Review

Crystal Chemistry of High-temperature Borates

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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– and BO4– 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 BO3– triangles (Δ) and BO4– 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., BO3– triangles and BO4– 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 2.3 Å, and in the edges of tetrahedral they are 2.43 Å [1,5] (Figure 2).

![Figure 2](image)

*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) 3∆, 2) 2∆ + 2t, 3) 2∆ + 1t and 4) 4∆ + 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 K$_2$O·2B$_2$O$_3$ [14] and layered α-Na$_2$O·2B$_2$O$_3$ [11], were single and double 1∆ + 2t and 3∆ + 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 K$_2$O·2B$_2$O$_3$ structure represents configurationally a strongly deformed diborate group.

In borates of divalent metals, namely CaB$_2$O$_4$, 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$_2$O$_4$ (III) [21], SrB$_2$O$_4$ [22], SrB$_2$O$_7$ and PbB$_2$O$_7$ [23] structures. The same rings, but without additional FSU were discovered in framework CaB$_2$O$_4$ (IV) [24]. Less widespread are quadruple (SrB$_2$O$_7$ and PbB$_2$O$_7$ [23]), sextuple (Zn$_2$O$_3$B$_2$O$_7$ [25]) and octuple (CuB$_2$O$_4$ [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) K₃(B₂O₆) [9]; (b) Li₂O·2B₂O₃ [10]; (c) Na₂O·2B₂O₃ [11,12]; (d) K₂O·5B₂O₅ [13]; (e) K₂O·2B₂O₅ [14]; (f) α-Na₂O·2B₂O₃ [11]; (g) Sr₂B₂O₅ [19]; (h) boracites [20]; (i) SrB₂O₅ [23]; (j) Zn₄O(BO₂)₆ [25]; (k) CuB₂O₅ [26]; (l) R(BO₂)₃ (R = La – Tb) [27]

In the borates of trivalent metals, CSU differing from the others have also been found, e.g., quaternary rings of two BO₃-triangles and two BO₄-tetrahedra in corrugated metachains of rare earth borates, R(BO₃)₃ with R = La – Tb [27] (Figure 3). In such chain, every BO₄ 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 BO₄ tetrahedra represent the anionic part of the structure of low-temperature GdB₂O₅ and its rare earth analogues. Borate with tetravalent cations are represented by ThB₂O₅ and ThB₂O₆ compounds. Thorium diborate, ThB₂O₅, exhibits α- and β- polymorphs. In the structure of β-ThB₂O₅ two corner sharing BO₃ triangles are linked forming an isolated B₂O₅ dimer [29]. Whereas, in the structure of α-modification boron atoms occupy corner sharing BO₄-tetrahedra and BO₃-triangles forming 1D zigzag chain [30]. ThB₂O₅ structure exhibits infinite chains, which consist of [B₂O₅]²⁻ tetrahedral borate groups that are connected through one common oxygen atom [31]. Monocationic borates of pentavalent elements have only isolated BO₄ 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 RCo(BO$_2$)$_5$ with R = La – Ho, Na$_2$ZnMnB$_{4.67}$O$_{11.5}$ and RAl$_2$B$_{10.5}$O$_{11}$ with R = La – Nd [33–37], one can identify sextuple, quadruple and binary three-membered rings (Figure 4b–f).

![Diagram](image1)

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

In the R-aluminum metaborates synthetized 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 Al$_2$BO$_5$O$_5$ = Al$_2$Al$_2$O$_7$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, boroaluminates 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 Y$_2$AlBeBO$_7$ [44]. In the first case, double (2tAl + 2tB) 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 [Al$_3$B$_7$O$_{16}$]$_{1D}$ composition in SrAlBO$_4$, where (2tAl + 1tB) rings can be identified, is similar to the metaborate chain in calciborite - [B$_2$O$_6$]$_{1D}$, 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) Be$_2$(BO$_3$)$_2$F, KBe$_2$(BO$_3$)$_2$ [40]; (b) and (c) Li$_3$AlBO$_6$ [41]; (d) SrAlBO$_4$ [43]; (e) stillwellite [45]; (f) danburite [46].

2.3. Complete Radicals of Polyaiions

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$_2$O$_4$ modifications [16,17,21], SrB$_2$O$_4$, CaB$_2$O$_4$, Ba$_2$B$_2$O$_7$, BaO-2B$_2$O$_3$, BaO-4B$_2$O$_3$ [23,47,48] (Figures 6–8) and in some others. A peculiar CRP is found in aluminum orthotriborate, A1$_2$(BO$_3$)$_2$O$_6$ [39] or, to be more precise, in aluminum-alumoborate A1$_2$(AlO$_2$)$_2$BO$_5$.

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. 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) $\alpha$-Na$_2$B$_8$O$_{13}$ [51]; (b) $\alpha$-Na$_2$O·3B$_2$O$_3$ [49]; (c) $\beta$-Na$_2$O·3B$_2$O$_3$ [50]; (d) $\alpha$-Na$_2$B$_8$O$_{13}$ [51]; (e) K$_2$O·2B$_2$O$_5$ [14]; (f) 5K$_2$O·19B$_2$O$_3$ [52]; (g) Cs$_2$O·9B$_2$O$_3$ [53]; (i) $\alpha$-Na$_2$O·4B$_2$O$_3$ [54].
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) CaB₂O₄ (II) [16]; (d) CaB₂O₄ (III) [21]; (e) CaB₂O₄ [57]; (f) CaB₂O₄ [58]; (g) SrO·2B₂O₃ [23]; (h) BaO·2B₂O₃ [47]; (i) BaO·4B₂O₃ [48]; (j) R(BO₃)₃ [27]; (k) johachidalite, CaAl₂(BO₃)₃ [34]; (l) RAl-metaborates (R = Ce-Nd) [35].
Figure 8. CRP in boroberyllates, boroaluminates 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) CaAl(BO$_3$)$_2$:O [59]; (b) 2SrO-Al$_2$O$_3$:B$_2$O$_3$ [43]; (c) 3LiO-Al$_2$O$_3$:2B$_2$O$_3$ [60]; (d) Al(BO$_3$)$_2$:O$_3$ [39].

3. Polymerization of Boron-oxygen Radicals

Polymerization degree of BO$_m$ anions can be defined by the ratio of $N = N_{BOO}/N_B$ (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 $N' = N_{MOO}/N_{BOO}$ 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 ofboron-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 $\alpha$-LiBO$_3$ [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$_2$O:2B$_2$O$_3$ [10]. In Na borates isolated groups of $3\Delta$ at $N = 1$ in Na$_3$(B$_2$O$_5$) [8] transform into two-dimensional nets of dipentaborate or triborate clusters with $n = n_{BOO} = 5/3$ ($N = 1/2$) in Na$_2$O:2B$_2$O$_3$ [11]. Then one can observed 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$_3$-tetrabora in the stable high-temperature form for $N = 1/3$ in $\alpha$-Na$_3$O:3B$_2$O$_5$ and $\beta$-Na$_3$O:3B$_2$O$_5$ [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 $3\Delta$ ($N = 1$) in K$_3$B$_2$O$_5$ [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$_2$O:2B$_2$O$_3$ [14]; b) of penta- triborate rings, additional BO$_3$-triangles and BO$_3$-tetrabora with $n = 14/5$ at $N = 5/19$ in 5K$_2$O:19B$_2$O$_5$ [52]; or c) of pentaborate CSU with $n = 4$ ($N = 1/5$) in K$_2$O:5B$_2$O$_3$ [13]. In rubidium and cesium borates isolated rings of $3\Delta$ ($N = 1$) transform into a three-dimensional framework of triborate clusters with $n = 2$ ($N = 1/3$) in Cs$_2$O:3B$_2$O$_5$ [12], then into twinned two-dimensional network of triborate and boroxol rings with $n = 8$ ($N = 1/9$) [64]. In the Ag-tetraborate AgO:4B$_2$O$_3$ the polyanion structure is similar to potassium one [65].

No isolated BO$_3$ groups have been found in monovalent metal borates. Isolated BF$_4$ tetrahexa are known only in the structures of fluoroborates NaBF$_4$ and NH$_4$BF$_4$ with $N = 1$ [66,67]. The maximal fraction of BO$_3$-tetrahexa ($n = 1$) is found in the framework lithium (Li$_2$O:2B$_2$O$_3$) and potassium (K$_2$O:2B$_2$O$_3$) borate structures with $N = 1/2$ but $1/n = 3/5$ [10,14], and in cesium borate Cs$_2$O:3B$_2$O$_5$ 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$_3$-tetrabora, 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., $N_{BOO}/N_{BOO} \geq 3$), only isolated BO$_3$-triangles are observed in the structures of monocationic and binary compounds. In pyroborates ($N = 1$), including binary $M^2$:$M'_{BOO}$ compounds, anions are represented by isolated BO$_3$ pyrogroups. Metaborate anions ($N = 1/2$) are more condensed: a) infinite metachains of BO$_3$-triangles (CaBO$_3$:I) [17], b) cyclic groups of three triangles bonded at common corners (BaO:3B$_2$O$_5$ [68], c) ring-shaped three-membered rings of BO$_3$-tetrabora in CuB$_2$O$_5$ [26]. Thus, in divalent metal metaborates besides BO$_3$-triangles, BO$_3$-tetrabora 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
SrB₄O₇ and PbB₂O₇ in which the three-dimensional anionic framework consists only of BO₃–tetrahedra [23]. In the three-dimensional boron-oxygen net of BaB₆O₁₃ (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 ≥ 1, only isolated BO₃–triangles (or isolated BO₃–tetrahedra in Fe₂BO₆ [69] and sinhalite MgAlBO₃ [70]) have been found. In simple R borates (N = 1/3), the polyanions are chain-like with n = 2. Simultaneously, in binary borates of tri- and divalent metals, for example, johachidolite CaAlB₂O₉ [34], synthetic RCo(BO₃)₅ [71] and RAl₃B₄O₁₃ [35] the polyanions are represented by layers of BO₃–tetrahedra or BO₃–tetrahedra together with BO₃–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 (Mg,Fe)Al₃SiBO₉ [72] (N = 2), the anion consists of isolated BO₃–triangles and SiO₄–tetrahedra, but in stillwellite LaBSiO₄ (N = 1/2), it is represented by BO₃–metachain encrusted with discrete SiO₄–tetrahedra [45]. In danburite Ca₃B₄SiO₉ (N = 1/4) a silicon-boron-oxygen framework of SiO₄– and B₂O₅–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 Ba₂Y₆(Si₄B₂O₁₁)F₂ [73]), whereas borosilicates enriched with silicon are quite numerous. The shortage of adequately interpreted structures for borooxaluminates (with the exception of synthetic Al₉(BO₃)O₆ [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 K₂B₂O₇ [63] is smaller than in sodium compound Na₂(B₂O₆) [8]. However, in lithium analogue Li₂BO₂ [62], the ring already becomes energetically disadvantageous orates. 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 BO₃–triangles and BO₃–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 BO₃–triangles are commonly widespread, but BO₃–tetrahedra with an even higher negative charge (–5) as well.
4. Polymorphism of $\text{Bo}_m$ 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 $\text{Bo}_4$-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           | $[\text{Bo}^n\text{O}_6] = [\text{BoO}_6]$ | $\alpha$-$\text{Na}_2\text{O} \cdot \text{BoO}_3$ |
|                          | $[\text{Bo}^n\text{O}_4] = [\text{BoO}_4]$ | K$_2$O-$\text{BoO}_3$ |
|                          |                                             | Rb$_2$O-$\text{BoO}_3$ |
| Chain (one-dimensional, 1D) | $[(\text{Bo}^n\text{O}_2)\text{Bo}^n\text{O}_2]_1 = [\text{BoO}_{12}]_1$ | Cs$_2$O-$\text{BoO}_3$ |
|                          |                                             | $\beta$-$\text{BaO} \cdot \text{BoO}_3$ |
|                          |                                             | $\alpha$-$\text{Li}_2\text{O} \cdot \text{BoO}_3$ |
|                          |                                             | CaO-$\text{BoO}_3$ (I) |
|                          |                                             | SrO-$\text{BoO}_3$ (I) |
|                          |                                             | $\text{Ln}_2\text{O}_3 \cdot 3\text{BoO}_3$ (exc. Mo, W) |
|                          |                                             | $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{BoO}_3$ |
|                          |                                             | $25\text{SrO} \cdot \text{Bo} \cdot \text{Al}_2\text{O}_3$ |
|                          |                                             | Stillwellite $\text{CeO}_3 \cdot \text{BoO}_3 \cdot 2\text{SiO}_2$ |
|                          |                                             | $\text{LaO}_3 \cdot \text{BoO}_3 \cdot 2\text{MoO}_3$ |
|                          |                                             | $\text{LaO}_3 \cdot \text{BoO}_3 \cdot 2\text{WO}_3$ |
| Layer (two-dimensional, 2D) | $[(\text{Bo}^n\text{O}_2)\text{Bo}^n\text{O}_2]_2 = [\text{BoO}_{20}]_2$ | $\text{Ltt}_2\text{O}_3 \cdot 2\text{CoO} \cdot 5\text{BoO}_3$ (exc. La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) |
|                          |                                             | $\gamma$-$\text{Li}_2\text{O} \cdot \text{BoO}_3$ |
|                          |                                             | $\text{CaO} \cdot \text{BoO}_3$ (II) |
|                          |                                             | SrO-$\text{BoO}_3$ (II) |
| Framework (three-dimensional, 3D) | $[\text{Bo}^n\text{O}_3]_1 = [\text{BoO}_3]_1$ | $\text{CuO} \cdot \text{BoO}_3$ |
|                          |                                             | $4\text{ZnO} \cdot 3\text{BoO}_3$ |
|                          |                                             | $\text{CaO} \cdot \text{BoO}_3$ (III) |
|                          |                                             | SrO-$\text{BoO}_3$ (III) |
|                          |                                             | $\text{Danburite} = \text{CaO} \cdot \text{BoO}_3 \cdot 2\text{SiO}_2$ |

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 $\gamma$-$\text{LiBO}_3$ 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., $\text{CaB}_2\text{O}_4$ (I), B and Ca atoms have triangular and eightfold coordination, respectively [17]. With the transition of this modification into $\text{CaB}_2\text{O}_4$ (II) synthesized at 12–15 kbar, half of the boron atoms increase their coordination number to four [16]. In $\text{CaB}_2\text{O}_4$ (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 $\text{CaB}_2\text{O}_4$ (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 [B₄O₇]₄⁻ polyanions (n = 1 and 2) is their high degree of polymerization. Only one of them, α-Na₂O·2B₂O₃ is layered, in all others representatives were found 3D anionic motifs (Table 2). In all borates having [B₄O₇]₄⁻ radicals, with the exception of α-Na₂O·2B₂O₃, SrO·2B₂O₃ and PbO·2B₂O₃, the anions contain equal amounts of triangular and tetrahedral boron-oxygen coordination. The ratio of n: n = 5/3 in α-Na₂O·2B₂O₃ is accompanied by part of BO₃ triangles being the corners unshared with other FSU, and in the exclusively tetrahedral frameworks of SrO·2B₂O₃ and PbO·2B₂O₃ part of oxygen atoms is coordinated with three boron atoms [23].

Table 2. Polyanions with [B₄O₇]₄⁻ and [B₄O₇]₄⁻ radicals.

| Type of polyanion | Composition of B₄O₇ based polyanion | Compound |
|------------------|------------------------------------|----------|
|_layers (two-dimensional, 2D) | [(B₂²B'O₃₃)(B₂²B'O₃₃)]₂D = [B₄O₄]₂D | α-Na₂O·2B₂O₃ |
| | | Li₂O·2B₂O₃ |
| | | Mg₂O·2B₂O₃ |
| | | Mn₂O·2B₂O₃ |
| Frameworks (three-dimensional, 3D) | [(B₂²B'O₃₃)(B₂²B'O₃₃)]₂D = [B₄O₄]₂D | Zn₂O·2B₂O₃ |
| | | CdO·2B₂O₃ |
| | | K₂O·2B₂O₃ |
| | | Ca₂O·2B₂O₃ |
| | | Sr₂O·2B₂O₃ |
| | | Pb₂O·2B₂O₃ |
| | | Ba₂O·2B₂O₃ |

The 3D polyanion of [B₄O₇]₄⁻ composition in borates with comparatively small cations is made up of 2Δ + 2t diborate groups only. For larger M⁺ 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 K₂O·2B₂O₃. In Ca₂O·3B₂O₃ diborate 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 B₂O₅ and B₂O₆, 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 simplicity, predominance of BO₃–triangles over BO₄–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 [B₂O₅]⁺ and [B₂O₆]⁺ radicals.

| Radical | Type of Polyanion | Composition B₂O₅ and B₂O₆ Based Polyanions | Compound |
|---------|------------------|--------------------------------------------|----------|
| B₂O₅    | Layers (two-dimensional, 2D) | [(B₂²B'O₅)(B₂²B'O₅)(B'O₅)]₃D = [B₄O₅]₃D | β'-Na₂O·3B₂O₅ |
|         | Frameworks (three-dimensional, 3D) | [(B₂²B'O₅)(B₂²B'O₅)]₃D = [B₄O₅]₃D | α'-Na₂O·3B₂O₅ |
|         | | [B₂²B'O₅]₃D = [B₄O₅]₃D | Cs₂O·3B₂O₅ |
| B₂O₆    | Frameworks (three-dimensional, 3D) | [(B₂²B'O₆)(B₂²B'O₆)]₃D = [B₄O₆]₃D | α'-Na₂O·4B₂O₆ |
|         | | [(B₂²B'O₆)(B₂²B'O₆)]₃D = [B₄O₆]₃D | 0.6AgO·0.4Na₂O·4B₂O₆ |
|         | | [B₂²B'O₆]₃D = [B₄O₆]₃D | BaO·4B₂O₆ |
5. Isostructural Series

Isostructural series are widely encountered among high-temperature borates. Two dozen borates $M^2^+M^3^+[BO_3]O_6$ 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 $M^3^+$ cations.

Isostructural with respect to one another are numerous borates of the ludwigite-vonsenite group, $M^2^+Fe^4+[BO_3]O_6$, 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$^{2+}$ 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 nordskoldid $CaSn[BO_3]_2$ [80] which is isostructural to dolomite. More than fifty compounds compose the boracite group [56], with six minerals among them: boracite, stassfurtite, gauseinite, 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 $MBO_3$, where $M = Mg$, Mn, Zn, Cd; $MBO_3$ with $M = Mg$, Mn, Fe, Co, Cd; and $MBO_3$ ($M = Na, K, Rb, Cs$) in which the size of cations differs considerably.

Structural peculiarities of rare-earths 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 $ca$ 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 $R(BO_3)_3$ metabolates, 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 $RCO(BO_3)_2$ metabolates.

Double orthoborates of the $R$Sr$(BO_3)_3$, $R$Ba$(BO_3)_3$ and $R$Ca$(BO_3)_3$ families are already isostructural with one another, although in some compounds the intensities of X-ray reflection do not coincide [84].

In $RM$(BO$\_3$)$_3$ ($M = Al, Ga, Sc, Fe, Cr$) 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, $RO_\_3$-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$(BO_3)_3$ compound, the symmetry of MO$\_6$-octahedron is increased, with some increase in the size of RO$\_3$-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$(BO_3)_3$. 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$(BO_3)_3$, and ScFe$(BO_3)_3$ 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 BO₆-triangles and BO₄-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 Li₂O·2B₂O₅ consists of 2t + 2t diborate groups [10] its chemical composition can be written out as [(B₂O₅)₂]³⁺ or in the abbreviated form as [B₂O₅]²⁻. The negative charge of one such radical is equal to two. The structural formula will, therefore, have the form of Li₂[B₂O₅]³⁻. In contradistinction to Li₂[B₂O₅]⁴, 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 Mg₂[B₂O₅]²⁻[54]. In the α-Na₂O·2B₂O₅ structure, the two-dimensional polyanionic net consists of dipentaborate and triborate CSU, with the latter each containing a free O atom [11]. Polyation composition of this sodium borate can be written as (B₂B₂O₅) + (B₂B₂O₅) = [B₂B₂O₅]²⁻ = [B₂O₅]²⁻; its negative charge is equal to four, and borate structural formula will be represented in the form of α-Na₂[B₂O₅]⁴⁻. In K₂O·2B₂O₅, the composition of three-dimensional polyanionic network, consisting of (2Δ + 2t) diborate and (1Δ + 2t) triborate groups with additional BO₆ triangles (1Δ) [14], is (B₂B₂O₅) + (B₂B₂O₅) + (B₂O₅) = [B₂B₂O₅]³⁻ = [B₂O₅]³⁻. The charge of this polyradical is four, the borate structural formula can be look like K₄[B₂O₅]⁴⁻.

The anionic motif of metastable β-Na₂O·3B₂O₅ consists of double two-dimensional networks represented by pentaborate (4Δ + 1t), triborate (2Δ + 1t) rings and additional tetrahedra (1t) [50], i.e., polyanion composition is [(B₂B₂O₅) + (B₂B₂O₅) + (B₂O₅)] × 2 = [B₂B₂O₅]²⁻[54]; and structural formula of this borate β-Na₂[B₂O₅]²⁻[54]. The composition of three-dimensional twinned α-Na₂O·3B₂O₅ polyanion made up of triborate (4Δ + 1t) and diborate (2Δ + 2t) CSU is the same as that of β-Na₂O·3B₂O₅[49]; [(B₂B₂O₅) + (B₂B₂O₅)] × 2 = [B₂B₂O₅]²⁻[54], and Na₂-triborate structural formula can be written as β-Na₂[B₂O₅]²⁻[54]. Cs₂O·3B₂O₅ has a simpler formula since its three-dimensional boron-oxygen network consists only of triborate groups (2Δ + 1t) [12] which build polymerized radical [B₂B₂O₅]₃⁻ in structural formula of this compound Cs[B₂O₅]₃⁻.

In the structures of α-Na₂O·4B₂O₅ (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 [(B₂B₂O₅) + (B₂B₂O₅)] × 2 = [B₂B₂O₅]²⁻[54] = [B₂O₅]²⁻ having charge four takes place in borate structural formula α-Na₂[B₂O₅]³⁻[54]. General formula, i.e., gross composition of 5K₂O·19B₂O₅ (K₂O:3.88B₂O₅, 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[B₂O₅] containing (B₂B₂O₅) + (B₂B₂O₅) + (B₂O₅) + (B₂O₅) + (B₂O₅) × 2 = [B₂B₂O₅]²⁻[54] × 2 = [B₂B₂O₅]³⁻ = [B₂O₅]³⁻ radical. Structural formulas of all other borates can be derived in a similar way.
### Table 4. Structural formulas of monocationic polyborates.

| Formula in Oxides (Bulk Composition) | Structural Formula | Abbreviated |
|--------------------------------------|--------------------|-------------|
| α-Li₃O·2B₂O₃ | α-Li[B₄O₁₀] | α-Li[B₄O₁₀] |
| γ-Li₂O·B₂O₃ | γ-Li[B₂O₃] | γ-Li[B₂O₃] |
| γ·3Li₂O·7B₂O₅·2LiCl | γ-LiCl[(B₄B₄O₁₃)(B₄B₄O₁₃)] | γ-LiCl[B₄B₄O₁₃] | γ-LiCl[B₄O₁₃] |
| Li₂O·2B₂O₃ | Li₂[B₂B₄O₁₀] | Li₂[B₂B₄O₁₀] |
| MₓO·B₂O₃ (M¹ = Na·Cs) | Mₓ[(B₄B₄O₁₃)] | Mₓ[B₄O₁₃] |
| α-Na₂O·2B₂O₃ | α-Na[B₂B₄O₁₀] | α-Na[B₂B₄O₁₀] |
| α·Na·O·3B₂O₃ | α·Na[(B₄B₄O₁₃)(B₄B₄O₁₃)] | α·Na[B₂B₄O₁₀] |
| β·Na·O·3B₂O₃ | β·Na[B₂B₄O₁₀] | β·Na[B₂B₄O₁₀] |
| α·Na·O·4B₂O₃ | α·Na[B₂B₄O₁₀] | α·Na[B₂B₄O₁₀] |
| Kₓ·O·2B₂O₃ | Kₓ[B₂B₄O₁₀] | Kₓ[B₂B₄O₁₀] |
| 5Kₓ·O·19B₂O₃ | 5Kₓ[B₂B₄O₁₀] | 5Kₓ[B₂B₄O₁₀] |
| α·Kₓ·O·5B₂O₃ | α·Kₓ[B₂B₄O₁₀] | α·Kₓ[B₂B₄O₁₀] |
| β·Mₓ·O·5B₂O₃ (M¹ = K, Rb) | β·Mₓ[B₂B₄O₁₀] | β·Mₓ[B₂B₄O₁₀] |
| CsO·3B₂O₃ | Cs[B₂B₄O₁₀] | Cs[B₂B₄O₁₀] |
| Cs·O·9B₂O₃ | Cs[B₂B₄O₁₀] | Cs[B₂B₄O₁₀] |
| 0.6AgO·0.4NaO·4B₂O₃ | Ag₂·Na₄[(B₄B₄O₁₀)(B₄B₄O₁₀)] | Ag₂·Na₄[B₂B₄O₁₀] |

5MₓO·7B₂O₅·Mₓ·A₁ — rhomb. and trig. boracites (M¹ = Mg, Mn, Zn, Cd, Co, Ni, Cu; A¹ = Cl, NO₃)—— rhomb. (M¹ = Mg, Mn, Zn, Fe, Co, Ni, Cu; A¹ = F, Cl) — trig. (M¹ = Mg, Mn, Zn, Cd) — cub. boracites (M¹ = Mg, Mn, Fe, Ni, Co, Cu; A¹ = Cl, Br, NO₃)

| Formula in Oxides (Bulk Composition) | Structural Formula | Abbreviated |
|--------------------------------------|--------------------|-------------|
| 5MₓO·7B₂O₅·Mₓ·A₁ | 5MₓA₁[(B₄B₄O₁₀)] | 5MₓA₁[B₂B₄O₁₀] |
| MₓO·2B₂O₃ | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] |
| MₓO·2B₂O₃ | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] |
| MₓO·2B₂O₃ | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] |
| MₓO·2B₂O₃ | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] |
| MₓO·2B₂O₃ | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] |
| MₓO·2B₂O₃ | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] |
| MₓO·2B₂O₃ | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] |
| MₓO·2B₂O₃ | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] | MₓA₁[B₂B₄O₁₀] |
| Compound                  | Structure Description                                                                 | Formula     |
|--------------------------|----------------------------------------------------------------------------------------|-------------|
| 2CaO·3B₂O₅               | Ca₂[(B₂B₃O₈)(B₂O₂)]₃D                                                                 | Ca₂[B₂B₃O₈]₃D|
| CaO·2B₂O₅+II             | Ca₂[(B₂B₃O₈)(B₂B₅O₇)(B₂O₂)]₃D                                                           | Ca₂[B₂B₅O₇]₃D|
| M⁺⁺O₂B₂O₅ (M⁺⁺ = Sr, Po) | M⁺⁺[(B₂O₇)]₃D                                                                          | M⁺⁺[B₂O₇]₃D|
| β-BaO·B₂O₅               | Ba₂[(B₂O₈)]₃D                                                                          | Ba₂[B₂O₈]   |
| BaO·2B₂O₅                | Ba₂[(B₂B₃O₈)(B₂B₅O₇)]₃D                                                                | Ba₂[B₂B₅O₇]₃D|
| BaO·4B₂O₅                | Ba₂[(B₂B₃O₈)(B₄B₂O₈)]₂D                                                                | Ba₂[B₄B₂O₈]₂D|
| 4ZnO·3B₂O₅               | Zn₄O[(B₄O₁₂)]₃D                                                                        | Zn₄O[B₄O₁₂]₃D|
| CuO·B₂O₅                 | Cu₃[(B₂O₇)]₃D                                                                          | Cu₃[B₂O₇]   |
| 5Al₂O·B₂O₅               | Al₂[(Al₂B₃O₈)]₃D                                                                        | Al₂[Al₂B₃O₈]₃D|
| R₂O·3B₂O₅ (R = La-Tb)    | R₂[(B₂B₃O₈)(B₂O₂)]₂D                                                                    | R₂[B₂B₃O₈]₂D|

M⁺ — monovalent metal; M⁺⁺ — divalent metal
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 polyanions; (1a) non-ringed with dimers of B(O,OH)₃ triangles and B(O,OH)₄ tetrahedra; (2) one-ringed triborates with isolated polyanions; (3) two-ringed borates with isolated polyanions; (4) three-ringed borates; (5) four-ringed borates; (6) borates with mixed polyanions 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 polyanions 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 polyanions (zero-, uni-, di-, tri-, tetra- and pentabasic) in [92].

As distinct from Tennyson’ systematic [93], in [91], borates with isolated BO₃-triangles and BO₄-tetrahedra are included into the section of insular borates, as well as borates with isolated “mono”-ions and dimmers. 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 Ba[B₆O₁₅]₂, included in the section of chainlike compounds, a year later proved to be insular [48]. Its structural formula should be written out as Ba{[(B₂O₇)₂]. Also, the crystallographic characteristics of Mg[B₄O₇] 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 2PbO·B₃O₅ appearing in the same group with B₃O₅ 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⁺[B₃O₆], where M⁺ = Li, Na, K, Rb, as well as Mg[B₄O₇]: have been included in the group of ringed three-dimensional compounds. However, the polyanion in β-NaO₃B₃O₆ happened to be a twinned layered one made up of pentaborate (4A + 1t), triborate (2A + 1t) groups and the additional BO₃ tetrahedra bonding them [50], and therefore its structural formula should be β-Na₂[B₄O₁₃]₃[20]. The three-dimensional α-modification of Na₃O·3B₂O₅ also with a 3D twinned polyanion of diborate (2A + 2t) and pentaborate (4A + 1t) CSU [49], can probably be better described by a similar structural formula α-Na₃[BO₆]₃[20]. In K₂triborate, cell parameters were determined only by that time [92]. For Li- and Rb- borates, no crystallographic data were known then and MgO·3B₂O₅ has been synthesized yet, in our knowledge. Layered sodium borate with N = Na₃:Na = 1/2 and, as established later [11], with the anion of triborate (2A + 1t) and diborate (3A + 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 α-Na₂[BO₆]₃[20]. By that time, there were no detailed structural data for some other 3D borates: Li₂[B₄O₆], Na[B₄O₆], Cs₂[B₄O₆], Cs₂[B₄O₆]₃, Cs[B₄O₆] and α-Cs₂O·5B₂O₅ with exception of their lattice cell parameters [92]. As for K₂[B₄O₆], only the structure of a compound with close composition, 5K₂O·19B₂O₅ (K₂O·3.8B₂O₅) has been solved [52]. Taking into account the X-ray diffraction studies performed later, the crystallochemical formulas of K₂[B₄O₆], Ca[B₄O₆], K[B₄O₆], Rb[B₄O₆], Na₂[B₄O₆], Ag₂[B₄O₆] and Ba₂[B₄O₆] seem to be not so adequate in Ref. [92]. Probably, it would be better to write them as K₂[B₄O₆]₃[20], Ca₂[B₄O₆]₃[20], α- and β-K₂[B₄O₆]₃[20], β-Rb₂[B₄O₆]₃[20], α-Na₂[B₄O₆]₃[20], Ag₂[B₄O₆]₃[20], and Ba₂[B₄O₆]₃[20], in correspondence with the composition of their polyanions. In all cases, 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 SrB₄O₇ 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 BO₃-triangles and BO₃-tetrahedra but also the edges of the tetrahedral [91]. In this connection, it is unlikely that approximately interpreted in [7] layered Na₂ZnMnB₄O₁₃ structure with a very close proximity of triple-charged B³⁺ 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 BO₄-triangles and BO₆-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 M₂O₆/B₂O₃ 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 Ca₂B₂O₇ structures and the Ca₂B₂O₉·xH₂O series, where 1 ≤ x ≤ 15. Isolated or bonded into chains and layers triborate groups of one BO₄-triangle and two BO₆-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 BO₄-triangles and three BO₆-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:
In crystal structures each boron atom is bonded with three or with four oxygen atoms in $\text{BO}_3$–triangles and $\text{BO}_4$–tetrahedra;

in one structure not only triangular or only tetrahedral coordination is possible, but both of them jointly as well;

isolated $\text{BO}_3$–triangles and $\text{BO}_4$–tetrahedra are not found jointly, insular polyanions;

a decrease in the $N = N_0/N_s$ 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 $n = n_s/n$ number (at $N \leq 1$), whereas an increase in cation charge causes the inverse tendency;

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);

in 3D and 2D polyanions (less frequently in chainlike and insular ones), $\text{BO}_3$–triangles and $\text{BO}_4$–tetrahedra tend to combine into comparatively compact CSU, i.e., diborate $(2\Delta + 2t)$, triborate $(2\Delta + 1t)$, pentaborate $(4\Delta + 1t)$, boroxol $(3\Delta)$, ditriborate $(1\Delta + 2t)$, dipentaborate $(3\Delta + 2t)$ and other single and double ringed boron-oxygen negative charged polymerized radicals;

complex polyanions of anhydrous borates of uni- and divalent metals tend to twinning;

in most of complex polyanions, each oxygen atom is bonded with two boron atoms, for such compounds as $M\text{O}_m\text{B}_2\text{O}_3$ with $m > 1$, there is $n = m - 1$ relationship (where $n = n_s/n$);

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 $\text{BO}_3$–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 BO₃-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 bivalve 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., Li₂O·4B₂O₅ borate seems to contain three-dimensional boron-oxygen nets with the ratio of n ≥ 1. The polyanions in Na₂O·5B₂O₅ and Na₂O·9B₂O₅ are most probably three-dimensional with n equal to 4 and 8, K₂O·3B₂O₅ 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 Cs₂O·4B₂O₅ and Cs₂O·5B₂O₅ 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: Acid + O²⁻ ↔ Base, the acid-base parameters of melts depend on the oxygen activity, thus, B₂O₅ + O²⁻ = B₂O₅⁺, which means that the pyroborate anion (2Δ) has higher oxygen activity in comparison with boron trioxide increasing its base component.

Therefore, the activity of O²⁻, and, correspondingly, the reactivity of boron-containing melts decreases with an increase in the Nₘ/Nₒ 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.

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 see that the increase of the N-factor increases the anion polymerization and the Nₘ/Nₒ 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 = nₛ/nᵢ, i.e., the ratio of the number of BO₃–triangles to BO₃–tetrahedra in the structures of compounds increases.
## 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 = Na/Na) |
|-------------------------------------|-----------------|--------------------------|-------------------------------------|
|                                     |                 |                          | 1 < N ≤ 1/2 | 1/2 < N ≤ 1/3 | N < 1/3 |
| Monovalent                          | a               | Li                       | Orthoborates with isolated BO$_3$ triangles | Metaborates, insular and chainlike ** | Polyborates, 3D and seldom - layered | Polyborates, 3D | Polyborates, 3D |
|                                     | b               | Ag                       | Same        | 0              | 0             | 0             | Same |
| Divalent                            | a               | Be                       | Same        | Pyroborates    | Metaborates, insular and chainlike ** | Polyborates, 3D | Same |
|                                     | b               | Zn, Cd, Mn, Fe, Co, Ni, Cu, Pb | Same        | Same           | Metaborates, 3D | Same | Same |
| Borates (simple)                    |                 |                           | Orthoborates with BO$_4$ tetrahedra | Orthoborates with BO$_3$ triangles | - | - | - |
|                                     | a               | Al                       | -           | Same           | -             | -             | - |
|                                     | b               | Sc, Ti, V, Cr, Ga, In    | Same        | -              | -             | -             | - |
| Trivalent                           | 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                       | -           | -              | -             | -             | - |
### Pentavalent Molecules

| Pentavalent | Orthoborates with BO₃ triangles | Orthocompounds | Metacompounds, chainlike | Polycompounds, 3D |
|-------------|---------------------------------|----------------|--------------------------|------------------|
| P, As, Ta, Nb | - | - | - | - |

### Borates

#### Binary and more complex

| Borates | Orthoborates with BO₃ triangles | Metaborates, layered (t) | Metaborates, layered (A + t) |
|---------|---------------------------------|--------------------------|-----------------------------|
| M⁺M²⁺ | - | - | - |

#### M²⁺M₃⁺

| M²⁺M₃⁺ | Orthoborates with BO₃ triangles and BO₄ tetrahedra | Metaborates with B tetrahedrons | - |
|---------|---------------------------------|--------------------------|-----------------------------|

### Boron silicates

| Boron silicates | Orthocompounds | Metacompounds, chainlike | Polycompounds, layered and 3D |
|-----------------|----------------|--------------------------|-----------------------------|
| M²⁺M₄⁺, M₅⁺, M₆⁺ | - | - | - |

### Boron aluminates

| Boron aluminates | Orthocompounds | Metacompounds, chainlike | Polycompounds, layered and 3D |
|-----------------|----------------|--------------------------|-----------------------------|
| M⁺, M³⁺ | - | - | - |

### Boron beryllates

| Boron beryllates | Orthocompounds | Metacompounds, chainlike | Polycompounds, layered and 3D |
|-----------------|----------------|--------------------------|-----------------------------|
| M⁺ | - | - | - |

### Boron carbonates

| Boron carbonates | Orthocompounds | Metacompounds, chainlike | Polycompounds, layered and 3D |
|-----------------|----------------|--------------------------|-----------------------------|
| M²⁺M₅⁺ | - | - | - |

### Boron molybdates and boron tungstate

| Boron molybdates and boron tungstate | Orthocompounds | Metacompounds, chainlike | Polycompounds, layered and 3D |
|-------------------------------------|----------------|--------------------------|-----------------------------|
| M⁺ | - | - | - |

* 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-LiBO₂, 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 | Cations |
|-----------------------------------|---------|
| Orthoborates (with isolated B triangles) | |
| N | Li | Na (Ag) | K | Rb | Cs | Tl |
| 5 | α-Li[BO$_3$] | | | | | |
| 3 | β from 0 | 0 | - | - | - | |
| 5/2 | - | 0 | - | - | - | |
| 2 | - | 0 | - | - | - | |
| 3/2 | 0 | 0 | - | - | - | |
| Fluoroborates (with isol. BF$_4$ tetr.) | |
| N | Li | Na[BF$_4$] | K[BF$_4$] | Rb[BF$_4$] | Cs[BF$_4$] | Tl[BF$_4$] |
| 1 | α-Li[BO$_3$]$_{10}$ | α-Na[BO$_3$]$_{10}$ | K$_n$[BO$_3$]$_{10}$ | α from -0 | Cs$_n$[BO$_3$]$_{10}$ | 0 |
| 2/3 | | | | | | |
| 4/7 | | | | | | |
| 1/2 | Li$_m$[BO$_3$]$_{10}$2(D) | (α)-Na$_m$[BO$_3$]$_{10}$ | K$_n$[BO$_3$]$_{10}$ | 0 | 0 | 0 |
| 2/5 | | | | | | |
| 1/3 | 0 | 0 | 0 | | | |
| 5/19 | | | | | | |
| 1/4 | | | | | | |
| 1/5 | | | | | | |
| 1/9 | | | | | | |
### II. Borates with Cations of Transition Metals

| N   | Zn | Cd | Mn   | Fe | Co | Ni   | Cu | Pb |
|-----|----|----|------|----|----|------|----|----|
| 3/2 | α-Zn[BO$_3$]$_2$ | 0 (α and β forms) | Mn$_2$[BO$_3$]F | -  | -  | -    | -  | -  |
| 5/4 | 0 (α and β forms) | -  | -    | Mn$_2$[BO$_3$]F | 0  | -  | -    | -  | -  |
| 1   | 0 (α and β forms) | Cd$_2$[BO$_3$] | Mn$_3$[BO$_3$]F | 0  | -  | 0    | -  | -  |
| 1/2 | 0 (α and β forms) | Zn$_4$O[B$_6$O$_{12}$] | Mn$_2$[BO$_3$]F | 0  | -  | 0    | -  | -  |
| 3/7 | cub., rhomb. and trig. F, Cl, Br, I and NO$_3$ | cub., rhomb. and trig. F, Cl, Br, I and NO$_3$ | cub., rhomb. and trig. F, Cl, Br, I and NO$_3$ | cub., rhomb. and trig. F, Cl, Br, I and NO$_3$ | cub., rhomb. and trig. F, Cl, Br, I and NO$_3$ | cub. and rhomb. Cl, Br, I and NO$_3$ | Cu$_3$[B$_4$O$_7$]$_2$ | -  |
| 1/3 | -  | Cl, Br, I and NO$_3$ | “boracites” | 0  | -  | -    | -  | -  |
| 1/4 | Zn$_2$[BO$_3$]$_2$ | cub., rhomb. and trig. F, Cl, Br, I and NO$_3$ | “boracites” | Mn$_2$[BO$_3$]F | -  | -  | -    | -  | Pb[BO$_3$] |
| 1/6 | 0  | -  | -    | -  | -  | -    | -  | -  |

* 3D γ-LiBO$_2$ 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.
Figure 9. Dependence of anion polymerization \((N_b/N_o, \text{i.e., ratio of metal atoms number to the ratio of boron atoms number, referred to as N-factor})\) on \(N_b/N_m\) in anhydrous alkali borate metal structures.

9. Conclusions

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) \(\text{BO}_3\)-triangles (\(\Delta\)) and \(\text{BO}_4\)-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 \(2\text{–}9\) 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 \(\text{BO}_3\)-triangles \(\text{BO}_4\)-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 \(\text{BO}_3\)-triangles and \(\text{BO}_4\)-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.

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