

Review

Crystal Chemistry of High-Temperature Borates

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Academic Editor: Derek J. McPhee

Received: 20 April 2020; Accepted: 22 May 2020; Published: 25 May 2020



Abstract: In recent years borate-based crystals has attracted substantial interest among the research community. The overall importance of this family of materials is reflected in miscellaneous articles and several reviews that have been published over the years. Crystalline borate materials exhibit numerous interesting physical properties, which make them promising for further practical applications. Diversity of functional characteristics results from their high structural flexibility caused in the linkage of planar/non-planar BO_3 groups and BO_4 tetrahedra, which can occur as isolated or condensed structural units. This report is a brief review on crystal chemistry and structure features of anhydrous/high-temperature borates. Polymorphism of boron-oxygen radicals has been considered basing on cations' nature and synthesis conditions. Analysis of the laws governing borates structures and general principles of their systematics was discussed. As a result, an alternative classification of anhydrous compounds has been considered. It is based on four orders of their subdivision: (1) by the variety of anion formers, (2) by the cation charge, (3) by the $N = N_M:N_B$, i.e., ratio of metal atoms number to the ratio of boron atoms number (N-factor) value indicating the borate structural type (if it is known), (4) by the cation type and size.

Keywords: high-temperature borates; anhydrous borates; crystal chemistry; fundamental structural units; boron-oxygen radicals

1. Introduction

A critical analysis of the existing literature data on melting diagrams of borate systems, hydrothermal synthesis and mineralogical field studies indicates that more than 1300 high-temperature (anhydrous) borates and their structural derivatives have been synthesized and also found in Nature [1]. Their crystal structures and structural types have been studied using X-ray diffraction methods. Most of them belong to orthorhombic, monoclinic or trigonal/hexagonal systems. As a rule, the symmetry of borate materials decreases with decreasing cation and the ratio between the number of metal and boron atoms in the compound [2].

Isolated BO_3 triangles predominate in the structures of anhydrous borates, especially, those of binary and more complex compounds (about 65%) [3]. Among the remaining borates, almost one-half are represented by framework structures containing three-dimensional boron-oxygen polyanions (exclusively monocationic compounds), followed by insular layered and chain structures, i.e., those with dispersed individual elements (pyrogroups of two BO_3 -triangles, rings of three triangles, groups of two BO_4 -tetrahedra). In these cases, BO_3 - and BO_4 - groups are joined by sharing common O atoms. Polyanions of compounds with cations of alkali and alkali-earth metals are most diverse. Then, it is followed by isolated (pyroborates and ring metaborates), network and chain-forming structures. There are about fifty types of boron-oxygen anions and polyanions proper (including the BF_4 group) and a dozen of borosilicate, boroaluminate and boroberyllate anions (Figure 1).

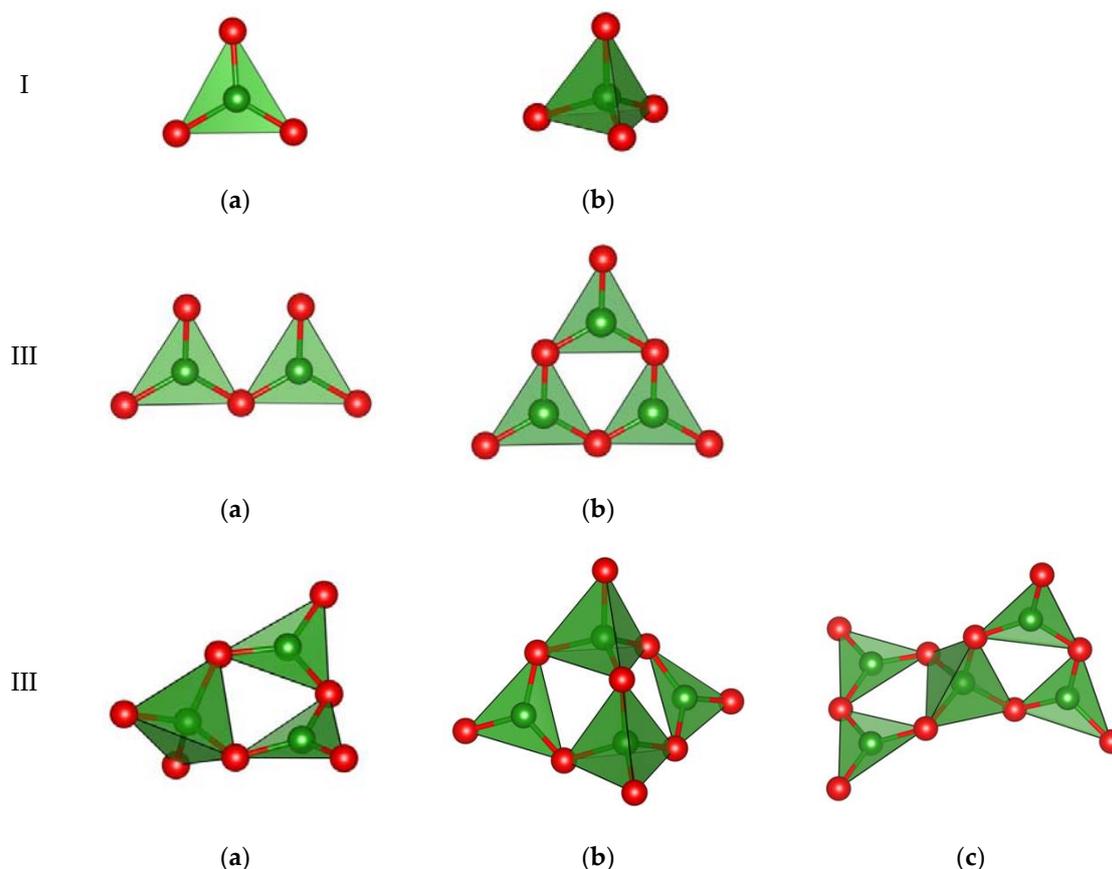


Figure 1. Examples of “building units” for anions and polyanions in anhydrous borates: (I) isolated fundamental units, only in orthoborates (a), (b); (II) island clusters, in pyroborates (a) and metaborates (b); (III) combined basic structural units in highly condensed polyanions (a), (b), (c). The green and red balls represent B, and O atoms, respectively.

As shown by our experimental studies [3,4], the regularities of the crystallization of borates with trivalent metals are in many respects determined by the specificity of their structure and the composition of crystallization medium. An increase in the content of anhydrous boric oxide in the melts facilitates the synthesis of borates with a higher polymerization of boron-oxygen radicals [2–4]. It should be also noted the tendency of boron atoms to tetrahedral coordination, and BO_3 - and BO_4 -groups-to polycondensation, when they prevail over other cations in the structures of compounds synthesized. Similar trends were also observed for some other groups of borates [5–7]. It is, therefore, worth assessing the extent to which the above peculiarities are typical for anhydrous borates in general.

2. Hierarchy of Basic Structural Clusters

This section provides a concise and precise description of the experimental results, their interpretation as well as the experimental conclusions that can be drawn. In polymeric boron-oxygen constructions of different composition one can easily identify, except for BO_3 -triangles (Δ) and BO_4 -tetrahedra (t), comparatively small groups formed by them, most of which are represented in many structures. First this clusters (radicals), but only isolated, were found in anhydrous potassium and sodium metaborates [8,9], and then in three-dimensional frameworks as well [10]. These comparatively small structural components (usually single or double rings), containing 2–5 triangles and tetrahedra, are designated below as combined basic structural units *CSU* in contradistinction to the fundamental (elementary) structural units (*FSU*), i.e., BO_3 -triangles and BO_4 -tetrahedra.

In polyanions of anhydrous borates, it is expedient to discern one more type of structural units. Structural units of this category are, as a rule, more complex and characterize the structures and the

structural types of compounds. It is appropriate to designate them, as complete radicals of polyanions (CRP). CRP can contain more than one CSU and/or additional triangles and tetrahedra. Thus, it represents a full repeating fragment of a polyanion (made up of 2–9 FSU) corresponding in composition or multiple of the boron-oxygen anion part in the structural formula of the compound.

2.1. Fundamental Structural Units

The B-O bond lengths in FSU vary within considerable limits, the range of variation being greater in complex structures. Their average values in triangles and tetrahedral amount to 1.37 Å and 1.48 Å, respectively. These values for O-O distances in the sides of triangles equal to 2.38 Å, and in the edges of tetrahedral they are 2.43 Å [1,5] (Figure 2).



Figure 2. FSU in orthoborate structures: (a) isolated BO_3 -triangles and (b) BO_4 -tetrahedra.

2.2. Combined Structural Units

The structures of alkali metal anhydrous monocationic borates contain a rather limited number of CSU of the same kind and their different combinations. In this framework, layered and isolated borate structures of this group most often are encountered single or paired triple rings of triangles and tetrahedra: 1) 3Δ , 2) $2\Delta + 2t$, 3) $2\Delta + 1t$ and 4) $4\Delta + 1t$ (Figure 3a–d), sometimes, they are variously mentioned in the literature as boroxol, diborate, triborate and pentaborate groups, respectively [9–13]. Occasionally, in framework $\text{K}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ [14] and layered $\alpha\text{-Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ [11], were single and double $1\Delta + 2t$ and $3\Delta + 2t$ rings (Figure 3e,f) encountered, not very aptly called ditriborate and dipentaborate groups. This is because the ditriborate group together with the additional BO_3^- triangle in $\text{K}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ structure represents configurationally a strongly deformed diborate group.

In borates of divalent metals, namely CaB_2O_4 , BO_3^- -triangles and BO_4^- -tetrahedra can form endless chains [15–17]. Apart from these, the most borates of divalent and trivalent metals also have other CSU. First of all, there is the pyroborate containing isolated pair of BO_3 triangles [18,19] (Figure 3g). The next one, a ring of three tetrahedra (Figure 3h) has been found in boracite, hausenite and their analogues [20], in CaB_2O_4 (III) [21], SrB_2O_4 [22], SrB_4O_7 and PbB_4O_7 [23] structures. The same rings, but without additional FSU were discovered in framework CaB_2O_4 (IV) [24]. Less widespread are quadruple (SrB_4O_7 and PbB_4O_7 [23]), sextuple ($\text{Zn}_4\text{OB}_6\text{O}_{12}$ [25]) and octuple (CuB_2O_4 [26]) rings of tetrahedra (Figure 3i–k). Overall, CSU here are more diversified than in the borates of alkali metals. Among them, the tetrahedral coordination of boron atoms predominates over the triangular one.

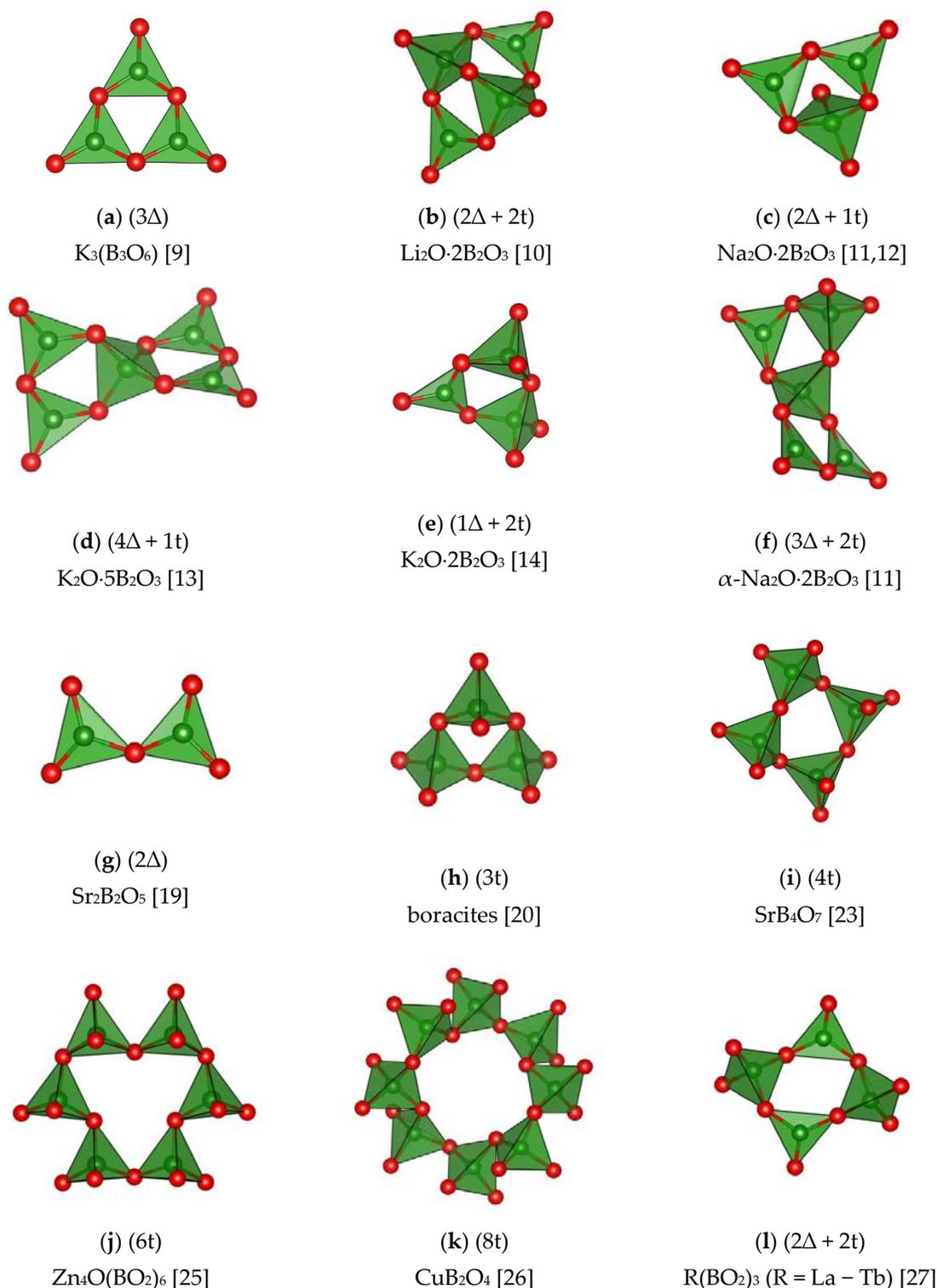


Figure 3. Examples of CSU in mono-, di- and trivalent metal simple (monocationic) borates (the green and red balls represent B, and O atoms, respectively). (a) $\text{K}_3(\text{B}_3\text{O}_6)$ [9]; (b) $\text{Li}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ [10]; (c) $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ [11,12]; (d) $\text{K}_2\text{O}\cdot 5\text{B}_2\text{O}_3$ [13]; (e) $\text{K}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ [14]; (f) $\alpha\text{-Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ [11]; (g) $\text{Sr}_2\text{B}_2\text{O}_5$ [19]; (h) boracites [20]; (i) SrB_4O_7 [23]; (j) $\text{Zn}_4\text{O}(\text{BO}_2)_6$ [25]; (k) CuB_2O_4 [26]; (l) $\text{R}(\text{BO}_2)_3$ ($\text{R} = \text{La} - \text{Tb}$) [27]

In the borates of trivalent metals, CSU differing from the others have also been found, e.g., quaternary rings of two BO_3 -triangles and two BO_4 -tetrahedra in corrugated metachains of rare earth borates, $\text{R}(\text{BO}_2)_3$ with $\text{R} = \text{La} - \text{Tb}$ [27] (Figure 3l). In such chain, every BO_4 tetrahedron belongs to two adjacent

rings, i.e., the oxygen corners of all the tetrahedra are shared with the triangles, while each of the triangles has one corner unbonded inside the chain. According to [28], isolated triple rings of BO_4 tetrahedra represent the anionic part of the structure of low-temperature GdBO_3 and its rare earth analogues. Borate with tetravalent cations are represented by ThB_2O_5 and ThB_4O_8 compounds. Thorium diborate, ThB_2O_5 , exhibits α - and β - polymorphs. In the structure of β - ThB_2O_5 two corner sharing BO_3 triangles are linked forming an isolated B_2O_5 dimer [29]. Whereas, in the structure of α - modification boron atoms occupy corner sharing BO_4 -tetrahedra and BO_3 -triangles forming 1D zigzag chain [30]. ThB_4O_8 structure exhibits infinite chains, which consist of $[\text{B}_2\text{O}_4]^{5-}$ tetrahedral borate groups that are connected through one common oxygen atom [31]. Monocationic borates of pentavalent elements have only isolated BO_4 tetrahedra [32].

The structures of binary and more complex borates predominantly contain isolated BO_3 triangles, less frequently tetrahedra or pyrogroups (Figure 4a). Only in four types of layered structures, i.e., in jochachidolite, synthetic $\text{RCo}(\text{BO}_2)_5$ with $R = \text{La} - \text{Ho}$, $\text{Na}_2\text{Zn}_2\text{MnB}_{4.67}\text{O}_{11}$ and $\text{RAl}_2\text{B}_4\text{O}_{10.5}$ with $R = \text{La} - \text{Nd}$ [33–37], one can identify sextuple, quadruple and binary three-membered rings (Figure 4b–f).

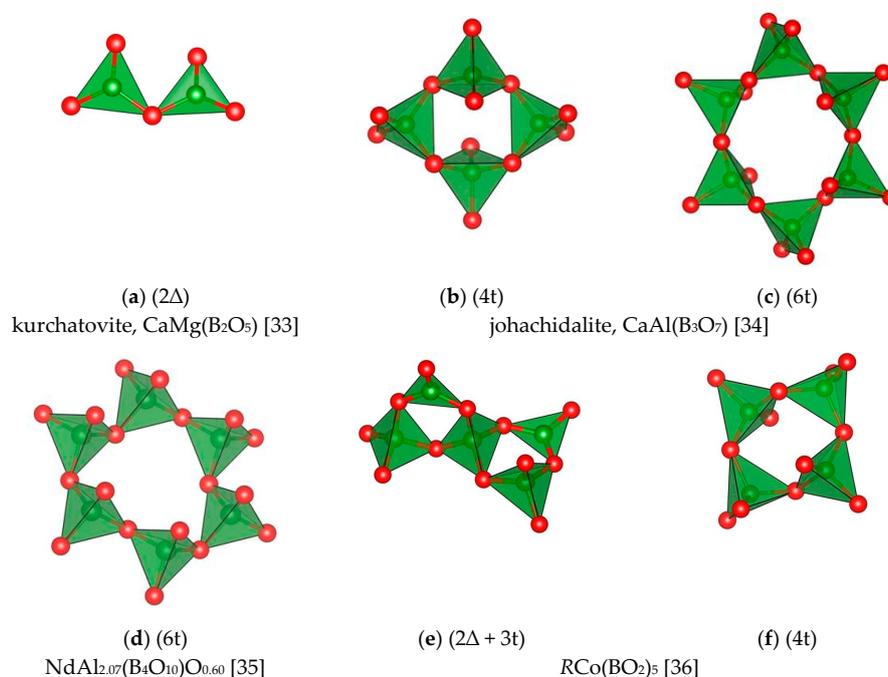


Figure 4. Examples of CSU in binary and more complex borates (the green and red balls represent B, and O atoms, respectively). (a) kurchatovite, $\text{CaMg}(\text{B}_2\text{O}_5)$ [33]; (b) and (c) johachidalite, $\text{CaAl}(\text{B}_3\text{O}_7)$ [34]; (d) $\text{NdAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.60}$ [35]; (e) and (f) $\text{RCo}(\text{BO}_2)_5$ [36].

In the R -aluminum metaborates synthesized by the authors of [38], the Al atoms are located in five-corner oxygen polyhedra, they can formally be regarded as a transitional compound between the borates proper and aluminoborates. Another type of “transitional” compounds can be represented by $\text{Al}_5(\text{BO}_3)\text{O}_6 = \text{Al}_2[\text{Al}_3\text{O}_6\text{BO}_3]$, in this structure 60% of Al atoms are located in AlO_4 -tetrahedra and 40% of them form AlO_6 -octahedra [39].

An individual group can be made up of CSU (in an overwhelming majority of cases - ring-shaped) in boroberyllates, borooaluminates and borosilicates where Be, Al and Si atoms with a tetrahedral coordination partially substitute boron (Figure 5) (see, for example, Ref. [40–46]). Unusual illustrations of trivalent Al and divalent Be in the role of boron are found in the structures of CaAlOBO_3 [42], SrAlBO_4 [43] and $\text{Y}_2\text{AlBeBO}_7$ [44]. In the first case, double (2 $t_{\text{Al}} + 2\Delta_{\text{B}}$) rings in the chains by their configuration resemble the diborate groups very often found in the polyanions of mono- and divalent metal borate structures. The alumoborate metachain, i.e., one-dimensional (1D) chain of $[\text{Al}_2\text{B}_2\text{O}_8]^{1-}$

composition in SrAlBO_4 , where $(2t_{\text{Al}} + 1\Delta_{\text{B}})$ rings can be identified, is similar to the metaborate chain in calciborite - $[\text{B}_4\text{O}_8]1\text{D}$, if the BO_4 tetrahedra in it are replaced by those of aluminum, i.e., by AlO_4 groups.

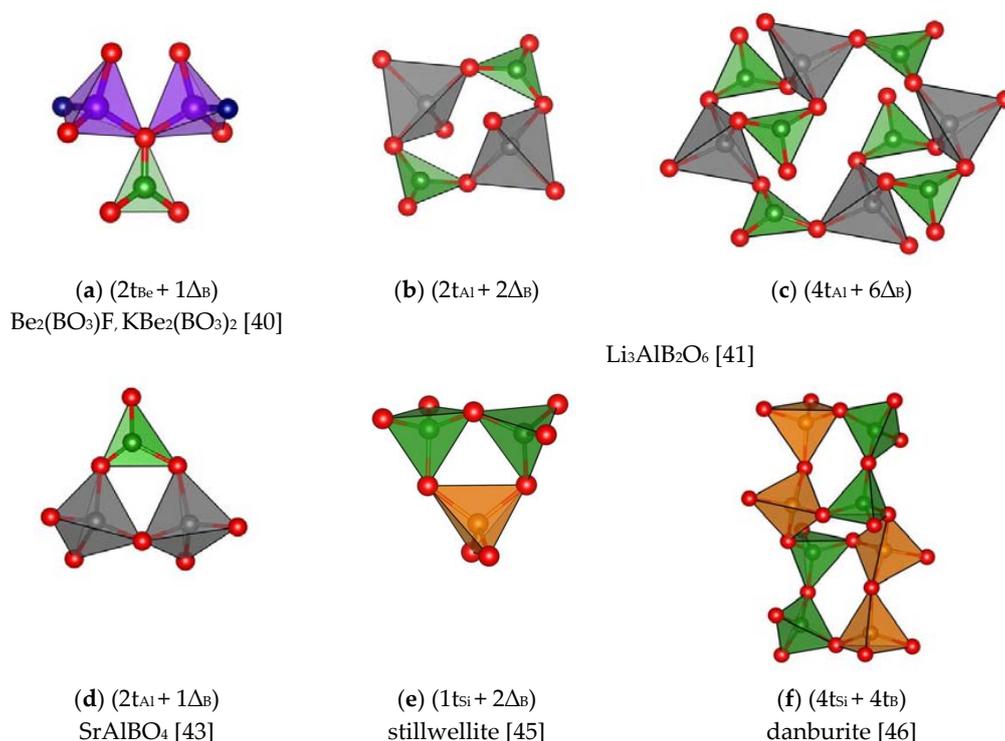


Figure 5. CSU in boroberyllates, boroaluminates and borosilicates (the green, red, violet, grey, and brown balls represent B, O, Be, Al, and Si atoms, respectively). (a) $\text{Be}_2(\text{BO}_3)\text{F}, \text{KBe}_2(\text{BO}_3)_2$ [40]; (b) and (c) $\text{Li}_3\text{AlB}_2\text{O}_6$ [41]; (d) SrAlBO_4 [43]; (e) stillwellite [45]; (f) danburite [46].

2.3. Complete Radicals of Polyanions

CRP in the structures of anhydrous borates are similar to some CSU shown in Figures 3 and 4 and they are identical with FSU in orthocompounds. The CRP have a comparatively complex structure in monovalent metal borates, for example, in boracite, as well as in a number of CaB_2O_4 modifications [16,17,21], SrB_2O_4 , $\text{Ca}_2\text{B}_6\text{O}_{11}$, CaB_4O_7 , $\text{BaO}\cdot 2\text{B}_2\text{O}_3$, $\text{BaO}\cdot 4\text{B}_2\text{O}_3$ [23,47,48] (Figure 6 Figures 7 and 8) and in some others. A peculiar CRP is found in aluminum orthotriborate, $\text{Al}_5(\text{BO}_3)_6$ [39] or, to be more precise, in aluminum-alumoborate $\text{Al}_2(\text{AlO}_2)_3\text{BO}_3$.

Thus, despite the great diversity of structural types of anhydrous borates, most of them contain only three configurations of the basic structural units: FSU, CSU, and CRP (Figures 6–8)

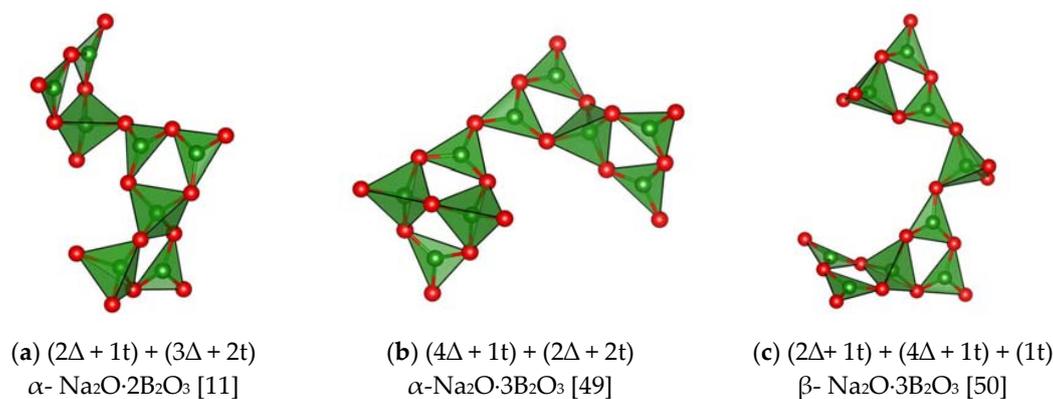


Figure 6. Cont.

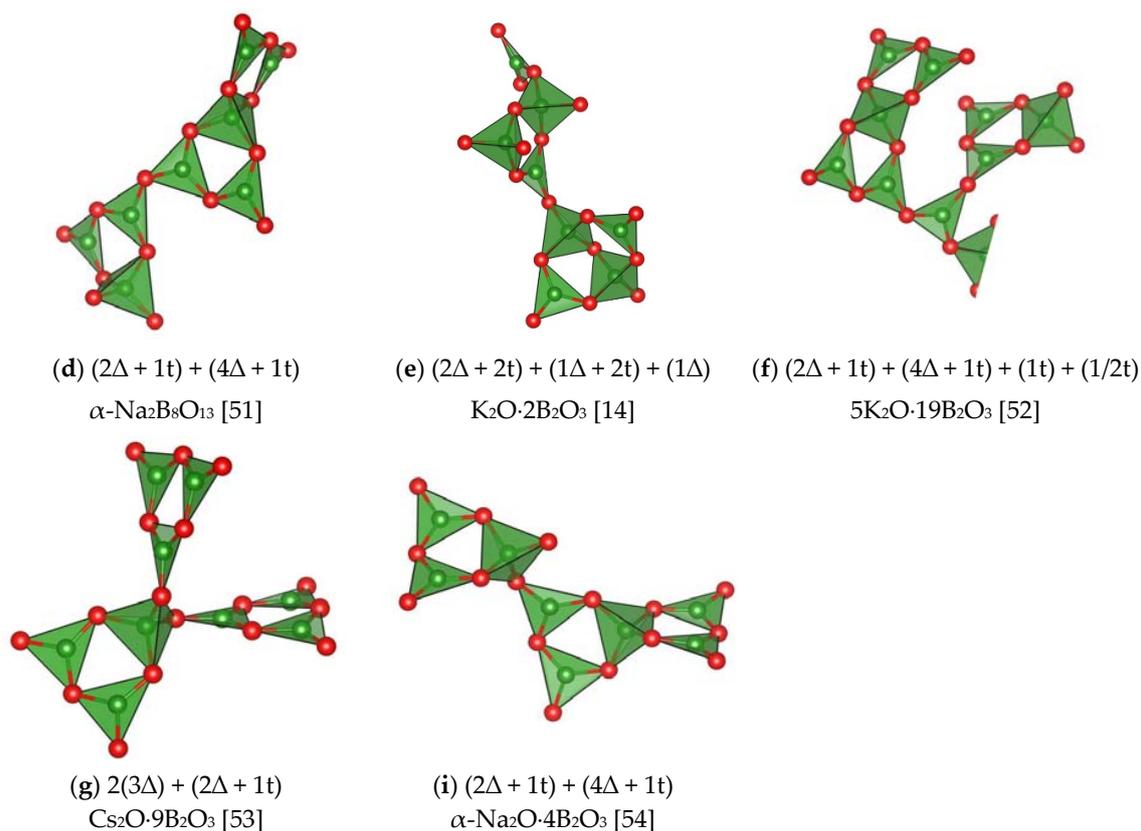


Figure 6. CRP in monovalent metal borates which are different from the FSU and CSU in these compounds (the green and red balls represent B, and O atoms, respectively). (a) $\alpha\text{-Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ [11]; (b) $\alpha\text{-Na}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ [49]; (c) $\beta\text{-Na}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ [50]; (d) $\alpha\text{-Na}_2\text{B}_8\text{O}_{13}$ [51]; (e) $\text{K}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ [14]; (f) $5\text{K}_2\text{O}\cdot 19\text{B}_2\text{O}_3$ [52]; (g) $\text{Cs}_2\text{O}\cdot 9\text{B}_2\text{O}_3$ [53]; (i) $\alpha\text{-Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$ [54].

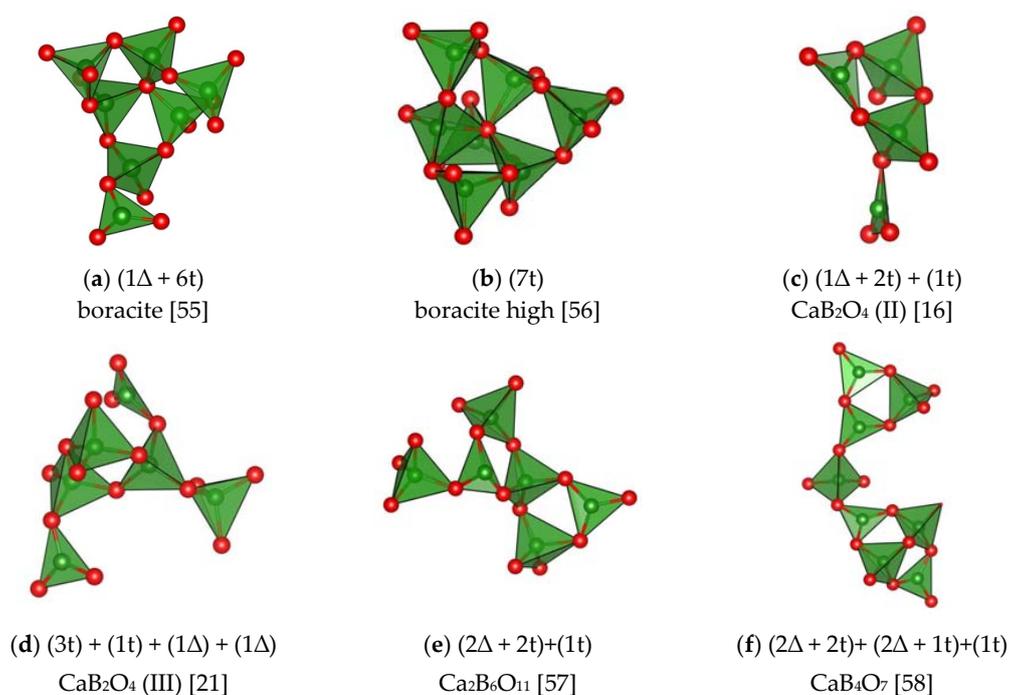


Figure 7. Cont.

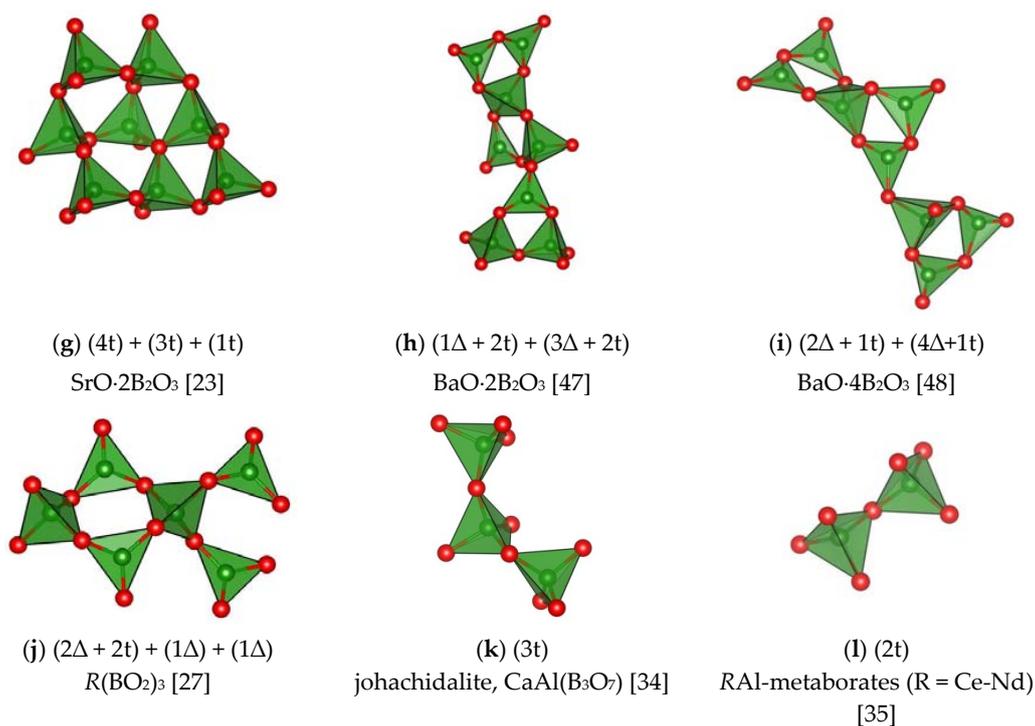


Figure 7. CRP in di- and trivalent metal borates different from the FSU and CSU in these compounds (the green and red balls represent B, and O atoms, respectively). (a) boracite [55]; (b) boracite high [56]; (c) CaB_2O_4 (II) [16]; (d) CaB_2O_4 (III) [21]; (e) $\text{Ca}_2\text{B}_6\text{O}_{11}$ [57]; (f) CaB_4O_7 [58]; (g) $\text{SrO} \cdot 2\text{B}_2\text{O}_3$ [23]; (h) $\text{BaO} \cdot 2\text{B}_2\text{O}_3$ [47]; (i) $\text{BaO} \cdot 4\text{B}_2\text{O}_3$ [48]; (j) $R(\text{BO}_2)_3$ [27]; (k) johachidalite, $\text{CaAl}(\text{B}_3\text{O}_7)$ [34]; (l) RAl-metaborates (R = Ce–Nd) [35].

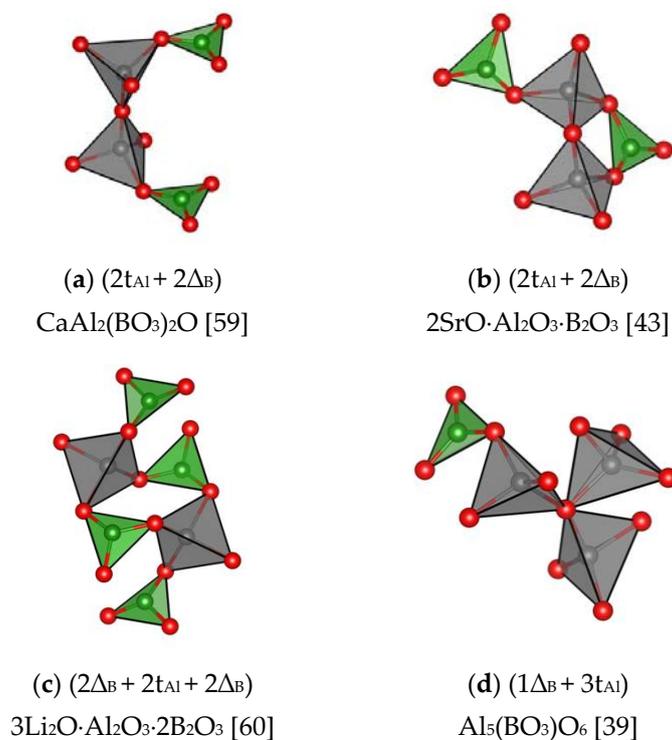


Figure 8. CRP in boroberyllates, borooaluminates and borosilicates different from the FSU and CSU in these compounds (the green, grey, and red balls represent B, Al and, O atoms, respectively). (a) $\text{CaAl}_2(\text{BO}_3)_2\text{O}$ [59]; (b) $2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ [43]; (c) $3\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$ [60]; (d) $\text{Al}_5(\text{BO}_3)\text{O}_6$ [39].

3. Polymerization of Boron-Oxygen Radicals

Polymerization degree of B_nO_m anions can be defined by the ratio of $N = N_M:N_B$ (called as N factor), i.e., by the relation between the number of atoms of a metal (metals, M) and B atoms in the formula of a compound. Generally it is equivalent to the $N' = N_{M \times O_y}:N_{B_2O_3}$ ratio. For monocationic borates with cations of odd valence, $N = N'$, but for those with even valence $N = N'/2$. The effect of the magnitude of N-factor on the type of boron-oxygen radicals and the degree of radicals polymerization should be analyzed for compounds with the same cations, i.e., separately for Li, Na, K, etc.

The most comprehensive X-ray diffraction data have been accumulated on alkali metal borates. A decrease in the value of N in these compounds leads polyanion complication and changing of structural type. For Li borates, obtained at normal pressure, isolated BO_3 -triangles ($N = 3$) in α - $Li_3B_3O_6$ [61] transform to one-dimensional chains of triangles ($N = 1$) in $LiBO_2$ [62], then to three-dimensional chains of $(4\Delta + 3t)$ groups ($N = 4/7$) [44] or $(2\Delta + 2t)$ groups for $N = 1/2$ in $Li_2O \cdot 2B_2O_3$ [10]. In Na borates isolated groups of 3Δ at $N = 1$ in $Na_3(B_3O_6)$ [8] transform into two-dimensional nets of dipentaborate or triborate clusters with $n = n_\Delta:n_t = 5/3$ ($N = 1/2$) in $Na_2O \cdot 2B_2O_3$ [11]. Then one can observe transformation to: 1) a double two-dimensional net of pentaborate, triborate rings with additional tetrahedra ($n = 2$) in a metastable low-temperature modification or 2) twinned three-dimensional framework of penta- and diborate groups with the same ratio of BO_3 -triangles and BO_4 -tetrahedra in the stable high-temperature form for $N = 1/3$ in α - $Na_2O \cdot 3B_2O_3$ and β - $Na_2O \cdot 3B_2O_3$ [49,50]. Finally, twinned three-dimensional network of penta- and triborate rings with $n = 3$ at $N = 1/4$ are formed in [54]. For potassium borates isolated rings of 3Δ ($N = 1$) in $K_3B_3O_6$ [9,63] change over to three-dimensional networks: a) of diborate, ditriborate groups having additional BO_3 -triangles with $n = 1$ at $N = 1/2$ in $K_2O \cdot 2B_2O_3$ [14]; b) of penta-, triborate rings, additional BO_3 -triangles and BO_4 -tetrahedra with $n = 14/5$ at $N = 5/19$ in $5K_2O \cdot 19B_2O_3$ [52]; or c) of pentaborate *CSU* with $n = 4$ ($N = 1/5$) in $K_2O \cdot 5B_2O_3$ [13]. In rubidium and cesium borates isolated rings of 3Δ ($N = 1$) transform into a three-dimensional framework of triborate groups with $n = 2$ ($N = 1/3$) in $Cs_2O \cdot 3B_2O_3$ [12], then into twinned two-dimensional network of triborate and boroxol rings with $n = 8$ ($N = 1/9$) [64]. In the Ag-tetraborate $AgO \cdot 4B_2O_3$ the polyanion structure is similar to potassium one [65].

No isolated BO_4 groups have been found in monovalent metal borates. Isolated BF_4 tetrahedra are known only in the structures of fluoroborates $NaBF_4$ and NH_4BF_4 with $N = 1$ [66,67]. The maximal fraction of BO_4 -tetrahedra ($n = 1$) is found in the framework lithium ($Li_2O \cdot 2B_2O_3$) and potassium ($K_2O \cdot 2B_2O_3$) borate structures with $N = 1/2$ but $1/n = 3/5$ [10,14], and in cesium borate $Cs_2O \cdot 3B_2O_3$ it is even smaller ($1/n = 1/2$) and shifts to $N = 1/3$ [12]. No clear-cut relationship was established between the value of n, the type of BO radical and the degree of the deformation of BO_3 -triangles and BO_4 -tetrahedra, with the exception that isolated *FSUs* are more regular.

With a decrease in the N number in borates of divalent metals, the same tendency is observed as in monovalent metal borates. At $N \geq 3/2$ (i.e., $N_{MO}:N_{B_2O_3} \geq 3$), only isolated BO_3 -triangles are observed in the structures of monocationic and binary compounds. In pyroborates ($N = 1$), including binary $M^{2+}M^{3+}B_2O_5$ compounds, anions are represented by isolated B_2O_5 pyrogroups. Metaborate anions ($N = 1/2$) are more condensed: a) infinite metachains of BO_3 -triangles (CaB_2O_4 -I) [17], b) cyclic groups of three triangles bonded at common corners ($BaO \cdot B_2O_3$ [68], c) ring-shaped three-membered rings of BO_4 -tetrahedra in CuB_2O_4 [26]. Thus, in divalent metal metaborates besides BO_3 -triangles, BO_4 -tetrahedra also appear under normal pressure.

Compounds with an even smaller N-factor exhibit only 3D frameworks. The amount of triangular and tetrahedral boron in the structures with $N = 1/4$ is the same, with the exception of SrB_4O_7 and PbB_4O_7 in which the three-dimensional anionic framework consists only of BO_4 -tetrahedra [23]. In the three-dimensional boron-oxygen net of BaB_8O_{13} ($N = 1/8$) triangularly coordinated boron ($n = 3$) predominates [48]. Although no clear-cut regularity is observed in the variation of the limits of B-O interatomic distances depending on the N value in divalent metal borates; they are more isometric in orthoborates.

In the structures of borates with trivalent metals at $N \geq 1$, only isolated BO_3 -triangles (or isolated BO_4 -tetrahedra in Fe_3BO_6 [69] and sinhalite MgAlBO_4 [70]) have been found. In simple R metaborates ($N = 1/3$), the polyanions are chain-like with $n = 2$. Simultaneously, in binary borates of tri- and divalent metals, for example, johachidolite CaAlB_3O_7 [34], synthetic $R\text{Co}(\text{BO}_2)_5$ [71] and $R\text{Al}_2\text{B}_4\text{O}_{10.5}$ [35] the polyanions are represented by layers of BO_4 -tetrahedra or BO_4 -tetrahedra together with BO_3 -triangles, even if the N value is equal to $2/3$, $2/5$ and $3/4$, respectively. Most likely, the nature of metals plays a significant role here. Both simple and binary pentavalent metal borates are not numerous and are not distinguished by any special diversity in the anion structure. For monocationic compounds, tetrahedral configuration of boron is preferable, but for binary compounds, it is triangular.

Decrease of the N ratio in borosilicates (in this case, it implies the ratio of the sum of metals to the sum of B and Si atoms) results to increasing of polymerization of the silicon-boron-oxygen motif. Thus, in the structure of grandidierite $(\text{Mg,Fe})\text{Al}_3\text{SiBO}_9$ [72] ($N = 2$), the anion consists of isolated BO_3 -triangles and SiO_4 -tetrahedra, but in stillwellite LaBSiO_5 ($N = 1/2$), it is represented by BO_4 -metachain encrusted with discrete SiO_4 -tetrahedra [45]. In danburite $\text{CaB}_2\text{Si}_2\text{O}_8$ ($N = 1/4$) a silicon-boron-oxygen framework of Si_2O_7 - and B_2O_7 -diorthogroups is observed [46]. If the sum of metals exceeds the total amount of Si and B atoms, the boron is coordinated by three oxygen atoms. Taking into account the stillwellite structure, boron-oxygen FSU are more predisposed to polymerization in comparison with silicon-oxygen ones. It is noteworthy that there are practically no minerals of anhydrous borosilicates with the amount of boron predominating over the silicon content (with the exception of cappelenite $\text{BaY}_6(\text{Si}_3\text{B}_6\text{O}_{24})\text{F}_2$ [73]), whereas borosilicates enriched with silicon are quite numerous. The shortage of adequately interpreted structures for borosilicates (with the exception of synthetic $\text{Al}_5(\text{BO}_3)\text{O}_6$ [39]) makes it impossible to disclose their regularities. Even smaller amount of structural data are published for boroberyllates.

Coordination metal-oxygen polyhedra is more regular in structures with large N value, i.e., when they constitute the base of these structures. At small N value, not numerous metal atoms adapt themselves to the anionic motif. In other words, coordination oxygen polyhedra of metals in highly polymerized borates seem to be mostly determined by the nature of free spaces in the boron-oxygen base, but not by the directed bonds.

Among the borates having high N -factor values, the tendency to anion polymerization increases in compounds with smaller cations. For example, the difference in B-O interatomic distances inside the ring of potassium metaborate $\text{K}_3\text{B}_3\text{O}_6$ [63] is smaller than in sodium compound $\text{Na}_3(\text{B}_3\text{O}_6)$ [8]. However, in lithium analogue LiBO_2 [62], the ring already becomes energetically disadvantageous. In the meantime, for highly condensed compounds the tendency of B-O anions to polymerize somewhat increases with an increase in the cation sizes.

An increase in the cation charge facilitates the weakening of the polymerization of BO_3 -triangles and BO_4 -tetrahedra and makes the tetrahedral coordination of boron atoms more preferable. In borates with comparatively weak singly charged and large divalent cations, the stability of the structure is ensured by the delocalization of anion charge, i.e., by a decrease in its formal specific charge during the polymerization process. In the case of cations with relatively high charge, which capable to form around themselves strong coordination polyhedral, making up the base of the structures, and the boron-oxygen anion stability is no longer of decisive importance. In such structures, therefore, not only isolated BO_3 -triangles are commonly widespread, but BO_4 -tetrahedra with an even higher negative charge (-5) as well.

4. Polymorphism of B_nO_m Polyanions

Metaborate radical of $[\text{BO}_2]_n$ composition, mostly widespread in polyborates, was found in isolated (0D), chain (1D), ribbon (1D), layered (2D) and three-dimensional (3D) borates (Table 1). Index n in the formula $[\text{BO}_2]_n$ for the currently known varieties of polyanions in metaborates assumes all the values from 1 to 6. With increasing polymerization of this metaradical, the triangular coordination

of boron atoms regularly changes into BO_4 -tetrahedra as one passes from the insular to chain, layered and 3D structures.

Table 1. Structural motifs based on the $[\text{BO}_2]_n$ metaborate radical.

Type of Metaborate Anion	Composition of $[\text{BO}_2]_n$ Polyanion	Compound
Isolated rings	$[\text{B}_3^{\Delta}\text{O}_6] = [\text{B}_3\text{O}_6]$	$\alpha\text{-Na}_2\text{O}\cdot\text{B}_2\text{O}_3$ $\text{K}_2\text{O}\cdot\text{B}_2\text{O}_3$ $\text{Rb}_2\text{O}\cdot\text{B}_2\text{O}_3$ $\text{Cs}_2\text{O}\cdot\text{B}_2\text{O}_3$ $\beta\text{-BaO}\cdot\text{B}_2\text{O}_3$
		$\alpha\text{-Li}_2\text{O}\cdot\text{B}_2\text{O}_3$ $\text{CaO}\cdot\text{B}_2\text{O}_3$ (I) $\text{SrO}\cdot\text{B}_2\text{O}_3$ (I)
Chain (one-dimensional, 1D)	$[\text{B}_2^{\Delta}\text{O}_4]_{1\text{D}} = [\text{B}_2\text{O}_4]_{1\text{D}}$	Calciborite $\text{CaO}\cdot\text{B}_2\text{O}_3$ (II)
	$[(\text{B}^{\Delta}\text{O}_2)_2\text{B}_2^{\text{t}}\text{O}_4]_{1\text{D}} = [\text{B}_4\text{O}_8]_{1\text{D}}$	$\text{Ln}_2\text{O}_3\cdot 3\text{B}_2\text{O}_3$ ($\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb}$)
	$[(\text{B}^{\Delta}\text{O}_2)_4\text{B}^{\text{t}}\text{O}_2]_{1\text{D}} = [\text{B}_6\text{O}_{12}]_{1\text{D}}$	$2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$
	$[(\text{B}^{\Delta}\text{O}_2)_2\text{Al}_2^{\text{t}}\text{O}_4]_{1\text{D}} = [\text{B}_2\text{Al}_2\text{O}_8]_{1\text{D}}$	$2\text{SrO}\cdot\text{B}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$
	$[\text{B}_3^{\text{t}}\text{O}_6]_{1\text{D}} = [\text{B}_3\text{O}_6]_{1\text{D}}$ (exc. Si)	Stillwellite $\text{Ce}_2\text{O}_3\cdot\text{B}_2\text{O}_3\cdot 2\text{SiO}_2$
	$[\text{B}_2^{\Delta}\text{O}_4]_{1\text{D}} = [\text{B}_2\text{O}_4]_{1\text{D}}$ (exc. Mo, W)	$\text{La}_2\text{O}_3\cdot\text{B}_2\text{O}_3\cdot 2\text{MoO}_3$ $\text{La}_2\text{O}_3\cdot\text{B}_2\text{O}_3\cdot 2\text{WO}_3$
Ribbon (one-dimensional, 1D)	$[(\text{B}^{\Delta}\text{O}_2)_4(\text{Al}^{\text{t}}\text{O}_2)_2]_{1\text{D}} = [\text{B}_4\text{Al}_2\text{O}_{12}]_{1\text{D}}$ $[(\text{B}^{\Delta}\text{O}_2)_4(\text{Ga}^{\text{t}}\text{O}_2)_2]_{1\text{D}} = [\text{B}_4\text{Ga}_2\text{O}_{12}]_{1\text{D}}$	$3\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{B}_2\text{O}_3$ $3\text{Li}_2\text{O}\cdot\text{Ga}_2\text{O}_3\cdot 2\text{B}_2\text{O}_3$
Layer (two-dimensional, 2D)	$[(\text{B}^{\Delta}\text{O}_2)_4\text{B}_6^{\text{t}}\text{O}_{12}]_{2\text{D}} = [\text{B}_{10}\text{O}_{20}]_{2\text{D}}$	$\text{Ln}_2\text{O}_3\cdot 2\text{CoO}\cdot 5\text{B}_2\text{O}_3$ ($\text{Ln} = \text{La-Nd, Sm-Ho}$)
Framework (three-dimensional, 3D)	$[\text{B}^{\text{t}}\text{O}_2]_{3\text{D}} = [\text{BO}_2]_{3\text{D}}$	$\gamma\text{-Li}_2\text{O}\cdot\text{B}_2\text{O}_3$
	$[\text{B}_3^{\text{t}}\text{O}_6]_{3\text{D}} = [\text{B}_3\text{O}_6]_{3\text{D}}$	$\text{CaO}\cdot\text{B}_2\text{O}_3$ (II) $\text{SrO}\cdot\text{B}_2\text{O}_3$ (II)
	$[\text{B}_3^{\text{t}}\text{O}_6]_{3\text{D}} = [\text{B}_3\text{O}_6]_{3\text{D}}$	$\text{CuO}\cdot\text{B}_2\text{O}_3$
	$[\text{B}_6^{\text{t}}\text{O}_{12}]_{3\text{D}} = [\text{B}_6\text{O}_{12}]_{3\text{D}}$	$4\text{ZnO}\cdot 3\text{B}_2\text{O}_3$
	$[(\text{B}_6^{\Delta}\text{O}_{2.5})(\text{B}^{\Delta}\text{O}_{1.5})\text{B}_4\text{O}_8]_{3\text{D}} = [\text{B}_6\text{O}_{12}]_{3\text{D}}$	$\text{CaO}\cdot\text{B}_2\text{O}_3$ (III) $\text{SrO}\cdot\text{B}_2\text{O}_3$ (III)
	$[(\text{B}_2^{\text{t}}\text{O}_4)(\text{Si}_2\text{O}_4)]_{3\text{D}} = [\text{Si}_2\text{B}_2\text{O}_8]_{3\text{D}}$	Danburite— $\text{CaO}\cdot\text{B}_2\text{O}_3\cdot 2\text{SiO}_2$

Pressure significantly affects the formation of metaborates' structural motifs. Thus, in lithium borate obtained at low pressure and temperature, the boron atoms are located in oxygen triangles that are condensed into chains [62], but $\gamma\text{-LiBO}_2$ crystals synthesized at 950 °C and a pressure of 15 kbar have 3D structures with tetrahedral coordination of boron atoms [74,75]. In the Ca metaborate structure, stable at normal temperature, i.e., CaB_2O_4 (I), B and Ca atoms have triangular and eightfold coordination, respectively [17]. With the transition of this modification into CaB_2O_4 (II) synthesized at 12–15 kbar, half of the boron atoms increase their coordination number to four [16]. In CaB_2O_4 (III), which can be obtained at 900 °C and 15–25 kbar pressure, the fraction of boron atoms that preserve their triangular coordination is already only 1/3 [21]. In this case, for one-third of Ca atoms the coordination number increases to ten. In the structure of CaB_2O_4 (IV) all the B atoms are located in oxygen tetrahedra, and the coordination number of Ca increases to 9–12 [24]. A similar situation was observed in Sr metaborate [23,76].

A distinguishing feature of $[\text{B}_4\text{O}_7]_n$ polyanions ($n = 1$ and 2) is their high degree of polymerization. Only one of them, $\alpha\text{-Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ is layered, in all others representatives were found 3D anionic motifs (Table 2). In all borates having $[\text{B}_4\text{O}_7]_n$ radicals, with the exception of $\alpha\text{-Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$, $\text{SrO}\cdot 2\text{B}_2\text{O}_3$ and $\text{PbO}\cdot 2\text{B}_2\text{O}_3$, the anions contain equal amounts of triangular and tetrahedral boron-oxygen coordination. The ratio of $n_{\Delta} : n_{\text{t}} = 5/3$ in $\alpha\text{-Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ is accompanied by part of BO_3 triangles being the corners unshared with other FSU, and in the exclusively tetrahedral frameworks of $\text{SrO}\cdot 2\text{B}_2\text{O}_3$ and $\text{PbO}\cdot 2\text{B}_2\text{O}_3$, part of oxygen atoms is coordinated with three boron atoms [23].

Table 2. Polyanions with $[B_4O_7]_n$ and $[B_8O_{14}]_n$ radicals.

Type of polyanion	Composition of B_4O_7 Based Polyanion	Compound
Layers (two-dimensional, 2D)	$[(B_2^{\Delta}B^tO_{5.5})(B_3^{\Delta}B_2^tO_{8.5})]_{2D} = [B_8O_{14}]_{2D}$	α - $Na_2O \cdot 2B_2O_3$
	$[B_2^{\Delta}B_2^tO_7]_{3D} = [B_4O_7]_{3D}$	LiO·2B ₂ O ₃
	$[B_2^{\Delta}B_2^tO_7]_{2(3D)} = [B_4O_7]_{2(3D)}$	MgO·2B ₂ O ₃ , MnO·2B ₂ O ₃ , ZnO·2B ₂ O ₃ , CdO·2B ₂ O ₃
Frameworks (three-dimensional, 3D)	$[(B_2^{\Delta}B_2^tO_7)(B^{\Delta}B_2^tO_{5.5})(B^{\Delta}O_{1.5})]_{3D} = [B_8O_{14}]_{3D}$	K ₂ O·2B ₂ O ₃
	$[(B_2^{\Delta}B_2^tO_7)(B_2^{\Delta}B^tO_5)(B^tO_2)]_{3D} = [B_8O_{14}]_{3D}$	CaO·2B ₂ O ₃
	$[B_4^tO_7]_{3D} = [B_4O_7]_{3D}$	SrO·2B ₂ O ₃ , PbO·2B ₂ O ₃
	$[(B_3^{\Delta}B_2^tO_{8.5})(B^{\Delta}B_2^tO_{5.5})]_{3D} = [B_8O_{14}]_{3D}$	BaO·2B ₂ O ₃

The 3D polyanion of $[B_4O_7]_n$ composition in borates with comparatively small cations is made up of $2\Delta + 2t$ diborate groups only. For larger M^{2+} cations the architectural principle was found in the twinning of 3D boron-oxygen nets, designated in Table 2 by doubling the contents of the square brackets. An increase in cation size leads to a strong deformation of diborate groups in $K_2O \cdot 2B_2O_3$. In $CaO \cdot 2B_2O_3$ triborate rings with additional tetrahedra are already stable, but a low-symmetry 3D net made up of dipentaborate and ditriborate *CSU* [47,76] is represented in the borate with the largest cation, barium.

The third and the fourth most widespread boron-oxygen clusters are B_3O_5 and B_8O_{13} , respectively (Table 3). The first one takes part in the formation of layered and 3D structures, and the second was found in 3D borates only. Common features of structures with these two radicals are their comparative complexity, predominance of BO_3 –triangles over BO_4 –tetrahedra, low symmetry and the twinning of boron-oxygen nets. On the whole, with an increase in the ratio of the total number of boron atoms to that of oxygen atoms in the polyanions their composition and structure become more complex.

Table 3. Polyanions based on $[B_3O_5]_n$ and $[B_8O_{13}]_n$ radicals.

Radical	Type of Polyanion	Composition B_3O_5 and B_8O_{13} Based Polyanions	Compound
B_3O_5	Layers (two-dimensional, 2D)	$[(B_4^{\Delta}B^tO_8)(B_2^{\Delta}B^tO_5)(B^tO_2)]_{2(2D)} = [B_9O_{15}]_{2(2D)}$	β - $Na_2O \cdot 3B_2O_3$
	Frameworks (three-dimensional, 3D)	$[(B_4^{\Delta}B^tO_8)(B_2^{\Delta}B_2^tO_7)]_{2(3D)} = [B_9O_{15}]_{2(3D)}$ $[B_2^{\Delta}B^tO_5]_{3D} = [B_3O_5]_{3D}$	α - $Na_2O \cdot 3B_2O_3$ $Cs_2O \cdot 3B_2O_3$
B_8O_{13}	Frameworks (three-dimensional, 3D)	$[(B_4^{\Delta}B^tO_8)(B_2^{\Delta}B^tO_5)]_{2(3D)} = [B_8O_{13}]_{2(3D)}$	α - $Na_2O \cdot 4B_2O_3$
		$[(B_4^{\Delta}B^tO_8)(B_2^{\Delta}B^tO_5)]_{2(3D)} = [B_8O_{13}]_{2(3D)}$	$0.6Ag_2O \cdot 0.4Na_2O \cdot 4B_2O_3$; BaO·4B ₂ O ₃

5. Isostructural Series

Isostructural series are widely encountered among high-temperature borates. Two dozen borates $M^{2+}M^{3+}[BO_3]O_3$ with warwickite-type structure and a considerable range of $M^{2+}:M^{3+}$ ratio are limited both by the sizes of trivalent cations close to Al^{3+} and lanthanides [77,78]. In this case, Ca^{2+} has the maximum radius value among M^{2+} cations.

Isostructural with respect to one another are numerous borates of the ludwigite-vonsenite group, $M^{2+}Fe^{3+}[BO_3]O_3$, where $M = Mg, Fe, Cu, Co, Ni$, partially Sn [77]. This structure is also preserved in Co compounds, where Fe^{3+} is substituted by Cr, Ga, V, Sc, as well as in Fe^{2+} borate [78]. Trivalent iron is almost half substituted by aluminium in aluminoludwigite. However, the substitution of Fe^{3+} by Mn^{3+} in pinakiolite and orthopinakiolite, as well as a substantial inclusion of Sn^{4+} in hulsite, cause a considerable reduction of the symmetry of the structures [79].

Another group of di- and tetravalent metal borates and binary borates of trivalent elements (is headed by nordenskiöldine $CaSn[BO_3]_2$ [80] which is isostructural to dolomite. More than fifty compounds compose the boracite group [56], with six minerals among them: boracite, stassfurtite, gauesinite, congolite, ericaite and chambersite. It is not only with various divalent cations anhydrous boracites were synthesized, but with chromium and lithium as well. One can also mention here the

isostructural groups of MB_4O_7 , where $M = Mg, Mn, Zn, Cd$; $M_2B_2O_5$ with $M = Mg, Mn, Fe, Co, Cd$; and $M_3B_3O_6$ ($M = Na, K, Rb, Cs$) in which the size of cations differs considerably.

Structural peculiarities of rare-earth borates should be specifically noted. Analysis shown that isostructural along the whole R series are only those compounds where the mutual linkage of these cations is comparatively small.

Orthoborates with the general formula $M^{3+}BO_3$ can be structurally subdivided into three groups: (1) isostructural to calcite; (2) isostructural to aragonite; (3) compounds with a structure close to the third modification of $CaCO_3$ –vaterite. Of them only $LuBO_3$, or, to be more specific, its low-temperature modification [81], belongs to the first group. The size of trivalent cation and the $c:a$ ratio in it are obviously close to the maximum limiting values at which borates with the structure of calcite are stable (these values seem to be minimal in $AlBO_3$ [82], synthesized only at high pressures [83]). It is thus seen that in monocationic orthoborates ($N = 1$) the characteristics of each R ion (electron shell structure, its radius) exert a decisive effect on the formation of the structure.

In $R(BO_2)_3$ metaborates, although the influence of R is less pronounced here, the replacement of cations by smaller ones still leads to the deformation of B–O metachains. Therefore, two structural types for them are known. The situation is approximately the same with $RCo(BO_2)_5$ metaborates.

Double orthoborates of the $R_2Sr_3(BO_3)_4$, $R_2Ba_3(BO_3)_4$ and $R_2Ca_3(BO_3)_4$ families are already isostructural with one another, although in some compounds the intensities of X-ray reflection do not coincide [84].

In $RM_3(BO_3)_4$ ($M = Al, Ga, Sc, Fe, Cr$) borates with the huntite-type structure, the R -oxygen polyhedra are essentially simplified and constitute trigonal prisms deformed to a different extent. In these structures, RO_6 -polyhedra are isolated from each other, and the base of the motif is formed by columns of Al, Ga, Sc, Fe, or Cr octahedra connected by isolated BO_3 -triangles [85–89]. When Al is substituted by Fe, and then by Ga, in the $NdM_3(BO_3)_4$ compound, the symmetry of MO_6 -octahedron is increased, with some increase in the size of RO_6 -prisms. The relative sharing of R ions is not great here, and their specific properties tell even less on the formation of the structure. It seems that in this family of double trivalent metal borates the critical values of the ratio of cation sizes are close to Al^{3+}/Nd^{3+} on the one side and to Fe^{3+}/Sc^{3+} on the other. Also, there is monoclinic structural modification of $NdAl_3(BO_3)_4$. In the case of large R cations of the cerium subgroup, layered double RAl -metaborates with $N = 3/4$ are also synthesized [38]. Despite out numerous attempts it was impossible to obtain $LaAl_3(BO_3)_4$, and $ScFe_3(BO_3)_4$ was also crystallized with difficulty in a narrow range of conditions [90].

6. Structural Formulas of Polyborates

In the above text formulas of all anhydrous borates are given in the form taken from the literature, i.e., mainly as a ratio of metal oxide to boron oxide. Although they clearly reflect the N' ratio, their structural formulas are undoubtedly more informative for polyborates with known crystal structure. Showing the ratio of cations and anions in the compounds, the CRP composition structure type (isolated anions, clusters, chains and ribbons, layers, 3D motifs), they can show, if necessary, the polyanion nature (simple or twinned), the amounts of triangularly and tetrahedrally coordinated boron atoms. Since most of the polyanions are built of single and double rings, it is useful to note this in the formula too. It could be provided them even more information, but because of the polyanions complexity, their structural formulas would become too bulky. Table 4 lists both complete and abbreviated structural formulas for some polyborates that have been studied.

The composition of repeating radical is enclosed in square brackets with the 1D, 2D or 3D symbols for various types of structures (one-, two- or three-dimensional polyanion, respectively). In the case of a twinned polyanion, the composition of one of the equivalent boron-oxygen nets is doubled (indicated by the figure of two after the square brackets). The maximum information is contained in the first complete version of the formula, where CSU are shown, as well as additional BO_3 -triangles and BO_4 -tetrahedra. The second version, as an alternative for writing out the formula, only shows a relationship between the triangularly and the tetrahedrally coordinated boron. For example, since the three-dimensional polyanion

in $\text{Li}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ consists of $2\Delta + 2t$ diborate groups [10] its chemical composition can be written out as $[(\text{B}_2^\Delta\text{B}_2^t\text{O}_7)]_{3\text{D}}$ or in the abbreviated form as $[\text{B}_4\text{O}_7]_{3\text{D}}$. The negative charge of one such radical is equal to two. The structural formula will, therefore, have the form of $\text{Li}_2[\text{B}_4\text{O}_7]_{3\text{D}}$. In contradistinction to $\text{Li}_2[\text{B}_4\text{O}_7]$, in Mg, Mn, Zn and Cd borates with $N' = 2$, the polyanions consist of twinned three-dimensional boron-oxygen nets. Therefore, their structural formula is $\text{M}_2^{\text{II}}[\text{B}_4\text{O}_7]_{2(3\text{D})}$. In the $\alpha\text{-Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ structure, the two-dimensional polyanionic net consists of dipentaborate and triborate *CSU*, with the latter each containing a free O atom [11]. Polyanion composition of this sodium borate can be written as $(\text{B}_3^\Delta\text{B}_2^t\text{O}_{8.5}) + (\text{B}_2^\Delta\text{B}^t\text{O}_{5.5}) = [\text{B}_5^\Delta\text{B}_3^t\text{O}_{14}]_{2\text{D}} = [\text{B}_8\text{O}_{14}]_{2\text{D}}$; its negative charge is equal to four, and borate structural formula will be represented in the form of $\alpha\text{-Na}_4[\text{B}_8\text{O}_{14}]_{2\text{D}}$. In $\text{K}_2\text{O}\cdot 2\text{B}_2\text{O}_3$, the composition of three-dimensional polyanionic network, consisting of $(2\Delta + 2t)$ diborate and $(1\Delta + 2t)$ triborate groups with additional BO_3 triangles (1Δ) [14], is $(\text{B}_2^\Delta\text{B}_2^t\text{O}_7) + (\text{B}^\Delta\text{B}_2^t\text{O}_{5.5}) + (\text{B}^t\text{O}_{1.5}) = [\text{B}_4^\Delta\text{B}_4^t\text{O}_{14}]_{3\text{D}} = [\text{B}_8\text{O}_{14}]_{3\text{D}}$. The charge of this polyradical is four, the borate structural formula can be look like $\text{K}_4[\text{B}_8\text{O}_{14}]_{3\text{D}}$.

Table 4. Structural formulas of monocationic polyborates.

Formula in Oxides (Bulk Composition)	Structural Formula		
	Complete	Complete	Abbreviated
$\alpha\text{-Li}_2\text{O}\cdot\text{B}_2\text{O}_3$	$\alpha\text{-Li}_2[\text{B}^\Delta_2\text{O}_4]_{1\text{D}}$	$\alpha\text{-Li}_2[\text{B}^\Delta_2\text{O}_4]_{1\text{D}}$	$\alpha\text{-Li}_2[\text{B}_2\text{O}_4]$
$\gamma\text{-Li}_2\text{O}\cdot\text{B}_2\text{O}_3$	$\gamma\text{-Li}[\text{B}^t\text{O}_2]_{3\text{D}}$	$\gamma\text{-Li}[\text{B}^t\text{O}_2]_{3\text{D}}$	$\gamma\text{-Li}[\text{BO}_2]$
$\gamma\text{-}3\text{Li}_2\text{O}\cdot 7\text{B}_2\text{O}_3\cdot 2\text{LiCl}$	$\gamma\text{-Li}_4\text{Cl}[(\text{B}^\Delta_3\text{B}^t_3\text{O}_{10.5})(\text{B}^\Delta\text{O}_{1.5})]_{3\text{D}}$	$\gamma\text{-Li}_4\text{Cl}[\text{B}^\Delta_4\text{B}^t_3\text{O}_{12}]_{3\text{D}}$	$\gamma\text{-Li}_4\text{Cl}[\text{B}_7\text{O}_{12}]$
$\text{Li}_2\text{O}\cdot 2\text{B}_2\text{O}_3$	$\text{Li}_2[(\text{B}^\Delta_2\text{B}^t_2\text{O}_7)]_{3\text{D}}$	$\text{Li}_2[\text{B}^\Delta_2\text{B}^t_2\text{O}_7]_{3\text{D}}$	$\text{Li}_2[\text{B}_4\text{O}_7]$
$\text{M}^{\text{I}}_2\text{O}\cdot\text{B}_2\text{O}_3$ ($\text{M}^{\text{I}} = \text{Na-Cs}$)	$\text{M}^{\text{I}}_3[(\text{B}^\Delta_3\text{O}_6)]$	$\text{M}^{\text{I}}_3[\text{B}^\Delta_3\text{O}_6]$	$\text{M}^{\text{I}}_3[\text{B}_3\text{O}_6]$
$\alpha\text{-Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$	$\alpha\text{-Na}_4[(\text{B}^\Delta_2\text{B}^t\text{O}_{5.5})(\text{B}^\Delta_3\text{B}^t_2\text{O}_{8.5})]_{2\text{D}}$	$\alpha\text{-Na}_4[\text{B}^\Delta_6\text{B}^t_3\text{O}_{15}]_{2\text{D}}$	$\alpha\text{-Na}_4[\text{B}_8\text{O}_{14}]$
$\alpha\text{-Na}_2\text{O}\cdot 3\text{B}_2\text{O}_3$	$\alpha\text{-Na}_6[(\text{B}_2^\Delta\text{B}^t_2\text{O}_7)(\text{B}^\Delta_4\text{B}^t\text{O}_8)]_{2(3\text{D})}$	$\alpha\text{-Na}_6[\text{B}^\Delta_6\text{B}^t_3\text{O}_{15}]_{2(3\text{D})}$	$\alpha\text{-Na}_6[\text{B}_9\text{O}_{15}]_2$
$\beta\text{-Na}_2\text{O}\cdot 3\text{B}_2\text{O}_3$	$\beta\text{-Na}_6[(\text{B}^\Delta_2\text{B}^t\text{O}_5)(\text{B}^\Delta_4\text{B}^t\text{O}_8)(\text{B}^t\text{O}_2)]_{2(2\text{D})}$	$\beta\text{-Na}_6[\text{B}^\Delta_6\text{B}^t_3\text{O}_{15}]_{2(2\text{D})}$	$\beta\text{-Na}_6[\text{B}_9\text{O}_{15}]_2$
$\alpha\text{-Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$	$\alpha\text{-Na}_4[(\text{B}^\Delta_2\text{B}^t\text{O}_5)(\text{B}^\Delta_4\text{B}^t\text{O}_8)]_{2(3\text{D})}$	$\alpha\text{-Na}_4[\text{B}^\Delta_6\text{B}^t_3\text{O}_{15}]_{2(3\text{D})}$	$\alpha\text{-Na}_4[\text{B}_8\text{O}_{13}]_2$
$\text{K}_2\text{O}\cdot 2\text{B}_2\text{O}_3$	$\text{K}_4[(\text{B}^\Delta\text{B}^t_2\text{O}_{5.5})(\text{B}^\Delta_4\text{B}^t\text{O}_8)(\text{B}^\Delta\text{O}_{1.5})]_{3\text{D}}$	$\text{K}_4[\text{B}^\Delta_4\text{B}^t_4\text{O}_{14}]_{3\text{D}}$	$\text{K}_4[\text{B}_8\text{O}_{14}]$
$5\text{K}_2\text{O}\cdot 19\text{B}_2\text{O}_3$	$\text{K}_{2.5}[(\text{B}^\Delta_2\text{B}^t\text{O}_5)(\text{B}^\Delta_4\text{B}^t\text{O}_8)(\text{B}^\Delta\text{O}_{1.5})(\text{B}^t\text{O}_{1.5})]_{3\text{D}}$	$\text{K}_5[\text{B}^\Delta_{14}\text{B}^t_5\text{O}_{31}]_{3\text{D}}$	$\text{K}_5[\text{B}_{19}\text{O}_{31}]$
$\alpha\text{-K}_2\text{O}\cdot 5\text{B}_2\text{O}_3$	$\alpha\text{-K}_2[(\text{B}^\Delta_4\text{B}^t\text{O}_8)]_{2(3\text{D})}$	$\alpha\text{-K}_2[\text{B}^\Delta_4\text{B}^t\text{O}_8]_{2(3\text{D})}$	$\alpha\text{-K}_2[\text{B}_5\text{O}_8]_2$
$\beta\text{-M}^{\text{I}}_2\text{O}\cdot 5\text{B}_2\text{O}_3$ ($\text{M}^{\text{I}} = \text{K, Rb}$)	$\beta\text{-M}^{\text{I}}_2[(\text{B}^\Delta_4\text{B}^t\text{O}_8)]_{2(3\text{D})}$	$\beta\text{-M}^{\text{I}}_2[\text{B}^\Delta_4\text{B}^t\text{O}_8]_{2(3\text{D})}$	$\beta\text{-M}^{\text{I}}_2[\text{B}_5\text{O}_8]_2$
$\text{Cs}_2\text{O}\cdot 3\text{B}_2\text{O}_3$	$\text{Cs}[(\text{B}^\Delta_2\text{B}^t\text{O}_5)]_{3\text{D}}$	$\text{Cs}[\text{B}^\Delta_2\text{B}^t\text{O}_5]_{3\text{D}}$	$\text{Cs}[\text{B}_3\text{O}_5]$
$\text{Cs}_2\text{O}\cdot 9\text{B}_2\text{O}_3$	$\text{Cs}_2[(\text{B}^\Delta_3\text{O}_{4.5})_2(\text{B}^\Delta_2\text{B}^t\text{O}_5)]_{2(3\text{D})}$	$\text{Cs}_2[\text{B}^\Delta_8\text{B}^t\text{O}_{14}]_{2(3\text{D})}$	$\text{Cs}_2[\text{B}_9\text{O}_{14}]_2$
$0.6\text{Ag}_2\text{O}\cdot 0.4\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$	$\text{Ag}_{2.4}\text{Na}_{1.6}[(\text{B}^\Delta_2\text{B}^t\text{O}_5)(\text{B}^\Delta_4\text{B}^t\text{O}_8)]_{2(3\text{D})}$	$\text{Ag}_{2.4}\text{Na}_{1.6}[\text{B}^\Delta_6\text{B}^t_3\text{O}_{15}]_{2(3\text{D})}$	$\text{Ag}_{2.4}\text{Na}_{1.6}[\text{B}_8\text{O}_{13}]_2$
$5\text{M}^{\text{II}}\text{O}\cdot 7\text{B}_2\text{O}_3\cdot \text{M}^{\text{I}}\text{A}^{\text{I}}_2$ —rhomb. and trig. Boracites ($\text{M}^{\text{II}} = \text{Mg, Mn, Zn, Cd, Co, Ni, Cu; A}^{\text{I}} = \text{Cl, NO}_3$)—rhomb. ($\text{M}^{\text{II}} = \text{Mg, Mn, Zn, Fe, Co, Ni, Cu; A}^{\text{I}} = \text{F, Cl}$)—trig.	$\text{M}_3^{\text{II}}\text{A}^{\text{I}}[(\text{B}^\Delta\text{O}_{1.5})_2(\text{B}^t\text{O}_{11.5})]_{3\text{D}}$	$\text{M}_3^{\text{II}}\text{A}^{\text{I}}[\text{B}^\Delta_6\text{B}^t_6\text{O}_{13}]_{3\text{D}}$	$\text{M}_3^{\text{II}}\text{A}^{\text{I}}[\text{B}_7\text{O}_{13}]$
$5\text{M}^{\text{II}}\text{O}\cdot 7\text{B}_2\text{O}_3\cdot \text{M}^{\text{I}}\text{A}^{\text{I}}_2$ —cub. Boracites ($\text{M}^{\text{II}} = \text{Mg, Mn, Fe, Ni, Co, Cu; A}^{\text{I}} = \text{Cl, Br, NO}_3$)	$\text{M}_3^{\text{II}}\text{A}^{\text{I}}[(\text{B}^t_7\text{O}_{13})]_{3\text{D}}$	$\text{M}_3^{\text{II}}\text{A}^{\text{I}}[\text{B}^t_7\text{O}_{13}]_{3\text{D}}$	$\text{M}_3^{\text{II}}\text{A}^{\text{I}}[\text{B}_7\text{O}_{13}]$
$\text{M}^{\text{II}}\text{O}\cdot 2\text{B}_2\text{O}_3$ ($\text{M}^{\text{II}} = \text{Mg, Mn, Zn, Cd}$)	$\text{M}_2^{\text{II}}[(\text{B}^\Delta_2\text{B}^t_2\text{O}_7)]_{2(3\text{D})}$	$\text{M}_2^{\text{II}}[\text{B}^\Delta_2\text{B}^t_2\text{O}_7]_{2(3\text{D})}$	$\text{M}_2^{\text{II}}[\text{B}_4\text{O}_7]_2$
$\text{M}^{\text{II}}\text{O}\cdot \text{B}_2\text{O}_3\text{-I}$ ($\text{M}^{\text{II}} = \text{Ca, Sr}$)	$\text{M}^{\text{II}}[(\text{B}^\Delta_2\text{O}_4)]_{1\text{D}}$	$\text{M}^{\text{II}}[\text{B}^\Delta_2\text{O}_4]_{1\text{D}}$	$\text{M}^{\text{II}}[\text{B}_2\text{O}_4]$
$\text{CaO}\cdot \text{B}_2\text{O}_3\text{-II}$ (calciborate)	$\text{Ca}_2[(\text{B}^\Delta\text{O}_2)_2(\text{B}^t_2\text{O}_4)]_{1\text{D}}$	$\text{Ca}_2[\text{B}^\Delta_2\text{B}^t_2\text{O}_4]_{1\text{D}}$	$\text{Ca}_2[\text{B}_4\text{O}_8]$
$\text{M}^{\text{II}}\text{O}\cdot \text{B}_2\text{O}_3\text{-III}$ ($\text{M}^{\text{II}} = \text{Ca, Sr}$)	$\text{M}_3^{\text{II}}[(\text{B}^\Delta\text{O}_{1.5})(\text{B}^t\text{O}_2)(\text{B}^t\text{O}_2)(\text{B}^t_3\text{O}_6)]_{3\text{D}}$	$\text{M}_3^{\text{II}}[\text{B}^\Delta_2\text{B}^t_4\text{O}_{12}]_{3\text{D}}$	$\text{M}_3^{\text{II}}[(\text{B}_6\text{O}_{12})]$
$\text{M}^{\text{II}}\text{O}\cdot \text{B}_2\text{O}_3\text{-IV}$ ($\text{M}^{\text{II}} = \text{Ca, Sr}$)	$\text{M}_3^{\text{II}}[(\text{B}^t_3\text{O}_6)_2]_{3\text{D}}$	$\text{M}_3^{\text{II}}[(\text{B}^t_3\text{O}_6)_2]_{3\text{D}}$	$\text{M}_3^{\text{II}}[(\text{B}^t_3\text{O}_6)_2]$
$2\text{CaO}\cdot 3\text{B}_2\text{O}_3$	$\text{Ca}_2[(\text{B}^\Delta_2\text{B}^t_2\text{O}_7)_2(\text{B}^t\text{O}_2)]_{3\text{D}}$	$\text{Ca}_2[\text{B}^\Delta_4\text{B}^t_4\text{O}_{11}]_{3\text{D}}$	$\text{Ca}_2[\text{B}_6\text{O}_{11}]$
$\text{CaO}\cdot 2\text{B}_2\text{O}_3\text{-II}$	$\text{Ca}_2[(\text{B}^\Delta_2\text{B}^t\text{O}_5)(\text{B}^\Delta_2\text{B}^t_2\text{O}_7)(\text{B}^t\text{O}_2)]_{3\text{D}}$	$\text{Ca}_2[\text{B}^\Delta_4\text{B}^t_4\text{O}_{14}]_{3\text{D}}$	$\text{Ca}_2[\text{B}_8\text{O}_{14}]$
$\text{M}^{\text{II}}\text{O}\cdot 2\text{B}_2\text{O}_3$ ($\text{M}^{\text{II}} = \text{Sr, Po}$)	$\text{M}^{\text{II}}[(\text{B}^t_4\text{O}_7)]_{3\text{D}}$	$\text{M}^{\text{II}}[\text{B}^t_4\text{O}_7]_{3\text{D}}$	$\text{M}^{\text{II}}[\text{B}_4\text{O}_7]$
$\beta\text{-BaO}\cdot \text{B}_2\text{O}_3$	$\text{Ba}_3[(\text{B}^\Delta_3\text{O}_6)_2]$	$\text{Ba}_3[(\text{B}^\Delta_3\text{O}_6)_2]$	$\text{Ba}_3[(\text{B}_3\text{O}_6)_2]$
$\text{BaO}\cdot 2\text{B}_2\text{O}_3$	$\text{Ba}_2[(\text{B}^\Delta\text{B}^t_2\text{O}_{5.5})(\text{B}^\Delta_3\text{B}^t_2\text{O}_{8.5})]_{3\text{D}}$	$\text{Ba}_2[\text{B}^\Delta_4\text{B}^t_4\text{O}_{14}]_{3\text{D}}$	$\text{Ba}_2[\text{B}_8\text{O}_{14}]$
$\text{BaO}\cdot 4\text{B}_2\text{O}_3$	$\text{Ba}_2[(\text{B}^\Delta_2\text{B}^t\text{O}_5)(\text{B}^\Delta_4\text{B}^t\text{O}_8)]_{2(3\text{D})}$	$\text{Ba}_2[\text{B}^\Delta_6\text{B}^t_3\text{O}_{15}]_{2(3\text{D})}$	$\text{Ba}_2[\text{B}_8\text{O}_{13}]_2$
$4\text{ZnO}\cdot 3\text{B}_2\text{O}_3$	$\text{Zn}_4\text{O}[(\text{B}^t_6\text{O}_{12})]_{3\text{D}}$	$\text{Zn}_4\text{O}[(\text{B}^t_6\text{O}_{12})]_{3\text{D}}$	$\text{Zn}_4\text{O}[\text{B}_6\text{O}_{12}]$
$\text{CuO}\cdot \text{B}_2\text{O}_3$	$\text{Cu}_3[(\text{B}^t_3\text{O}_6)_2]_{3\text{D}}$	$\text{Cu}_3[(\text{B}^t_3\text{O}_6)_2]_{3\text{D}}$	$\text{Cu}_3[(\text{B}_3\text{O}_6)_2]$
$5\text{Al}_2\text{O}_3\cdot \text{B}_2\text{O}_3$	$\text{Al}_2[(\text{Al}^t_3\text{O}_6)(\text{B}^\Delta\text{O}_3)]_{3\text{D}}$	$\text{Al}_2[\text{Al}^t_3\text{B}^\Delta\text{O}_9]_{3\text{D}}$	$\text{Al}_2[\text{Al}_3\text{BO}_9]$
$\text{R}_2\text{O}_3\cdot 3\text{B}_2\text{O}_3$ ($\text{R} = \text{La-Tb}$)	$\text{R}_2[(\text{B}^\Delta_2\text{B}^t_2\text{O}_8)(\text{B}^\Delta\text{O}_2)]_{1\text{D}}$	$\text{R}_2[\text{B}^\Delta_4\text{B}^t_2\text{O}_{12}]_{1\text{D}}$	$\text{R}_2[\text{B}_6\text{O}_{12}]$

M^{I} —monovalent metal; M^{II} —divalent metal.

The anionic motif of metastable $\beta\text{-Na}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ consists of double two-dimensional networks represented by pentaborate ($4\Delta + 1t$), triborate ($2\Delta + 1t$) rings and additional tetrahedra ($1t$) [50], i.e., polyanion composition is $[(\text{B}_4^\Delta\text{B}^t\text{O}_8) + (\text{B}_2^\Delta\text{B}^t\text{O}_5) + (\text{B}^t\text{O}_2)] \times 2 = [\text{B}_6^\Delta\text{B}_3^t\text{O}_{15}]_{2(2\text{D})} = [\text{B}_9\text{O}_{15}]_{2(2\text{D})}$; and structural formula of this borate $\beta\text{-Na}_6[\text{B}_9\text{O}_{15}]_{2(2\text{D})}$. The composition of three-dimensional twinned

α -Na₂O·3B₂O₃ polyanion made up of triborate (4Δ + 1t) and diborate (2Δ + 2t) CSU is the same as that of β-Na₂O·3B₂O₃ [49]: [(B₄^ΔB^tO₈) + (B₂^ΔB₂^tO₇)] × 2 = [B₆^ΔB₃^tO₁₅]_{2(3D)}, and Na-triborate structural formula can be written as β-Na₆[B₉O₁₅]_{2(3D)}. Cs₂O·3B₂O₃ has a simpler formula since its three-dimensional boron-oxygen network consists only of triborate groups (2Δ + 1t) [12] which build polymerized radical [B₂^ΔB^tO₅]_{3D} in structural formula of this compound Cs[B₃O₅]_{3D}.

In the structures of α-Na₂O·4B₂O₃ (and silver borate of similar composition) the binary three-dimensional anionic motif is represented by pentaborate (4Δ + 1t) and tetraborate (2Δ + 2t) CSU [54]. Its polymerized radical [(B₄^ΔB^tO₈) + (B₂^ΔB^tO₅)] × 2 = [B₆^ΔB₂^tO₁₃]_{2(3D)} = [B₈O₁₃]_{2(3D)} having charge four takes place in borate structural formula α-Na₄[B₈O₁₃]_{2(3D)}. General formula, i.e., gross composition of 5K₂O·19B₂O₃ (K₂O·3.8B₂O₃, which has a similar boron content, a three-dimensional polyanion built of triborate (2Δ + 1t), pentaborate (4Δ + 1t) groups, additional tetrahedra (1/2t) and triangles (1Δ) [52] corresponds to K₅[B₁₉O₃₁] containing (B₄^ΔB^tO₈) + (B₂^ΔB^tO₅) + (B_{0.5}^tO) + (B^ΔO_{1.5}) × 2 = [B₇^ΔB_{2.5}^tO_{15.5}] × 2 = [B₁₄^ΔB₅^tO₃₁]_{3D} = [B₁₉O₃₁]_{3D} radical. Structural formulas of all other borates can be derived in a similar way.

7. Classification

Any systematic is usually aimed at finding particular regularities in the system studied, in order to predict a variation of its characteristic features. Classification of numerous borates with their specific structural features is far from a simple matter, but in many respects, it implies the progress of their study. The chemical, crystallochemical and genetic systematics undertaken with the accumulation of factual data reflects a considerable extent of knowledge that had been acquired by the moment of classification. Each subsequent classification is, as a rule, superior to the previous one. The schemes proposed by 1966 were thoroughly and critically discussed in the review [91]. Therefore, there is a sense in dwelling shortly on some of them here.

In [92], by analogy with silicates, the following borate subclasses are described: (1) “nesoborates”, i.e., compounds with isolated BO₃ triangles and BO₄ tetrahedra, (2) “soroborates” (grouped), (3) “inoborates” (chainlike), (4) “phyloborates” (layered) and (5) “tectoborates” (three-dimensional). Its main shortcoming is the absence of a definite regularity in the systematics of isolated boron-oxygen polyanions, including a great number of other structural units. As a result, it was not possible to ascertain the relations between borates belonging to different groups and to include a number of synthetic borates.

The crystallochemical classification of borates suggested in [91] is based on two main characteristics: the structure of boron-oxygen polyanions and the manner in which they are combined. It also takes into account the peculiarities of the borate structures, consisting in a much greater variety of their polyanions, in comparison with silicates, phosphates, etc. In this classification, boron-oxygen isolated polyanions, as well as chainlike, layered, and 3D motifs are examined in detail. In addition, possible ways of combining anions and polyanions are analyzed and their general formulas are derived. All borates are subdivided into four orders (subclasses): insular, chainlike, layered and three-dimensional.

Insular borates are divided into eight suborders: (1) isolated non-ringed with isolated polyions; (1a) non-ringed with dimers of B(O,OH)₃ triangles and B(O,OH)₄ tetrahedra; (2) one-ringed triborates with isolated polyions; (3) two-ringed borates with isolated polyions; (4) three-ringed borates; (5) four-ringed borates; (6) borates with mixed polyions and (7) borosilicates. Three-ringed borates have no representatives, only one four-ringed borate was known, as well as one borosilicate. In all the other borosilicates whose structures were interpreted by that time, B and Si atoms constituted the general motif. In suborders (1), (1a) and (2), the families of oxygen-containing and hydroxyl borates were singled out, but tetra- and pentaborates were fallen into the third suborder.

Chainlike borates have been subdivided into following categories: (1) non-ringed; (2) one-ringed; (3) two-ringed; (4) three-ringed; (5) borates with mixed polyions and (6) borosilicates. For the fourth and the sixth suborders, there were no representatives, and only two borates were fallen into the fifth suborder. In non-ringed chainlike borates, the families of oxygen-containing and hydroxyl

borates (one compound) were identified, and the families of tetra- and pentaborates represent the two-ringed compounds.

Layered and three-dimensional borates are also regarded as having six similar suborders. Three-ringed three-dimensional borates were yet unknown, but non-ringed three-dimensional representatives are divided into oxygen-containing and hydroxyl (only one compound) borates, and the tetra- and pentaborate families are fallen into the two-ringed suborder.

Within most of the suborders and families, the compounds were classified by the basicity of individual polyions (zero-, uni-, di-, tri-, tetra- and pentabasic) in [92].

As distinct from Tennyson' systematic [93], in [91], borates with isolated BO_3 -triangles and BO_4 -tetrahedra are included into the section of insular borates, as well as borates with isolated "mono"-ions and dimers. The classification described in Ref. [91] comprises practically all the borates and many borosilicates known at the time, both with interpreted and hypothetical structures, and reflects the regularities of the polymerization of borates (mainly, hydrated ones). A place was found in it for 119 of the more than six hundreds known by that time anhydrous borates and their polymorphic modifications. All of them were mainly attributed to the section of insular borates, a small part was assigned to three-dimensional and to chainlike compounds, but no comment is made on layered borates. Detailed systematics of boron-oxygen radicals can be considered as a progressive step in understanding the crystal chemistry of this unusual class of inorganic polymer compounds.

Nowadays, the number of anhydrous high-temperature borates with interpreted structures and structural types is several times in comparison with the middle of last century. It is, therefore, quite natural that some of them, mainly those with hypothetical and approximately solved structures, after the interpretation or refinement had to be moved from one section of the classification scheme to another. For this reason, for example, barium metaborate with crystal chemical formula of $\text{Ba}[\text{B}_2\text{O}_4]$, included in the section of chainlike compounds, a year later proved to be insular [48]. Its structural formula should be written out as $\text{Ba}_3[(\text{B}_3\text{O}_6)_2]$. Also, the crystallographic characteristics of $\text{Mg}[\text{B}_2\text{O}_4]$ were unknown before to be assigned to the same order on the strength of the data [92]. should be noted that in a later work [76] the authors doubt whether this compound actually exists. The situation is approximately the same with $2\text{PbO}\cdot\text{B}_2\text{O}_3$ appearing in the same group with B_2O_5 dimers among insular borates [76].

The subsequent refinements and interpretations of crystal structures have also revealed numerous inaccuracies in the classification of 3D borates. For instance, triborates with the general structural formula $M^{1+}[\text{B}_3\text{O}_5]$, where $M^{1+} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$, as well as $\text{Mg}[\text{B}_2\text{O}_5]_2$ have been included in the group of ringed three-dimensional compounds. However, the polyanion in $\beta\text{-NaO}\cdot 3\text{B}_2\text{O}_3$ happened to be a twinned layered one made up of pentaborate ($4\Delta + 1t$), triborate ($2\Delta + 1t$) groups and the additional BO_4 tetrahedra bonding them [50], and therefore its structural formula should be $\beta\text{-Na}_6[\text{B}_9\text{O}_{15}]_{2(2D)}$. The three-dimensional α -modification of $\text{Na}_2\text{O}\cdot 3\text{B}_2\text{O}_3$, also with a 3D twinned polyanion of diborate ($2\Delta + 2t$) and pentaborate ($4\Delta + 1t$) *CSU* [49], can probably be better described by a similar structural formula $\alpha\text{-Na}_6[\text{B}_9\text{O}_{15}]_{2(3D)}$. In K-triborate, cell parameters were determined only by that time [92]. For Li- and Rb- borates, no crystallographic data were known then and $\text{MgO}\cdot 3\text{B}_2\text{O}_3$ has not synthesized yet, in our knowledge. Layered sodium borate with $N = N_M:N_B = 1/2$ and, as established later [11], with the anion of triborate ($2\Delta + 1t$) and diborate ($3\Delta + 2t$) *CSU*, has been placed by the authors of [90] into the section of two-ringed three-dimensional tetraborates with 3D polyanions. However, its more realistic structural formula might be written as $\alpha\text{-Na}_4[\text{B}_8\text{O}_{14}]_{2D}$. By that time, there were no detailed structural data for some other 3D borates: $\text{Li}_2[\text{B}_8\text{O}_{13}]$, $\text{Na}[\text{B}_5\text{O}_8]$, $\text{Cs}_2[\text{B}_4\text{O}_7]$, $\text{Cs}_2[\text{B}_8\text{O}_{13}]$, $\text{Cs}[\text{B}_5\text{O}_8]$ and $\alpha\text{-Cs}_2\text{O}\cdot 5\text{B}_2\text{O}_3$, with exception of their lattice cell parameters [92]. As for $\text{K}_2[\text{B}_8\text{O}_{13}]$, only the structure of a compound with close composition, $5\text{K}_2\text{O}\cdot 19\text{B}_2\text{O}_3$ ($\text{K}_2\text{O}\cdot 3.8\text{B}_2\text{O}_3$) has been solved [52]. Taking into account the X-ray diffraction studies performed later, the crystallochemical formulas of $\text{K}_2[\text{B}_4\text{O}_7]$, $\text{Ca}[\text{B}_4\text{O}_7]$, $\text{K}[\text{B}_5\text{O}_8]$, $\text{Rb}[\text{B}_5\text{O}_8]$, $\text{Na}_2[\text{B}_8\text{O}_{13}]$, $\text{Ag}_2[\text{B}_8\text{O}_{13}]$ and $\text{Ba}_2[\text{B}_8\text{O}_{13}]$ seem to be not so adequate in Ref. [92]. Probably, it would be better to write them as $\text{K}_4[\text{B}_8\text{O}_{14}]_{3D}$, $\text{Ca}_2[\text{B}_8\text{O}_{14}]_{3D}$, α - and β - $\text{K}_2[\text{B}_5\text{O}_8]_{2(3D)}$, β - $\text{Rb}_2[\text{B}_5\text{O}_8]_{2(3D)}$, $\alpha\text{-Na}_4[\text{B}_8\text{O}_{13}]_{3D}$, $\text{Ag}_4[\text{B}_8\text{O}_{13}]_{2(3D)}$, and $\text{Ba}[\text{B}_8\text{O}_{13}]_{2(3D)}$, in correspondence with the

composition of their polyanions. In addition, boracite was regarded as non-ringed, because of the insufficiently accurate interpretation of its structure [94].

Finally, it should be noted that in accordance with [23], the first SrB_4O_7 structure determination by the author of [95] was also incorrect. Namely, based on this example it was assumed possible for the polymerization to take place not only by the combining of the corners of BO_3 -triangles and BO_4 -tetrahedra but also the edges of the tetrahedral [91]. In this connection, it is unlikely that approximately interpreted in [7] layered $\text{Na}_2\text{Zn}_2\text{MnB}_{4.67}\text{O}_{11}$ structure with a very close proximity of triple-charged B^{3+} can be stable.

Another attempt to systematize borates (including organic compounds) was undertaken by G. Heller [96]. It was based on the cation type and the number of boron atoms in the polyanion structural unit. This classification schematically presents the possible polyanions and gives several examples of different structures (many of which later proved to be incorrect) set out in accordance with the number of boron atoms in the basic polyanion structural unit and the type of the anionic radical (isolated, chainlike, layered, three-dimensional). An attempt to encompass numerous anhydrous, hydrated borates and organoboron compounds has made it very cumbersome and led to a number of errors and discrepancies, including representation of the crystallochemical formulas of some compounds.

Christ and Clark [6] have proposed a rational crystallochemical classification of the anions of hydrated borates. The authors have identified the basic polyanion structural units, suggested an abbreviated notation, and the rules of their formation. They have also deduced crystallochemical formulas from the structural data at hand, and the other compounds were combined in a separate group. It was assumed that polymerization could be realized in the following schemes: (1) by the corners of BO_3 -triangles and BO_4 -tetrahedra being combined, (2) by elimination of water from isolated boron groups, (3) by complication of anions into additional groups. The most probable sequence was shown for the addition of protons to the oxygen atoms in hydrous borates.

Therefore, every systematics of borates has made a contribution to the development of the crystallochemistry of this class of compounds. New data on borate crystal structures require further refinement and the revision of existing classifications. This primarily concerns numerous anhydrous compounds the peculiarities of whose structure and crystallization have not been analyzed taking into account the latest data.

The major source of errors in all the systematics is associated with underestimating the regularities of the polymerization of boron oxygen anions. That is why some borates are often prematurely placed into certain sections of the classification schemes. Moreover, this is not surprising since in the course of their study a number of characteristic features previously not taken into account became known. For instance, all crystallochemical systematics did not take into consideration that a part of oxygen atoms in highly condensed 2D and 3D polyanions being cannot be not coordinated not only with two, which is usual, but also with one, three and even four boron atoms. All this, as well as a number of other factors, have introduced substantial uncertainties into the classification of compounds with unknown structures.

In order to avoid such ambiguities, borates with unknown structure should not be included in the crystallochemical systematics. On this way, however, one of the main objectives of classification will not be met, i.e., it will not serve as a basis for theoretical and experimental research, will not favor to forecast structures and properties of new materials. In the case of distribution and redistribution of numerous subsequently studied anhydrous borates among the sections of a latest crystallochemical systematics, similar (with the same cations and having close $M_x\text{O}_y/\text{B}_2\text{O}_3$ ratios) compounds and even borates with analogous structure will be placed into unsuitable for them units. This is because only the structure and composition of the anion (polyanion) were taken into account leaving aside the cation type, size and charge. At times it will be difficult to explain the difference between structures with polyanions of similar composition but with different cations, in order to understand the nature of boron-oxygen radicals polymerization, etc. As a result, it seems impossible to expect a tangible assistance from such systematics on the way of interpretation and refinement of structures, and predicting new compounds.

Ways of searching for a more flexible classification can be based on the general regularities in the structure of this class of borate materials, and on knowledge about the previous systematics of borates and other compounds [97]. Analysis of anhydrous borates structure, composition and conditions shows that there is a sense to examine them separately within the framework of the general classification of borates. In addition, this is because of the specificity of their structures. Thus, e.g., Christ and Clark have shown that in every known hydrated borate structure, in contradistinction to anhydrous borates, there is only one type of the basic structural unit in the anion [6]. The difference between them is clearly illustrated by the comparison of $\text{Ca}_2\text{B}_6\text{O}_{11}$ structures and the $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot x\text{H}_2\text{O}$ series, where $1 \leq x \leq 15$. Isolated or bonded into chains and layers triborate groups of one BO_3 -triangle and two BO_4 -tetrahedra represent anions of all the hydrated Ca borates. In the anhydrous 3D borates, usually regarded as the end member of this series, the paired rings of two BO_3 -triangles and three BO_4 -tetrahedra are bonded into a framework by additional tetrahedra [96]. For this reason G. Christ and J. Clark emphasized the difference in the structure of anhydrous and hydrated borates and suggested the necessity of their independent analysis.

When classifying anhydrous high-temperature borates, therefore, one should bear in mind the set of the following prerequisites, most of which are individually well known:

- (1) In crystal structures each boron atom is bonded with three or with four oxygen atoms in BO_3 -triangles and BO_4 -tetrahedra;
- (2) In one structure not only triangular or only tetrahedral coordination is possible, but both of them jointly as well;
- (3) Isolated BO_3 -triangles and BO_4 -tetrahedra are not found jointly, insular polyanions;
- (4) A decrease in the $N = N_M/N_B$ ratio (N-factor), as well as an increase in cation size (although to a smaller extent), leads to an increase in the degree of polymerization of the anion and raises the $n = n_\Delta/n_t$ number (at $N \leq 1$), whereas an increase in cation charge causes the inverse tendency;
- (5) Polymerization, or the formation of chains, layers and frameworks, is actualizing by the sharing corners of triangles and tetrahedra (the sharing edges has up to now not been proved conclusively);
- (6) In 3D and 2D polyanions (less frequently in chainlike and insular ones), BO_3 -triangles and BO_4 -tetrahedra tend to combine into comparatively compact CSU, i.e., diborate ($2\Delta + 2t$), triborate ($2\Delta + 1t$), pentaborate ($4\Delta + 1t$), boroxol (3Δ), ditriborate ($1\Delta + 2t$), dipentaborate ($3\Delta + 2t$) and other single and double ringed boron-oxygen negative charged polymerized radicals;
- (7) Complex polyanions of anhydrous borates of uni- and divalent metals tend to twinning;
- (8) In most of complex polyanions, each oxygen atom is bonded with two boron atoms, for such compounds as $M_xO \cdot m\text{B}_2\text{O}_3$ with $m > 1$, there is $n = m - 1$ relationship (where $n = n_\Delta/n_t$);
- (9) As an exclusion for 2D and 3D highly condensed polyanions, the coordination numbers of oxygen atoms (relative to boron) can be equal to one or three (in cubic boracite even to four).

The first (primary) classification level, successfully used in inorganic chemistry and mineralogy, is known to be based on the type of the anion-forming element (sulphides, halides, silicates, borates, phosphates, etc.). This reflects the characteristic common features of all classes of compounds, determined by the position of anion forming elements in the Periodic table of the elements. The second order (sublevel) represents the subdivision of classes and is usually also based on the composition of compounds or on their structure. For silicates, e.g., in their overwhelming majority natural and, therefore, of complex composition, in which it is sometimes difficult to identify the predominant cations, the crystallochemical classification reflecting the functional dependence between the composition and the structure of the anion has proved to be the most expedient. This, however, does not mean that this approach should be used for systematics onto the other classes of compounds as well.

When the main cations and the above nine prerequisites are considered together, it becomes possible to move the structural principle onto a higher rank (level) of the classification scheme. It is because the structure of polyanions, the polymerization degree, the ratio of the BO_3 triangles number

to the amount of tetrahedra are determined, to a considerable extent, by the N-factor and the type of cation.

The first level of the systematics of anhydrous borates can be subdivided by the quantitative composition of anions and polyanions into the following sublevels:

- (a) Borates proper (also, there is a sense to divide this very numerous group, having diverse cations, into two subgroups: aI—monocationic or “simple” borates and all-binary and more complex compounds);
- (b) Borosilicates;
- (c) Boroaluminates;
- (d) Boroberyllates;
- (e) Borocarbonates;
- (f) Boromolybdates and borotungstates.

It is reasonable to carry out the next, second, order (sublevel) of classification by the value of cation charge. Then, inside these subdivisions, compounds can be ranked in accordance with their decreasing N factor, indicating its value and structural type, if the structure has been studied. Therefore, the third level is structural. Moreover, finally, the fourth order of this scheme should as far as possible represent the change in the type and size of cations having the same charge. It is also expedient to single out the isostructural and isomorphic series, that especially characteristic for borates with isolated BO_3 -triangles.

An example of the scheme of classification of high-temperature anhydrous borates is given in Tables 5 and 6, where the example of systematics of monocationic mono- and bivalent anhydrous metal compounds is shown. This systematics allows to cover all known anhydrous borate compounds, and to develop an understanding of variations of their properties, limits of stability, as well as the possibility of synthesizing new compounds of these series. Following [98], e.g., $\text{Li}_2\text{O}\cdot 4\text{B}_2\text{O}_3$ borate seems to contain three-dimensional boron-oxygen nets with the ratio of $n \geq 1$. The polyanions in $\text{Na}_2\text{O}\cdot 5\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}\cdot 9\text{B}_2\text{O}_3$ are most probably three-dimensional with n equal to 4 and 8, $\text{K}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ possibly also contains three-dimensional nets of triborate groups with $n = 2$. The structure of polyanions in Rb-borates is close to that in the corresponding potassium compounds. The structures of $\text{Cs}_2\text{O}\cdot 4\text{B}_2\text{O}_3$ and $\text{Cs}_2\text{O}\cdot 5\text{B}_2\text{O}_3$ are evidently also three-dimensional with $n = 3$ and 4.

8. Structural Aspects of Acid-Base Properties

Understanding of growth kinetics and mechanism of borate crystals from melts and fluxed melts is still a problem and leads to deterioration in crystal quality. Thus, it is useful to consider a correlation between the polymerization of anions in the structures of anhydrous borates and their derivatives in order to explain the capability of these inorganic polymers to crystallize.

There were some attempts to estimate acid-base properties for oxide compounds, both solids and melts. The most popular of them is the Lux-Flood's acid-base theory [99]. This concept seems to be more effective for assessment of the acid-base characteristics of anhydrous borates finding of promising solvents for the flux growth of high-temperature borate crystals. According to the Lewis-Lux's equation: $\text{Acid} + \text{O}^{2-} \leftrightarrow \text{Base}$, the acid-base parameters of melts depend on the oxygen activity, thus, $\text{B}_2\text{O}_3 + \text{O}^{2-} = \text{B}_2\text{O}_5^{4-}$, which means that the pyroborate anion (2Δ) has higher oxygen activity in comparison with boron trioxide increasing its base component.

Therefore, the activity of O^{2-} , and, correspondingly, the reactivity of boron-containing melts decreases with an increase in the N_B/N_O ratio, and a tendency to glass formation is observed due to the features of their structure, for which the B–O bond energy is 519 kJ/mol [100]. Since atoms and other particles in such viscous systems move slowly, the glasses obtained by rapid quenching retain pronounced traces of frozen processes.

Table 5. Classification scheme of anhydrous borates.

By the Composition of Anion Formers	By Cation Valency	By Cation Type (and Size)	By the Value of N Factor ($N = N_M/N_B$)						
			$N > 1$	$N = 1$	$n = n_A/n_B = m - 1$, where m —coeff. from $M_xO_mB_2O_3$ *				
					$1 < N \leq 1/2$	$1/2 < N \leq 1/3$	$N < 1/3$		
Borates	Monocationic (simple)	Monovalent	a	Li ↓ Cs	Orthoborates with isolated BO_3 triangles	Metaborates, insular and chainlike **	Polyborates, 3D and seldom - layered	Polyborates, 3D and seldom - layered	Polyborates, 3D
			b	Ag Tl	Same	0	0	0	Same
		Divalent	a	Be ↓ Ba	Same	Pyroborates	Metaborates, insular and chainlike**	Polyborates, 3D	Same
			b	Zn, Cd, Mn, Fe, Co, Ni, Cu, Pb	Same	Same	Metaborates, 3D	Same	Same
		Trivalent	a	Al	Orthoborates with BO_4 tetrahedra	Orthoborates with BO_3 triangles	-	-	-
			b	Sc, Ti, V, Cr, Ga, In	-	Same	-	-	-
			c	Fe	Orthoborates with BO_4 tetrahedra	Same	-	-	-
			d	Y, La-Nd, Sm-Yb	0	Same	-	Metaborates, chainlike	-
			e	Bi	Orthoborates with BO_3 triangles	-	-	0	0
		Tetravalent	Th	-	-	0	-	-	
		Pentavalent	P, As, Ta, Nb	-	Orthoborates with BO_3 triangles	-	-	-	
		1	2	3	4	5	6	7	8
		Borates	Binary and more complex	M^+M^{2+}	Orthoborates with BO_3 triangles	-	-	-	-
				M^+M^{3+}	Same	0	0	-	-
				M^+M^{5+}	Same	Pyroborates	-	-	-
$M^{2+}M^{2+}$	-			Same	-	-	-		
$M^{2+}M^{3+}$	Orthoborates with BO_3 triangles and BO_4 tetrahedra			-	Metaborates, layered (t)	Metaborates, layered ($\Delta + t$)	-		
$M^{2+}M^{4+}$	-			Orthoborates with BO_3 triangles	-	-	-		
$M^{3+}M^{3+}$	-			Orthoborates with BO_3 triangles	Metaborates with B tetrahedrons	-	-		
Boron silicates	$M^{2+}M^{3+}, M^{3+}, M^{2+}$	Orthocompounds	Metacompounds, chainlike	-	-	Polycompounds, 3D			
Boron aluminates	M^{2+}, M^{3+}	-	Same	Polycompounds, layered and 3D	-	-			
Boron beryllates	M^+	-	-	Polycompounds, layered	Polycompounds, layered and 3D	-			
Boron carbonates	$M^{2+}M^{3+}$	Orthocompounds	-	-	-	-			
Boron molybdates and boron tungstates	M M^{3+}	-	-	Metacompounds, chainlike	-	-			

* Simple mono- and divalent metal borates having polyanions with coordination number of oxygen atoms with respect to boron are equal to two obey this rule. ** 3D γ - $LiBO_2$, Ca and Sr metaborates obtained at high pressure are an exception. Note: Symbols “-” and “0” indicate that this compound is unknown (“-”) or it is known but its structure was not solved (“0”).

Table 6. Classification of mono- and divalent metal borates.

I. Borates of Monovalent Elements									
	N	Cations							
		Li	Na (Ag)	K	Rb	Cs	Tl		
Orthoborates (with isolated B triangles)	5	-	0	-	-	-	-	-	-
	3	α -Li ₃ [BO ₃] β from - 0	0	-	-	-	-	-	Tl ₃ [BO ₃]
	5/2	-	0	-	-	-	-	-	-
	2	-	0	-	-	-	-	-	-
	3/2	0	0	-	-	-	-	-	-
Fluoroborates (with isol. BF ₄ tetr.)	1	-	Na[BF ₄]	K[BF ₄]	Rb[BF ₄]	Cs[BF ₄]	Tl[BF ₄]		
Metaborates (ins. with boroxol gr.) *	1	α -Li ₂ [B ₂ O ₄] _{1D} γ -Li[BO ₂] _{3D}	α -Na ₃ [B ₃ O ₆] β phase - 0	K ₃ [B ₃ O ₆]	α from - 0	Cs ₃ [B ₃ O ₆]			0
Polyborates (skeletal, sometimes compounds, layered with diborate - D, triborate - T, pentaborate - P, boroxol - B, ditriborate - DT, dipentaborate - DP rings and additional B triangles and tetrahedrons; $n = n_{\Delta}/n_t = m - 1$)	2/3	-	0	-	-	-	-	-	-
	4/7	α and β Cl, Br and I "boracites" - 0 γ -Li ₄ Cl[B ₇ O ₁₂] _{3D}	-	-	-	-	-	-	-
	1/2	Li ₄ [B ₄ O ₇] _{2(3D)} 2(D)	(α)-Na ₄ [B ₈ O ₁₄] _{2D} ** (T+DP) β and γ phase - 0	K ₄ [B ₈ O ₁₄] _{3D}	0	0	0	0	0
	2/5	0	0	-	-	-	-	-	-
	1/3	0	α -Na ₆ [B ₉ O ₁₅] _{2(3D)} 2(D + P) β -Na ₆ [B ₉ O ₁₅] _{2(2D)} 2(P + T + t) γ -form - 0	0	0	0	Cs ₃ [B ₃ O ₅] _(3D) (T)	0	0
	5/19	-	-	K ₅ [B ₁₉ O ₃₁] _{3D}	-	-	-	-	-
	1/4	0	α -(Na,Ag) ₄ [B ₈ O ₁₃] _{2(3D)} 2(T + P) β modification - 0	0	0	0	0	0	0
	1/5	-	α , β and γ phases - 0	α -K ₂ [B ₅ O ₈] _{2(3D)} 2(P) β -K ₂ [B ₅ O ₈] _{2(3D)} 2(P), γ phase - 0	α phase - 0 β -Rb ₂ [B ₅ O ₈] _{2(3D)} 2(P)	α , β , γ phases - 0	0	0	0
	1/9	0	α , β , and γ phases - 0	0	0	0	Cs ₂ [B ₉ O ₁₄] _{2(3D)} 2(B + T) β phase	-	-
II. Borates with Cations of Transition Metals									
	N	Cations							
		Zn	Cd	Mn	Fe	Co	Ni	Cu	Pb
Orthoborates (with isolated BO ₃ triangles)	3	-	-	Wiserite Mn ₃ [BO ₃] ₃ F ₃	-	-	-	-	-
	2	-	-	Mn ₂ [BO ₃] ₂ F	-	-	-	-	0 (α and β forms)
	3/2	α -Zn ₃ [BO ₃] ₂	0 (α and β forms)	Jimboite Mn ₃ [BO ₃] ₂	-	0	Ni ₃ [BO ₃] ₂	0	-
	5/4	0 (α and β forms)	-	-	-	-	-	-	-
Pyroborates (with isol.2)	1	-	Cd ₂ [B ₂ O ₅]	Mn ₂ [B ₂ O ₅]	Fe ₂ [B ₂ O ₅]	Co ₂ [B ₂ O ₅]	0	-	0 (α and β forms)
Metaborates (skeletal)	1/2	0 (α and β forms) Zn ₄ O[B ₆ O ₁₂] [*] (t)	-	0	0	0	0	Cu ₃ [(B ₃ O ₆) ₂] (t)	0
Polyborates (skeletal)	3/7	cub., rhomb. and trig. F, Cl, Br, I and NO ₃ "boracites"	Cl, Br, I and NO ₃ "boracites"	cub., rhomb. and trig. F, Cl, Br, I and NO ₃ "boracites"	cub. and trig. F, Cl, Br, I and NO ₃ "boracites"	cub., rhomb. and trig. F, Cl, Br, I and NO ₃ "boracites"	cub. and rhomb. Cl, Br, I and NO ₃ "boracites"	cub. and rhomb. Cl, Br, I and NO ₃ "boracites"	-
	1/3	-	0	-	-	-	-	-	-
	1/4	Zn ₂ [B ₄ O ₇] ₂	Cd ₂ [B ₄ O ₇] ₂	Mn ₂ [B ₄ O ₇] ₂	-	-	-	-	Pb[B ₄ O ₇] (t)
	1/6	0	-	0	-	-	-	-	-

* 3D γ -LiBO₂ obtained at high pressure is an exception. ** By its $n = 5/3$ number is an exception; in a part of O atoms coordination number with respect to boron is equal to 1.

Taking into consideration the above borate classification and the Lux-Flood's concept, it is intuitively obvious that the simplest way to assess quantitatively acid-base properties of the anhydrous borates is to estimate the dependence of polymerization of anions in the borate structures on the sizes and valences of cations, and also on the N-factor (Figure 9). From the crystallochemical point of view, it can be seen that the increase of the N-factor increases the anion polymerization and the N_B/N_O ratio. This leads to a decrease in the oxygen activity factor and simultaneously to an increase in the acid component of these compounds. Also, the value of $n = n_{\Delta}/n_t$, i.e., the ratio of the number of BO_3 -triangles to BO_4 -tetrahedra in the structures of compounds increases.

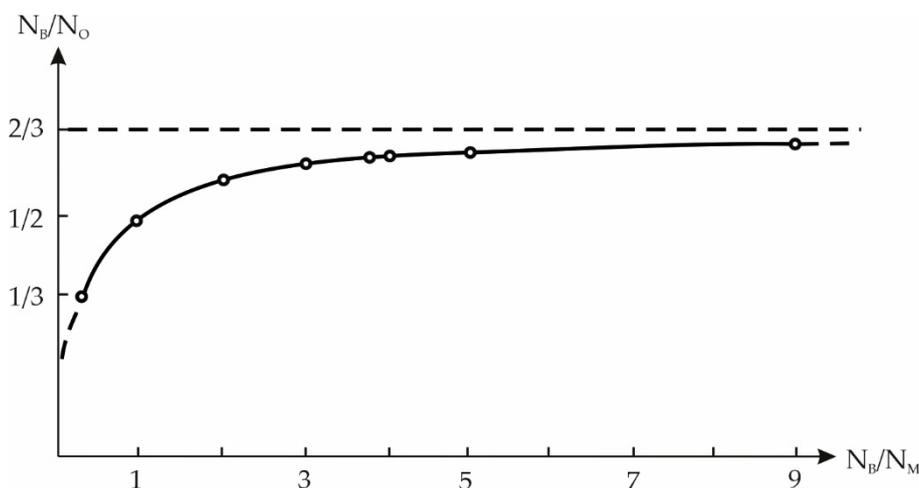


Figure 9. Dependence of anion polymerization (N_B/N_O , i.e., ratio of metal atoms number to the ratio of boron atoms number, referred to as N-factor) on N_B/N_M in anhydrous alkali borate metal structures.

9. Summary

This review is an alternative approach by the authors to present the structural aspects of high-temperature anhydrous borates in the way of synthesis and growth of crystals of new technologically attractive materials from this numerous family of borates. They can be described by only three types according to the level of complexity of structural units: (1) BO_3 -triangles (Δ) and BO_4 -tetrahedra (t) as fundamental (elementary) structural units (*FSU*) constituting the anions of all borates (only triangles, only tetrahedra or both the triangles and tetrahedra); (2) the second level of structural units is represented by combined basic units (*CSU*) which usually built up of several *FSU* (from 2 to 5) joined by sharing common O atoms occurring in many structures; (3) the third type of borate structural units corresponds to complete radicals of polyanions (*CRP*) which constructed of 2–9 *FSU*, i.e., with a composition equal or aliquot to the anionic portions of the compound structural formulas. With a decrease in the $N = N_M/N_B$ ratio, i.e., N-factor, as well as with an increase in the cation size (though to a smaller extent), the anion polymerization degree and the $n = n_{\Delta}/n_t$ number (at $N < 1$) regularly increase. An increase in the cation charge causes the reverse tendency. It facilitates the attenuation of the polycondensation of BO_3 -triangles BO_4 -tetrahedra. In borates with highly charged cations, the boron atoms prefer tetrahedral coordination. Highly charged cations are, however, capable to form around themselves rigid coordination polyhedra, usually making up the basis of the structure. Stability of the boron-oxygen anion here loses its decisive importance. This encourages the formation of borate structures with isolated both BO_3 -triangles and BO_4 -tetrahedra having comparatively large charges, -3 and -5 respectively. Tendency to polymerization and, therefore, to more acidic properties makes it possible to forecast new phase systems for the synthesis of predicted borate structures. A new approach to borates classification is proposed, and an improved systematics of anhydrous compounds has been performed. The place of a borate in this scheme, including those with an unsolved structure, characterizes to a certain extent its structure and properties.

Author Contributions: Conceptualization, N.I.L. and V.V.M.; validation, N.I.L., V.V.M. and E.A.V.; formal analysis, N.I.L.; writing—original draft preparation, N.I.L. and E.A.V.; project administration, N.I.L.; funding acquisition, N.I.L. Every author contributed to this overview. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Russian Science Foundation, grant number 19-12-00235.

Conflicts of Interest: The authors declare no conflicts of interests.

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