tetragonal ($P4_1 = C_4^2$) $TlBO_2$ with the notation $2:\infty(\triangle + T)$ consists of one boron-oxygen triangle and one boron-oxygen tetrahedron linked together to form an infinite $(B_2O_4)_n^{2n-}$ ion [213].

2.4.2 Metaborates With M^{2+} Cations, $M^{2+}[BO_2]_2$

2.4.2.1 $Mg[BO_2]_2$ Type

The polymer $(Mg[BO_2]_2)_n$ type has been investigated only by Debye-Scherrer photographs [439].

2.4.2.2 $Ca[BO_2]_2$-I Type

To the orthorhombic (Pnca = D_{2h}^{14}) $Ca[BO_2]_2$-I type with the short-hand notation $1:\infty(\triangle)$, chains, belong $Ca[BO_2]_2$-I [440]; $Sr[BO_2]_2$-I [441,442]; and $Eu[BO_2]_2$ = α-$Eu[B_2O_4]$ [443].

2.4.2.3 $Ca[BO_2]_2$-II = Calciborite Type

This type is represented only by the orthorhombic (Pccn = D_{2h}^{10}) $Ca[BO_2]_2$-II = mineral *calciborite* with the notation $2:\infty(\triangle + T)$, chains [410,443,444].

2.4.2.4 $Ca[BO_2]_2$-III Type

To the orthorhombic ($Pna2_1 = C_{2v}^9$) $Ca[BO_2]_2$-III type with the anion $B_6O_{12}^{6-}$ and with the notation $6:\infty_3[3T + (2\triangle + T)]$, network, belong $Ca[BO_2]_2$-III [445]; $Sr[BO_2]_2$-III [441]; and $Eu[BO_2]_2$-III [446].

2.4.2.5 $Ca[BO_2]_2$-IV Type

To the cubic ($Pa3 = T_h^6$) $Ca[BO_2]_2$-IV type with $B_3O_6^{3-}$ rings and the notation $3:\infty_3(3T)$, network, belong $Ca[BO_2]_2$-IV [447]; $Sr[BO_2]_2$-IV [441]; and $Eu[BO_2]_2$-IV [446].

2.4.2.6 $Ba[BO_2]_2$-I Type

This type is represented by the trigonal ($R\bar{3}c = D_{3d}^6$) high-temperature phase β-$Ba[BO_2]_2$-I with nearly planar $B_3O_6^{3-}$ rings and the notation $3:\infty_3(3\triangle)$, network [442, 448].

2.4.2.7 $Ba[BO_2]_2$-II Type

The trigonal ($R\bar{3}c = C_{3v}^6$) low-temperature phase α-$Ba[BO_2]_2$-II is also likely to contain $B_3O_6^{3-}$ rings [449].

2.4.2.8 $Cu[BO_2]_2$ Type

To the tetragonal ($I\bar{4}2d = D_{2d}^{12}$) $Cu[BO_2]_2$ type with $B_3O_6^{3-}$ rings and the notation $3:\infty_3(3T)$, network, belong $Cu[B_2O_4] = Cu[BO_2]_2$ [450,451]; and $Pd[B_2O_4] = Pd[BO_2]_2$ [452].

2.4.3 Metaborates With M^{3+} Cations, $M[BO_2]_3$

2.4.3.1 $La[BO_2]_3$ Type

To the monoclinic ($I2/a = C_{2h}^6$) $La[BO_2]_3$ type with $[B_6O_{12}]^{6-}$ ions combined to chains and the notation $6:\infty(4\triangle + 2T)$, chains (Fig. 3d), belong $La[BO_2]_3$ [453,454,455]; $Ce[BO_2]_3$ [456]; $Pr[BO_2]_3$ [456]; $Nd[BO_2]_3$ [321,456,457]; $Sm[BO_2]_3$ [456,458]; $Eu[BO_2]_3$ [456]; $Gd[BO_2]_3$ [456,458,459]; and $Tb[BO_2]_3$-I [456].

2.4.3.2 $Tb[BO_2]_3$-II Type

This orthorhombic ($Pbnm = D_{2h}^{16}$ or $Pbn2_1 = C_{2v}^9$) type is represented only by $3\,B_2O_3 \cdot Tb_2O_3$-II = $Tb[BO_2]_3$-II [459].

2.4.3.3 $Bi[BO_2]_3$ Type

A new monoclinic ($C2 = C_2^3$) type has been found in $Bi[B_3O_6] = 3\,B_2O_3 \cdot Bi_2O_3 = Bi[BO_2]_3$ with $B_3O_6^{3-}$ rings and the notation $3:\infty_2(2\triangle + T)$, sheets [460].

2.4.4 Metaborates With $M^{6+}O_2$ Cations

2.4.4.1 $UO_2[BO_2]_2$ Type

$UO_2[BO_2]_2$ crystallizes in a monoclinic space group; the presence of twins prevented an assignment [461].

2.4.5 Metaborates With M^{2+} and M^{3+}

2.4.5.1 $CoSm[BO_2]_5$ Type

To the monoclinic ($P2_1/c = C_{2h}^5$) $CoSm[B_5O_{10}]$ type with $B_5O_{10}^{5-}$ layers and the notation $5:\infty_2(2\triangle + 3T)$, layers (Fig. 3c), belong

$LaMg[BO_2]_5$ [462]; $CeMg[BO_2]_5$ [462] $PrMg[BO_2]_5$ [462];
$NdMg[BO_2]_5$ [462]; $SmMg[BO_2]_5$ [462]; $EuMg[BO_2]_5$ [462]
$GdMg[BO_2]_5$ [462]; $TbMg[BO_2]_5$ [462]; $DyMg[BO_2]_5$ [462];
$HoMg[BO_2]_5$ [462]; $ErMg[BO_2]_5$ [462]; $YCo[BO_2]_5$ [463,464];
$LaCo[BO_2]_5$ [465]; $NdCo[BO_2]_5$ [466]; $SmCo[BO_2]_5$ [467];
$HoCo[BO_2]_5$ [284,468].

2.4.6 Metaborates $M_4^{2+}[O(BO_2)_6]$ or $M_4^{2+}[S(BO_2)_6]$ or $M_4^{2+}[Se(BO_2)_6]$

2.4.6.1 $Zn_4[O(BO_2)_6]$ Type

The cubic ($I\bar{4}3m = T_d^3$) $Zn_4[O(BO_2)_6]$ type contains BO_4 tetrahedra in $[B_6O_{12}]^{6-}$ rings that build a network; the notation is $6:\infty_3(6T)$, network. To this type belong $Zn_4[O(BO_2)_6]$ [469,470,471]; $Hg_4[O(BO_2)_6]$ [472]; $Zn_4[S(BO_2)_6]$ [473,474,475]; $Co_4[S(BO_2)_6]$ [473,474,475]; and $Zn_4[Se(BO_2)_6]$ [475].

2.4.7 Metaborate BO_2^- Besides PO_4^{3-}

In the trigonal ($P\bar{3} = C_{3i}^1$) $Sr_{9.4}Na_{0.3}(PO_4)_6(BO_2)$ linear BO_2 groups with two-coordinate boron have been found [476].

2.4.8 Metaborate BO_2^- Besides WO_4^{2-} or MoO_4^{2-}

Compounds of the types $Re[WBO_6]$, $(RE)_2[WB_2O_9]$, or $(RE)_4[WB_2O_{12}]$ had been discussed in Chapts. 2.2.1.11 and 2.2.1.15, respectively.

2.5 Diborates, $[B_2O_5]^{4-}$

2.5.1 $Na_4[B_2O_5]$ Type

The monoclinic ($C2/c = C_{2h}^6$) compound $Na_4[B_2O_5]$ has two nearly planar condensed BO_3^{3-} groups with an angle B—O—B of 120.6° [477]; see Fig. 3e; notation $2:2\triangle$, isolated.

2.5.2 Suanite Type

The monoclinic ($P2_1/a = C_{2h}^5$) $Mg_2[B_2O_5]$-II = mineral *suanite* has two planar BO_3^{3-} groups linked via O atoms with an angle B—O—B of 138.0° and 22.9° for Mg—O [478–480].

2.5.3 $Sr_2[B_2O_5]$ Type

To the monoclinic ($P2_1/a = C_{2h}^5$) $Sr_2[B_2O_5]$-type with two planar BO_3^{3-} groups linked via O atoms with an B—O—B angle of 138.9° belong the compound $Ca_2[B_2O_5]$ [224]; $Sr_2[B_2O_5]$ [481]; α-$Mn_2[B_2O_5]$ [482]; and $Eu_2[B_2O_5]$ [443].

2.5.4 $Co_2[B_2O_5]$ Type

To the triclinic $Co_2[B_2O_5]$ type with two planar BO_3^{3-} groups linked via O atoms with an B—O—B angle of 134.5° and 16° for Mg—O belong the compounds $Mg_2[B_2O_5]$-I [480, 482]; β-$Mn_2[B_2O_5]$-I [482]; $Fe_2[B_2O_5]$ [482]; $Co_2[B_2O_5]$ [464,483]; and $Cd_2[B_2O_5]$ [484,485].

2.5.5 $MgCa[B_2O_5]$ Type

To the monoclinic ($P2_1 = C_{2h}^5$) $MgCa[B_2O_5]$ type with an angle B—O—B of 122 to 127.7° belong the compounds $MgCa[B_2O_5]$ [486]; $CaMn[B_2O_5]$ [487]; and (Mg,Fe)Ca-$[B_2O_5]$ = mineral *α-kurchatovite* [488].

2.5.6 β-Kurchatovite Type

The orthorhombic ($Pc2_1b = C_{2v}^5$) β-kurchatovite type is represented by the compound $Mg_5Ca_6Mn[B_2O_5]_6$ = mineral *β-kurchatovite* [489].

2.5.7 Other Not Fully Characterized Types

Other not fully structurally characterized compounds are the orthorhombic or monoclinic $Li_4[B_2O_5]$ [433]; monoclinic ($P2/m = C_{2h}^1$ or $P2 = C_2^1$ or $Pm = C_S^1$) $Ba_2[B_2O_5]$ [490]; and monoclinic ($C2/m = C_{2h}^3$) $Th[B_2O_5]$ [491].

2.5.8 The Ion $[B_2O_5]^{4-}$ Besides O^{2-} Ions

While the orthorhombic ($Pna2_1 = C_{2v}^9$) $TlNb[BO_3]_2 = Tl(NbO)[B_2O_5]$ contains trigonal boron [303], the hexagonal ($P\bar{6}2m = D_{3h}^3$) $NdAl_2[O_{0.5}(B_2O_5)_2] = NdAl_{1.67+0.67x}[B_4O_{10}]O_x$ ($0.5 \leqq x \leqq 0.6$) contains tetrahedral boron and consists of infinite $[B_2O_5]_n^{4n-}$ chains; the ideal composition $NdAl_3[B_4O_{10}]O_2$ corresponds with the mineral *muscovite*, $KAl_2[Si_3AlO_{10}](OH)_2$ [492–494].

2.5.9 The Ion $[B_2O_5]^{4-}$ Besides Halogenide Ions

For $Al_2[(B_2O_5)F_2]$, powder diffraction data have been given [495].

2.6 Triborates

2.6.1 The Ion $[B_3O_5]^-$

2.6.1.1 Li[B_3O_5] Type

This orthorhombic ($Pna2_1 = C_{2v}^9$) type is represented only by $Li[B_3O_5]$, containing a six-membered $[B_3O_3O_{4/2}]$ ring (see Fig. 3f) with the short-hand notation $3\infty:2\triangle + T$, chains [496,497].

2.6.2 $Na[B_3O_5]$-I Type

To the monoclinic ($P2_1/c = C_{2h}^5$) $Na[B_3O_5]$-I type with $[B_9O_{15}]^{3-}$ rings (see Fig. 3o) and the notation $9:\infty_3(5:4\triangle + T, 4:2\triangle + 2T)$, network, belongs only α-$Na[B_3O_5]$-I = $Na_3[B_9O_{15}]$ [498].

2.6.3 $Na[B_3O_5]$-II Type

To the monoclinic ($P2_1/c = C_{2h}^5$) $Na[B_3O_5]$-II type with $[B_9O_{15}]^{3-}$ rings, but the notation $9:\infty_2(3:2\triangle + T, 5:4\triangle + T, 1T)$, belongs β-$Na[B_3O_5]$ = β-$Na_3[B_9O_{15}]$ [499].

2.6.4 $Cs[B_3O_5]$ Type

The orthorhombic ($P2_12_12_1 = D_2^4$) $Cs[B_3O_5]$ type contains $[B_3O_5]^-$ rings with the notation $3\infty:2\triangle + T$, chains; the structure type of $Cs[B_3O_5]$ [500] may be also in $Tl[B_3O_5]$ [501].

2.6.5 Other Not Fully Characterized Types

Triclinic γ-Na$[B_3O_5]$-III [498] and triclinic (but pseudohexagonal) K$[B_3O_5]$ [503] with $[B_9O_{15}]^{3-}$ rings are not yet fully characterized.

2.6.6 The Ion $[B_3O_7]^{5-}$

The ion $[B_3O_7]^{5-}$ with three four-coordinate boron atoms occurs in the orthothombic (Cmma = D_{2h}^{21}) CaAl$[B_3O_7]$ = mineral *johachidolite* [420,421].

2.7 Tetraborates

2.7.1 The Ion $[B_4O_7]^{2-}$

2.7.1.1 $Li_2[B_4O_7]$ Type

The tetragonal ($I4_1cd$ = C_{4v}^{12}) $Li_2[B_4O_7]$ type contains $B_4O_7^{2-}$ groups building two three-dimensional connected networks, but with the notation 4:2△ + 2T, isolated; it is only represented by $Li_2[B_4O_7]$ [504,505].

2.7.1.2 $Na_2[B_4O_7]$ Type

The triclinic $Na_2[B_4O_7]$ consists of $[B_8O_{14}]^{4-}$ ions with one non-bridging O atom; the notation is $8:\infty_3$(5:3△ + 2T, 3:2△ + T), network (Fig. 3h) [502].

2.7.1.3 $K_2[B_4O_7]$ Type

Triclinic $K_2[B_4O_7]$ also contains $[B_8O_{14}]^{4-}$ ions, but the notation is $8:\infty_3$(4-1:2△ + 2T, 3:△ + 2T, +1△), network [506].

2.7.1.4 $Cd[B_4O_7]$ Type

To the orthorhombic (Pbca = D_{2h}^{15}) Cd$[B_4O_7]$ type with $B_4O_7^{2-}$ ions that build up a framework (see Fig. 3g) with the notation $4\infty_3$:2△ + 2T, network, belong Mg$[B_4O_7]$ [507]; Mn$[B_4O_7]$ [508]; Fe$[B_4O_7]$ [509]; Zn$[B_4O_7]$ [510]; Cd$[B_4O_7]$ [511]; and Hg$[B_4O_7]$ [290].

2.7.1.5 $Ca[B_4O_7]$ Type

The monoclinic ($P2_1/n$ = C_{2h}^5) Ca$[B_4O_7]$ type contains $B_8O_{14}^{4-}$ ions, consisting of BO_2^-, $B_3O_5^-$, and $B_4O_7^{2-}$ ions with the notation $8:\infty_3$(3:2△ + T, 1T, 4:2△ + 2T), network (see Fig. 3i); it has been found only in Ca$[B_4O_7]$ [512,513].

2.7.1.6 $Sr[B_4O_7]$ Type

To the orthorhombic ($P2_1nm$ = C_{2v}^7) Sr$[B_4O_7]$ type consisting of a three-dimensional network of BO_4 tetrahedra with one of the O atoms coordinated to three B atoms and the notation $4:\infty_3$(4T), network belong Sr$[B_4O_7]$ [514,515] and Pb$[B_4O_7]$ [515].

2.7.1.7 $Ba[B_4O_7]$ Type

The monoclinic ($P2_1/c$ = C_{2h}^5) Ba$[B_4O_7]$ type contains (like the Ca compound) $B_8O_{14}^{4-}$ ions, but consisting of a pentaborate and a triborate unit with the notation $8:\infty_3$(3:△ + 2T, 5:3△ + 2T), network; see Fig. 3k [516].

2.7.1.8 α-Eu[B_4O_7] Type

A similar structure as Sr[B_4O_7] has the orthorhombic ($Pnm2_1 = C_{2v}^2$) α-Eu[B_4O_7] [517].

2.7.1.9 Other Not Fully Characterized Tetraborate Types

Not yet fully characterized are the structures of tetragonal $Cu_2[B_4O_7]$ [518]; hexagonal β-Eu[B_4O_7] [519]; orthorhombic ($Ammm = D_{2h}^{19}$ or $Amm2 = C_2^{14}$) α-$Tl_2[B_4O_7]$; and trigonal-rhomboedric ($P\bar{3} = C_{3i}^1$ or $P3 = C_3^1$) β-$Tl_2[B_4O_7]$ [520].

2.7.2 The Ion $[B_4O_9]^{6-}$

The ion $[B_4O_9]^{6-}$ seems to exist in the two modifications of $Li_6[B_4O_9]$ [433] as well as in the orthorhombic $Na_4[Cd(B_4O_9)]$ [521].

2.7.3 The Ion $[(B_4O_{10})O_{0.5}]^{9-}$

The ion $[B_4O_{10})O_{0.5}]^{9-}$ can be formulated in $NdAl_{1.67+0.67x}(B_4O_{10})O_x$ [492–494]; see diborates.

2.7.4 The Ion $[B_4O_{11}]^{10-}$

The ion $[B_4O_{11}]^{10-}$ seems to exist in the triclinic $Li_4[Zn_3(B_4O_{11})]$ [300].

2.8 Pentaborates

2.8.1 The Ion $[B_5O_8]^-$

2.8.1.1 K[B_5O_8]-I Type

The orthorhombic ($Pbca = D_{2h}^{15}$) high-temperature phase α-K[B_5O_8]-I contains double ring $B_5O_8^-$ groups (Fig. 31) combined into two interlocking networks; the notation is 5:4△ + T, isolated [522].

2.8.1.2 K[B_5O_8]-II Type

To the orthorhombic ($Pbca = D_{2h}^{15}$) phase β-K[B_5O_8]-II which contains the double ring $B_5O_8^-$ with the notation 5:4△ + T, isolated, but in another three-dimensional network which can be described as consisting of helix chains, belong β-K[B_5O_8]-II [523]; β-Rb[B_5O_8]-II [524]; and perhaps Tl[B_5O_8] [501].

2.8.1.3 Other Not Fully Characterized Types

Not fully characterized pentaborate types are the monoclinic low-temperature phase γ-K[B_5O_8]-III [503]; and the monoclinic ($P2_1/a = C_{2h}^5$ or $P222_1 = D_2^2$) α-Cs[B_5O_8] [525].

2.8.2 The Ion $[B_5O_{11}]^{7-}$

The orthorhombic ($Pnma = D_{2h}^{16}$) $Bi_3O[B_5O_{11}]$ type = $Bi_3[B_5O_{12}]$ contains $[B_5O_{11}]^{7-}$ ions with the notation 5:3△ + 2T, isolated [526].

2.8.3 The Ion $[B_{4.67}O_{11}]^{8-}$

The monoclinic (Cc = C_s^4) $Na_2Zn_2Mn[B_{4.67}O_{11}]$ type consists of BO_4 tetrahedra and BO_3 triangles in ratio 1:1 [527].

2.8.4 The Ion $[B_5O_9X]^{4-}$ (X = Cl, Br)

2.8.4.1 $Ca_2[B_5O_9Br]$ Type

To the orthorhombic (Pnn2 = C_{2v}^{10}) $Ca_2[B_5O_9Br]$ type with the $[B_5O_9]^{3-}$ ion and the notation $5:\infty_3(2\triangle + 3T)$, network, belong the following compounds:

$Ca_2[B_5O_9Cl]$ [528, 529];	$Ca_2[B_5O_9Br]$ [528];	$Sr_2[B_5O_9Br]$ [529];
$Ba_2[B_5O_9Cl]$ [530];	$Ba_2[B_5O_9Br]$ [530];	$Eu_2[B_5O_9Cl]$-I [401, 531];
$Eu_2[B_5O_9Br]$ [401, 531, 532];	$Ca_{2-x}Eu_x[B_5O_9Cl]$ [530];	$Sr_{2-x}Eu_x[B_5O_9Br]$ [401];
$Sr_{2-x}Eu_x[B_5O_9I]$ [530];	$Pb_2[B_5O_9Cl]$ [530];	$Pb_2[B_5O_9Br]$ [530].

2.8.4.2 $Sr_2[B_5O_9Cl]$ Type

To the tetragonal ($P4_22_12$ = D_4^6) $Sr_2[B_5O_9Cl]$ type with the $[B_5O_9]^{3-}$ ion and the notation $5:\infty_3(2\triangle + 3T)$, network, belong $Sr_2[B_5O_9Cl]$ [529]; $Ba_2[B_5O_9Cl]$ [529]; $Eu_2[B_5O_9Cl]$-II [532]; $Sr_{2-x}Eu_x[B_5O_9Cl]$ [401]; $Ba_{2-x}Eu_x[B_5O_9Cl]$ [529]; $Ca_{2-x-y}Ba_xEu_y[B_5O_9Cl]$ [529]; and $Sr_{2-x-y}Ba_xEu_y[B_5O_9Cl]$ [529].

2.8.4.3 Hilgardite Type

For $Ca_2[B_5O_9Cl] \cdot H_2O$ = mineral *hilgardite* [154–159], see Chapt. 1.6.

2.9 Hexaborates

2.9.1 The Ion $[B_6O_{10}]^{2-}$

The ion $[B_6O_{10}]^{2-}$ seems to be present in $3\,B_2O_3 \cdot CaO = Ca[B_6O_{10}]$ [533].

2.9.2 The Ion $[B_6O_{11}]^{4-}$

The ion $[B_6O_{11}]^{4-}$ has been found in monoclinic ($P2_1/b$ = C_{2h}^5) $3\,B_2O_3 \cdot 2\,CaO = Ca_2[B_6O_{11}]$ with the notation $6:\infty_3(5:2\triangle + 3T, 1T)$, A = B, network; a pentaborate unit and a single BO_4 tetrahedron are connected to build up a three-dimensional network [534].

2.9.3 The Ion $[B_6O_{17}]^{16-}$

It may be that the ion $[B_6O_{17}]^{16-}$ exists in monoclinic $Li_8Zn_4[B_6O_{17}]$ [300].

2.10 Heptaborates, Boracites

The boracites are three-dimensional, highly symmetrical, rigid boron-oxygen frame networks with tetrahedral boron, in the holes of which M^{2+} cations and X (or Y) anions are situated; the divalent cation is surrounded by four O^{2-} and two X^- ions constituting an irregular octahedron.

2.10.1 The Ion $[B_7O_{12}X]^{4-}$

2.10.1.1 The $Li_4[B_7O_{12}Cl]$-I Type

To the γ-$Li_4[B_7O_{12}Cl]$-I type, which is very similar to the cubic ($F\bar{4}3c = T_d^5$) high-boracite type, belong the high-temperature phase γ-$Li_4[B_7O_{12}Cl]$-I [535,536] and $Li_4[B_7O_{12}I]$ [537].

2.10.1.2 The $Li_4[B_7O_{12}Cl]$-II Type

This cubic ($P\bar{4}3n = T_d^4$) type is represented only by β-$Li_4[B_7O_{12}Cl]$-II [535].

2.10.1.3 The $Li_4[B_7O_{12}Cl]$-III Type

To this trigonal ($R3 = C_3^4$) type belong α-$Li_4[B_7O_{12}Cl]$-III [535,536]; $Li_4[B_7O_{12}Br]$ [535,537]; and $Li_4[B_7O_{12}Cl_{0.7}Br_{0.3}]$ [535].

2.10.2 The Ion $[B_7O_{12+x/2}X]^{(4+x)-}$

2.10.2.1 The $Li_5[B_7O_{12.5}Cl]$ Type

To the cubic ($F23 = T^2$) $Li_5[B_7O_{12.5}Cl]$ type belong the compounds $Li_5[B_7O_{12.5}Cl]$ [538]; $Li_5[B_7O_{12.5}Br]$ [538]; and $Li_{4+x}[B_7O_{12+x/2}Cl]$ [539,540].

2.10.3 The Ions $[B_7O_{12+x}Y_{1-y}]^{6-}$

2.10.3.1 The Ion $[B_7O_{12.5}\square_{0.5}Y_{1.0}]^{6-}$

This high-boracite type ($F\bar{4}3 = T_d^5$) is represented by $Mg_3[B_7O_{12.5}S]$ [474] and $Mn_3^{2+}[B_7O_{12.5}S]$ [474].

2.10.3.2 The Ion $[B_7O_{12.65}\square_{0.35}Y_{0.85}\square_{0.15}]^{6-}$

The following compounds belong to this high-boracite ($F\bar{4}3 = T_d^5$) type:
$Mg_3[B_7O_{12.65}S_{0.85}]$ [473,475]; $Mn_3[B_7O_{12.65}S_{0.85}]$ [473,475]; $Fe_3[B_7O_{12.65}S_{0.85}]$ [473,475]; $Cd_3[B_7O_{12.65}S_{0.85}]$ [473,475]; $Mn_3[B_7O_{12.65}Se_{0.85}]$ [475]; $Fe_3[B_7O_{12.65}Se_{0.85}]$ [475]; $Cd_3[B_7O_{12.65}Se_{0.85}]$ [475,541]; $Mn_3[B_7O_{12.65}Te_{0.85}]$ [475].

2.10.4 The Ions $[B_7O_{13}X]^{6-}$

2.10.4.1 The High-Boracite = $Mg_3[B_7O_{13}Cl]$-I Type

The cubic ($F\bar{4}3 = T_d^5$) high-boracite type consists of a B—O network containing the B atoms and 12 of the 13 O atoms, while the M^{2+} and X^- ions are located in the holes; the last O atom is tetrahedrally coordinated by four B atoms. To this type belong: the high temperature phase α-$Mg_3[B_7O_{13}Cl]$-I = mineral α-boracite [474,542,543];
$Cr_3[B_7O_{13}F]$ [544]; $Cr_3[B_7O_{13}Cl]$-I [543,545]; $Cr_3[B_7O_{13}Br]$-I [543]; $Cr_3[B_7O_{13}I]$ [543]; $Mn_3[B_7O_{13}Cl]$-I [543]; $Mn_3[B_7O_{13}Br]$-I [543]; $Mn_3[B_7O_{12}I]$-I [543]; $(Mg_{1-x}Mn_x)_3[B_7O_{13}Br]$ [546]; $Fe_3[B_7O_{13}Cl]$-I [543,547]; $Fe_3[B_7O_{13}Br]$-I [543,547]; $Fe_3[B_7O_{13}I]$-I [543,547]; $(Mg_{1-x}Fe_x)_3[B_7O_{13}Br]$ [546]; $Co_3[B_7O_{13}Cl]$-I [543]; $Co_3[B_7O_{13}Br]$-I [543]; $Co_3[B_7O_{13}I]$-I [543,548];

$Ni_3[B_7O_{13}Cl]$-I [543]; $Ni_3[B_7O_{13}Br]$-I [543] $Ni_3[B_7O_{13}I]$-I [549,550];
$Ni_3[B_7O_{13}Cl_{0.5}Br_{0.5}]$-I [543]; $Ni_3[B_7O_{13}Br_{0.9}I_{0.1}]$-I [543]; $Ni_3[B_7O_{13}I_{1-x}(OH)_x]$ [551];
$(Co,Ni)_3[B_7O_{13}(NO_3)]$-I [544]; $Cu_3[B_7O_{13}Cl]$-I [543]; $Cu_3[B_7O_{13}Br]$-I [543,548];
$Cu_3[B_7O_{13}(NO_3)]$-I [544]; $Zn_3[B_7O_{13}Cl]$-I [543,547]; $Zn_3[B_7O_{13}Br]$-I [543];
$Zn_3[B_7O_{13}I]$-I [543]; $Cd_3[B_7O_{13}Cl]$-I [543]; $Cd_3[B_7O_{13}Br]$-I [543];
$Cd_3[B_7O_{13}I]$-I [543].

2.10.4.2 The Low-Boracite = $Mg_3[B_7O_{13}Cl]$-II Type

The orthorohombic ($Pca2_1 = C_{2v}^5$) low-boracite type is similar to $Mg_3[B_7O_{13}Cl]$-I, but the Mg^{2+} ions are shifted 24 pm along the z-axis and the Cl^- ions 21 pm along the cubic (111) direction. To this type belong:
the low-temperature phase β-$Mg_3[B_7O_{13}Cl]$-II [543,552]
$Cr_3[B_7O_{13}Cl]$-II [543];
$Cr_3[B_7O_{13}Br]$-II [543]; $Mn_3[B_7O_{13}Cl]$-II = mineral *chambersite* [474,545,553];
$Mn_3[B_7O_{13}Br]$-II [474]; $Mn_3[B_7O_{13}I]$-II [474,543]; $Fe_3[B_7O_{13}Cl]$-II [543,547];
$Fe_3[B_7O_{13}Br]$-II [543,547]; $Fe_3[B_7O_{13}I]$-II [543,554]; $(Mn_{1-x}Fe_x)_3[B_7O_{13}Br]$-II [546];
$Co_3[B_7O_{13}Cl]$-II [543]; $Co_3[B_7O_{13}Br]$-II [543]; $Co_3[B_7O_{13}I]$-II [543];
$Co_3[B_7O_{13}(NO_3)]$-II [544]; $Ni_3[B_7O_{13}Cl]$-II [543]; $Ni_3[B_7O_{13}Br]$-II [543,555];
$Ni_3[B_7O_{13}I]$-II [543]; $Ni_3[B_7O_{13}Cl_{0.5}Br_{0.5}]$-II [543,555]; $Ni_3[B_7O_{13}Br_{0.9}I_{0.1}]$-II [543];
$Ni_3[B_7O_{13}(NO_3)]$-II [544]; $(Co,Ni)_3[B_7O_{13}(NO_3)]$-II [544]; $Cu_3[B_7O_{13}Cl]$-II [543];
$Cu_3[B_7O_{13}Br]$-II [543]; $Cu_3[B_7O_{13}(NO_3)]$-II [544]; $Zn_3[B_7O_{13}Cl]$-II [543,547];
$Zn_3[B_7O_{13}Br]$-II [543]; $Zn_3[B_7O_{13}I]$-II [543]; $Zn_3[B_7O_{13}(NO_3)]$-II [544];
$Cd_3[B_7O_{13}Cl]$-II [543]; $Cd_3[B_7O_{13}Br]$-II [543]; $Cd_3[B_7O_{13}I]$-II [543];
$Cd_3[B_7O_{13}(NO_3)]$-II [544].

2.10.4.3 The Ericaite = $(Mg,Fe)_3[B_7O_{13}Cl]$-III Type

To the trigonal ($R3c = C_{3v}^6$) ericaite type belong $Mg_3[B_7O_{13}F]$ [544]; $Mn_3[B_7O_{13}F]$ [544]; $Mn_3[B_7O_{13}F_{0.44}(OH)_{0.56}]$ [544]; $Mn_3[B_7O_{13}(OH)]$ [474]; $Fe_3[B_7O_{13}F]$ [544]; $Fe_{2.4}Mg_{0.6}[B_7O_{13}Cl]$ = mineral *ericaite* [553]; $Fe_{2.676}Mg_{0.243}Mn_{0.081}[B_7O_{13}Cl]$ = mineral *congolite* [556]; $Fe_3[B_7O_{13}Cl]$-III [547,557]; $Fe_3[B_7O_{13}Br]$-III [557]; $Fe_3[B_7O_{13}I]$-V [547,554]; $Co_3[B_7O_{13}F]$ [544]; $Zn_3[B_7O_{13}F]$ [544]; and $Zn_3[B_7O_{13}Cl]$-III [547,557].

2.10.4.4 $Fe_3[B_7O_{13}I]$-III and $Fe_3[B_7O_{13}I]$-IV

$Fe_3[B_7O_{13}I]$-III as well as $Fe_3[B_7O_{13}I]$-IV crystallize in the monoclinic $Pc = C_S^2$ space group [554].

2.11 Higher Borates

2.11.1 The Ion $[B_8O_{13}]^{2-}$

2.11.1.1 The $Na_2[B_8O_{13}]$ Type

This monoclinic ($P2_1/a = C_{2h}^5$) type with the notation $8:\infty_2(5:4\triangle + T, 3:2\triangle + T)$, layers (see Fig. 3m), is represented by α-4 $B_2O_3 \cdot Na_2O$ = α-$Na_2[B_8O_{13}]$ [558].

2.11.1.2 The $Ag_2[B_8O_{13}]$ Type

To this monoclinic ($P2_1 = C_{2h}^5$) type with the notation $8:\infty_3(5:4\triangle + T, 3:2\triangle + T)$, network, belong β-$Ag_2[B_8O_{13}]$ and the mixed $Ag_{0.6}Na_{0.4}[B_8O_{13}]$ [559].

2.11.1.3 The $Ba[B_8O_{13}]$-II Type

This orthorhombic ($P222_1 = D_2^2$) type with pseudotetragonal symmetry and the notation $8:\infty_2(5:4\triangle + T, 3:2\triangle + T)$, chains that build up three-dimensional networks, is represented by $4\ B_2O_3 \cdot BaO$-II $= Ba[B_8O_{13}]$-II [560].

2.11.1.4 Other Types

Not yet fully characterized are pseudocubic $Cs_2[B_8O_{13}]$ [561] and tetragonal $Ba[B_8O_{13}]$-I [562].

2.11.2 The Ion $[B_8O_{14}]^{4-}$

For compounds with the anion $[B_8O_{14}]^{4-}$, see $[B_4O_7]^{2-}$, above.

2.11.3 The Ion $[B_8O_{15}]^{6-}$

The ion $[B_8O_{15}]^{6-}$ occurs in monoclinic ($P2_1/c = C_{2h}^5$ or $Pc = C_S^2$) $8\ B_2O_3 \cdot 3\ K_2O \cdot Al_2O_3 = K_3[AlB_8O_{15}]$; the aluminoborate polyanion is built up from the double-ring pentaborate group, the single-ring triborate group and a single AlO_4 tetrahedron, connected to an infinite two-dimensional double layer; the notation is therefore $8:\infty_2(5:4\triangle + T, 3:2\triangle + T, Al:1T)$, layers, modified; it is similar to β-$Na_3[B_9O_{15}]$ crystals, except for replacement of B by Al at the tetrahedral sites [563].

2.11.4 The Ion $[B_8O_{17}]^{8-}$

The ion $[B_8O_{17}]^{8-}$ may exist in $Na_4Ga_4[B_8O_{17}]$, for which only the powder diagram has been given [564].

2.11.5 The Ion $[B_9O_{14}]^{-}$

The pseudotetragonal, orthorhombic refined ($P4_122 = D_4^3$ or $P222_1 = D_2^2$) α-$Cs[B_9O_{14}]$ contains planar boroxine groups and one $[B_3O_5]^{-}$ group; the notation is therefore $9:\infty_3(2\times3:3\triangle, 3:2\triangle + T)$, network (Fig. 3n); the monoclinic β-$Cs[B_9O_{14}]$ has not yet been fully characterized [561, 565].

2.11.6 The Ion $[B_9O_{15}]^{3-}$

For compounds with the anion $[B_9O_{15}]^{3-}$, see $[B_3O_5]^{-}$ above.

2.11.7 The Ion $[B_{10}O_{21}]^{12-}$

The triclinic $5\ B_2O_3 \cdot 6\ PbO = Pb_6[B_{10}O_{21}]$ contains the ion $[B_{10}O_{21}]^{12-}$. It is built up from two $[B_4O_7]^{2-}$ groups which are connected by two planar BO_3^{3-} triangles; the notation is $10:(2\times4:2\triangle + 2T, 2\triangle)$, isolated [566].

2.11.8 The Ion $[B_{10}O_{30}]^{30-}$

The triclinic compound $B_2O_3 \cdot 3\,CuO = Cu_3[B_2O_6]$ is better formulated as $Cu_{15}[B_{10}O_{30}] = Cu_{15}[O_2(B_2O_5)_2(BO_3)_6]$; it forms a layer structure consisting of almost planar $[B_2O_5]^{4-}$ groups, planar isolated BO_3^{3-} groups, and isolated O^{2-} ions; the notation is $10:\infty_2(6\times\triangle, 2\times 2\triangle, 2\,O)$, layers, modified; it should have also been cited in the Chapts. 2.2.1 and/or 2.5 [567].

2.11.9 The Ion $[B_{12}O_{29}]^{22-}$

The ion $[B_{12}O_{29}]^{22-}$ may exist in triclinic $Ba_5[Al_4B_{12}O_{29}]$, studied only by powder diffraction [381].

2.11.10 The Ion $[B_{19}O_{31}]^{5-}$

The monoclinic ($C2/c = C_{2h}^6$) compound $3.8\,B_2O_3 \cdot K_2O = 19\,B_2O_3 \cdot 5\,K_2O = K_5[B_{19}O_{31}]$ contains a three-dimensional network of two connected pentaborate, two triborate groups, two BO_3 triangles and one BO_4 tetrahedron; the notation is, therefore, $19:\infty_3(2\times 5{:}4\triangle + T,\ 2\times 3{:}2\triangle + T,\ 2\triangle,\ 1T)$, network; see Figure 3p [568].

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