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Crystal chemistry of borates: the classification and algebraic description by topological type of fundamental building blocks

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The structural characteristics of all the borates available were analyzed using the Inorganic Crystal Structure Database. The fundamental building blocks (FBBs) in 841 borates were systematically classified into 6 types in terms of their topological structures. By including the polymerization of the FBBs in the borate structure, a novel systematic classification and an algebraic description of borates have been proposed. The current systematic borate classification, in which all the identical FBBs can be classified into the same type, is more reasonable and provides new insight into the structural differences between various borates. The current, simpler, algebraic description is more extensive and can reflect more of the structural information of borates. This thus provides an impetus for elucidating the topological features of borates. Our work also provides much useful information on the design and search for novel borates, which is also helpful to classify newly synthesized borates and to strengthen the understanding of the overall scope of borate structures.

1. Introduction

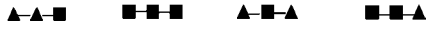
A systematic classification of topologically unique compounds, which is often relevant to their nomenclature, provides a useful insight into the structural relationships between different compounds. Classification studies of polymer molecules (Tezuka & Oike, 2001), zirconosilicates (Ilyushin & Blatov, 2002), protein compounds (Fukunishi *et al.*, 2006), nickel hydroxide (Ramesh *et al.*, 2006), orthosilicates (Ilyushin *et al.*, 2002) and so on have been successfully carried out in recent years. Structurally speaking, the topology of a compound often forms the basis on which their properties and functions can be controlled in both static and dynamic states, either in bulk or in the solution phase (Gan *et al.*, 2000). In the last few decades, borates have developed into an important field in mineralogical and industrial applications. A series of new crystalline borates has been developed (Becker, 1998), with excellent second-harmonic generation (SHG) properties. New borate compounds can be generated from a great diversity of borate crystal structures. The 70-year history of borate structure determinations has illustrated the unique chemistry of borates, characterized by the following distinguishing features (Becker, 2001; Filatov & Bubnova, 2000; Touboul *et al.*, 2003):

(i) In borate crystal structures, the B atoms can have both threefold [Bφ_3] and fourfold [Bφ_4] coordinations to oxygen or hydroxyl groups ($\varphi = O^{2-}$, OH^-), boron–oxygen bonds are of much higher bond-valence (≥ 0.7 v.u., where v.u. = valence unit) than the interstitial cation–oxygen bonds (≤ 0.3 v.u.).

(ii) Both Bϕ_3 triangles (Δ) and Bϕ_4 tetrahedra (T) can be connected to each other *via* common corners (O atoms; not

Table 1
Topological structures of branched FBBs.

A planar description of branched FBBs with the number of both Bφ_3 (filled triangle) and Bφ_4 (filled square) ranging from 2 to 5. The corresponding configuration of each topological structure is given in the supplementary data (see Fig. S3).

No. of B atoms	Topological structure†
2	
3	
4	
5	

† B—φ—B bonds are shown as a single line connecting two B atoms, following Burns *et al.* (1995).

via faces but a few *via* edges; Huppertz & von der Eltz, 2002) of the coordination polyhedra to form rigid boron–oxygen groups. These groups represent the anionic repeating units of the borate structures, which are known as fundamental building blocks (FBBs; Christ & Clark, 1977; Burns *et al.*, 1995; Burns, 1995).

(iii) FBBs can polymerize into complex borate polyanions such as those with infinite chains, layers and network anions.

Therefore, borates are more than suitable for a hierarchical classification on the basis of their structural units. In particular, the fundamental topology theory of FBBs has been an interesting subject for investigation. However, to the best of our knowledge, up until now there have only been a few attempts at a topological description (Christ & Clark, 1977; Heller, 1986; Burns *et al.*, 1995; Touboul *et al.*, 1984; Touboul *et al.*, 2003) and the systematic classification (Xie, 1964; Strunz, 1997; Grice *et al.*, 1999) of borates, and most of them still have some disadvantages. For example, in these classifications borates with identical FBBs that are connected differently are unfortunately classified into different types. On the other hand, much work has been done to synthesize new borates (Wu *et al.*, 2006; Ewald *et al.*, 2006; Wen *et al.*, 2006) and to search for the structure–property realtionships of borates (Xue & Zhang, 1998; Klimin *et al.*, 2005; Yu & Xue, 2006). Therefore, it is desirable to propose a new systematic borate classification and to rectify those descriptions available.

Burns *et al.* (1995) derived finite clusters of the form $B_n\varphi_m$ ($3 \leq n \leq 6$) which were topologically and metrically possible. However, many of these clusters cannot actually be found in borate crystal structures; some clusters were even proven to be unstable or unlikely to exist (Burns, 1995). Actually, the FBBs with the lowest energy are those which are available in known borate structures (Becker, 2001). Therefore, we used the Inorganic Crystal Structure Database (ICSD, 2004) as our data source and structurally analyzed all the borates available (except some multi-anion compounds in which the boron anions are not dominant). In the current work, around 100 types of FBBs in 841 borates were found and classified into six types according to their topological structures. Furthermore, we proposed a new systematic borate classification and employed it to classify all the borates available. In our proposed classification, all the identical FBBs will occur together and the linkages between FBBs will simply be an additional distinction. On the other hand, a new algebraic description was also introduced to describe a variety of topologically unique FBB architectures. A comparison with other available descriptions indicates that our simpler algebraic description can provide more structural information on borates.

2. Topological structure of FBBs in borates and their application in borate classification

2.1. Topological types of the structure of FBBs

It is necessary here to introduce the general principle for extracting the FBB from a borate. The FBB, by definition, should be the simplest unit that can reflect the basic structural information of an assigned crystallographic frame (see the example in the supplementary material, Fig. S1[1]). The linkages between FBBs can create an assigned crystallographic frame with whole borate polyanions as the repeating unit (Christ & Clark, 1977; Burns *et al.*, 1995; Burns, 1995; Becker, 2001). In this regard, one borate can only contain one FBB, but several different borates may have the same FBB. All cations have been omitted to analyze the borate structures in the current work (more details are given in the supplementary material). On the basis of this treatment, a statistical analysis of different borate FBBs was carried out to survey the variety of FBBs in borate crystal structures. The results show that there are *ca* 100 types of FBBs in all 841 borates. Based on the topological similarity of different FBB structures, we proposed that these FBBs can be classified into six types: single Bφ_3 or Bφ_4, branched FBBs, normal-ring FBBs, bridge-ring FBBs, '8'-shaped-ring FBBs and combined-ring FBBs.

(i) Single Bφ_3 or Bφ_4 FBBs: there are numerous borates whose structures are formed from only a single Bφ_3 and a few from a single Bφ_4, as listed in Table S1 of the supplementary material.

(ii) Branched FBBs: the characteristic typical of these FBBs is their branched (but not ringed) appearance, as shown in Table 1.

(iii) Normal-ring FBBs: some typical normal-ring FBBs of borates were selected and their topological structures are shown in Table 2 (type 1). In type 2 these groups, in which a

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS5036). Services for accessing these data are described at the back of the journal.

Table 2
Selected topological structures of normal-ring FBBs.

Some typical topologies of normal-ring FBBs are shown here as examples. The corresponding configuration of each topological structure is given in the supplementary data (see Fig. S4).

Normal-ring FBB	Topological structure
Type 1†	
Type 2‡	
Type 3§	

† A normal-ring consisting of $B\varphi_3$ and (or) $B\varphi_4$ polyhedra. ‡ A linear combination of a normal-ring FBBs with one or more BO_3 (or BO_4) polyhedra. § A linear combination of several normal-ring FBBs.

normal-ring FBB has a linear combination with one or more BO_3 (or BO_4) polyhedra, still belong to normal-ring FBB. Type 3 gives the topologies of a linear combination of several normal-ring FBBs. The linear combination means that two groups connect together *via* one O atom, as illustrated in Fig. 1(*a*).

(iv) Bridge-ring FBBs: when two normal-ring FBBs share two borate tetrahedra, a bridge-ring FBB forms (Fig. 1*c*). Some bridge-ring FBBs and their relevant topological constructions are given in Table 3. Among them, type 1 exhibits typical bridge-ring-shaped constructions; a FBB with type 2 structures is called a double-bridge-ring FBB because of the two oxygen bridges traversing the 6-normal-ring. In addition, a particular structure is found only in hydrated borates (type 3), which can be called a 6-bridge-ring FBB because of six oxygen bridges across a 12-normal-ring FBB. In type 4 structures, one central O atom is simultaneously bonded to three B atoms, like a large bridge traversing the 6-normal-ring FBB. Therefore, these homothetic structures of type 4 can be classified as bridge-ring FBBs and called the big-bridge-ring FBBs.

(v) '8'-shaped-ring FBBs: when two normal-ring FBBs share one borate tetrahedron in the center, the '8'-shaped-ring FBB forms (Fig. 1*b*). As shown in Table 4 (Type 1), typical FBBs have an obvious '8'-shaped appearance. Similarly, when three normal-rings share two borate tetrahedra, a double-'8'-shaped-ring forms, which is considered to be another type of '8'-shaped-ring FBB (Type 2). In addition, a linear combination of several '8'-shaped-ring FBBs can also be treated as a kind of '8'-shaped-ring FBB (Type 3).

(vi) Combined-ring FBBs: when a normal-ring FBB has a linear combination with a bridge-ring FBB, the structure formed is considered to be a combined-ring FBB. Similarly, the groups in which two or more different types of ring connect together by O atoms, are also regarded as a combined-ring FBB (such as Type 1 in Table 5). Furthermore, there is another type of combined-ring FBB as shown in Table 5 (Type 2). In this type of FBB a normal-ring FBB (or bridge-ring or '8'-shaped-ring FBBs), as a unit, takes part in the formation of another new ring. These FBBs exist in several hydrated borates.

There are various FBBs in hundreds of borates. However, any FBB can be classified into the current six types of FBB. For the purposes of analyzing and classifying each FBB (especially complex FBB) more easily, it is necessary to introduce some useful rules.

Rule 1: The group in which a normal-ring FBB has a linear combination with one or more $B\varphi_3$ (or $B\varphi_4$), still belongs to normal-ring FBBs (such as Type 2 in Table 2). The assignment of bridge-ring and '8'-shaped-ring FBBs obeys the same rule.

Rule 2: The group consisting of several linear combinatorial normal-ring FBBs still belongs to normal-ring FBBs. The same rule is applicable to bridge-ring and '8'-shaped ring FBBs (such as Type 3 in Table 4).

Rule 3: The group which consists of more than one kind of linear combinatorial ring (*e.g.* a normal-ring FBB having a

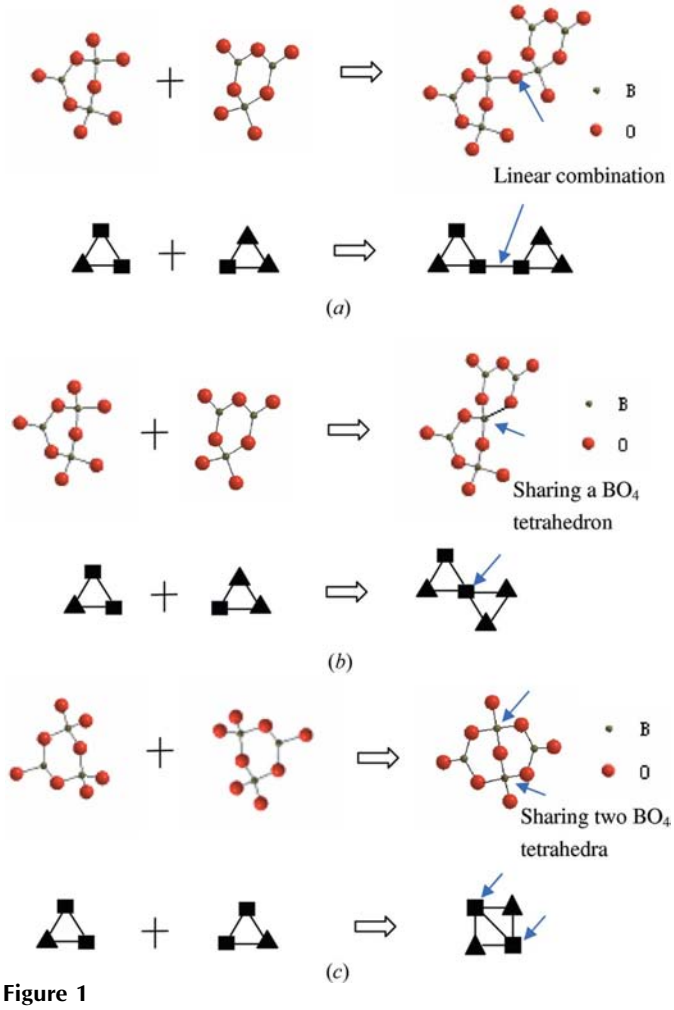


Figure 1
Some different linkages in borate structures and their corresponding topologies: (*a*) two normal-ring FBBs connected by an O atom, which is the so-called 'linear combination'; (*b*) two normal-ring FBBs connected by a borate tetrahedron, which form an '8'-shaped-ring FBB; (*c*) two normal-ring FBBs connected by two borate tetrahedra, which form a bridge-ring FBB.

Table 3
Selected topological structures of bridge-ring FBBs.

Some typical topologies of bridge-ring FBBs are shown here as examples. The corresponding configuration of each topological structure is given in the supplementary data (see Fig. S5).

Bridge-ring FBB	Topological structure
Type 1†	
Type 2‡	
Type 3§	
Type 4¶	

† Typical bridge-ring, bridge-ring FBBs with branches, and a linear combination of bridge-ring FBBs. ‡ Double-bridge-ring FBB and a linear combination of a double-bridge-ring FBB with one or more BO_3 (or BO_4) polyhedra. § 6-bridge-ring FBB. ¶ Big-bridge-ring FBB and a linear combination of a big-bridge-ring FBB with one or more BO_3 (or BO_4) polyhedra.

linear combination with a bridge-ring FBB *etc.*), belongs to the combined-ring FBBs.

According to these rules it is easy to determine the assigned complex FBB. Take the case of $Pb_6B_{10}O_{21}$ (ICSD 2641) as an example. It has a complex FBB, as shown in Fig. 2(*a*), in which there are two bridge-ring FBBs and two BO_3 units (these four units connect together by O atoms). The FBB of $Pb_6B_{10}O_{21}$ can thus be classified as a bridge-ring FBB (rule 2). The FBB of $Rb_3B_7O_{12}$ (ICSD 412539), as shown in Fig. 2(*b*), consists of two '8'-shaped-ring FBBs, one normal-ring FBB and one BO_4 unit, and thus belongs to a combined-ring FBB (rule 3).

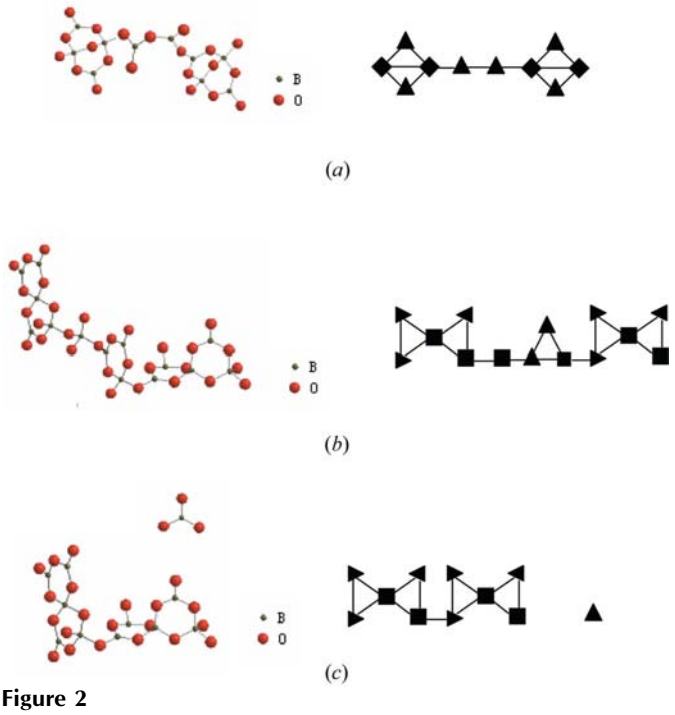


Figure 2
Structures and topologies of FBBs in some borates: (*a*) $Pb_6B_{10}O_{21}$; (*b*) $Rb_3B_7O_{12}$; (*c*) $Sr_2B_{11}O_{16}(OH)_5(H_2O)$.

2.2. Borate classification based on the topological structure of FBBs

The degree of polymerization of FBBs in a crystal structure (isolated, chain, layer and network) is a common factor in previous borate classifications (Xie, 1964; Strunz, 1997; Grice *et al.*, 1999). Classifying various FBBs into six types makes the topological structure of the FBB another characteristic of borates. Based on these two varying characteristics of FBBs, we proposed a new systematic classification scheme for borates.

Fig. 3 illustrates our systematic borate classification. The primary division is based on the topological structure of the FBBs (single Δ or T borates, branched borates, normal-ring borates, bridge-ring borates, '8'-shaped-ring borates and combined-ring borates). A subsequent subdivision is related to the degree of linkage between these FBBs (isolated, chains, layers and networks). Further subdivision is based on the crystal symmetry (non-centrosymmetric and centrosymmetric borates). Terminal subdivision is according to the number of B atoms in one chemical formula. In terms of such a classification scheme, 545 anhydrous borates and 296 hydrated borates are separately

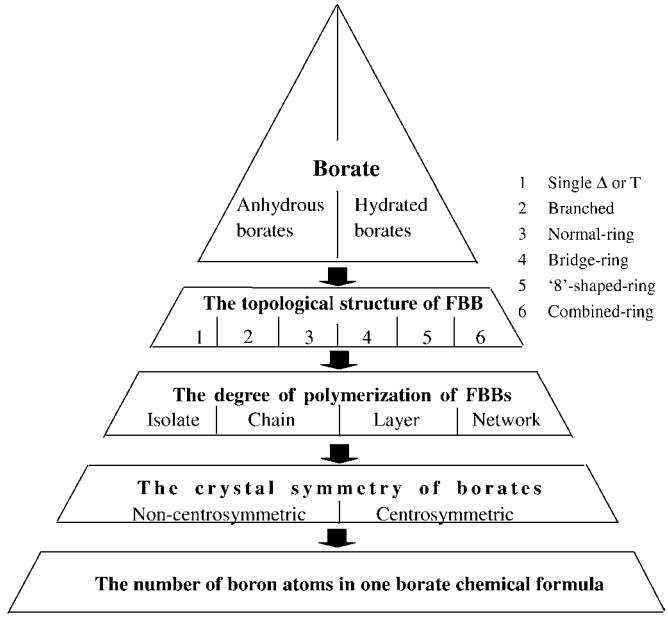
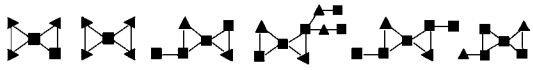
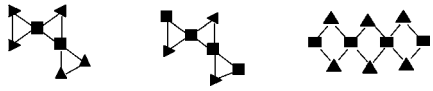
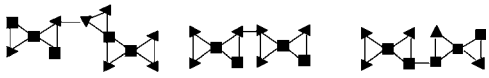


Figure 3
Schemes of the current borate classification.

Table 4
Selected topological structures of '8'-shaped-ring FBBs.

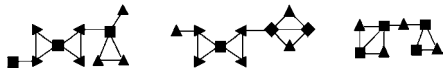
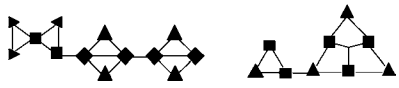
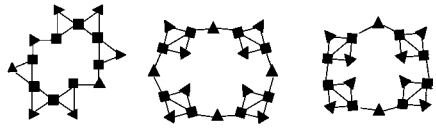
Some typical topologies of '8'-shaped-ring FBBs are shown here as examples. The corresponding configuration of each topological structure is given in the supplementary data (see Fig. S6).

'8'-shaped-ring FBB	Topological structure
Type 1†	
Type 2‡	
Type 3§	

† '8'-shaped-ring FBB and a linear combination of a '8'-shaped-ring FBB with one or more BO_3 (or BO_4) polyhedra. ‡ Double-'8'-shaped-ring FBB. § A linear combination of various '8'-shaped-ring FBBs.

Table 5
Selected topological structures of combined-ring FBBs.

Some typical topologies of combined-ring FBBs are shown here as examples. The corresponding configuration of each topological structure is given in the supplementary data (see Fig. S7).

Combined-ring FBB	Topological structure
Type 1†	
	
Type 2‡	

† A linear combination of several types of rings. ‡ A new ring constructed by a combination of ring units.

classified and tabulated (classification tables are listed in the supplementary material).

It should be noted that there are several special borates in which the FBBs consist of two unconnected parts. For example, the FBB of $Sr_2B_{11}O_{16}(OH)_5(H_2O)$ (ICSD 2942) is composed of two parts: one '8'-shaped-ring FBB and one single $B\varphi_3$ triangle (Fig. 2*c*). The '8'-shaped-ring FBBs link to each other to form layers and there is no linkage between the '8'-shaped-ring FBB and the $B\varphi_3$ triangle. The FBB of $Sr_2B_{11}O_{16}(OH)_5{\cdot}H_2O$ can be treated as an '8'-shaped-ring FBB, since the '8'-shaped-ring can reflect the dominant characteristic and the primary structure of borate polyanions. In this regard, $Sr_2B_{11}O_{16}(OH)_5(H_2O)$ was classified as an '8'-shaped-ring layered borate. Here, the number of borates which have these FBBs is very few (only 17 in 841) and each of them can be classified into one of the current six types [treated as in the case of $Sr_2B_{11}O_{16}(OH)_5{\cdot}H_2O$; see those compounds marked with an asterisk in the classification tables in the supplementary material].

3. Proposed algebraic description for FBBs and their polymerization in borate structures

To conveniently describe the structures and linkages of FBBs, a new algebraic description is introduced which is based on our topological classification and previous description schemes (Touboul *et al.*, 2003; Burns *et al.*, 1995). The descriptor proposed here is based on:

(i) the number of borate polyhedra in the FBB,

(ii) the degree of polymerization of the FBB in the borate structure,

(iii) the connectivity of the polyhedral groups in the FBB,

(iv) the presence of different rings in the FBB and

(v) the connectivity of different rings within the FBB.

The descriptor has the general form n: $\infty^r A$, where n is the number of borate polyhedra in the FBB, ∞^r reflects the degree of polymerization of the FBB in the borate structure (r may take the value 1, 2 or 3 if the FBB forms the chains, sheets or networks; when an isolated FBB exists in the structure the symbol ∞^r is removed) and A is a characteristic string [$m\ \langle b\Delta c\mathrm{T}\rangle + m'\ \langle b'\Delta c'\mathrm{T}\rangle^b + m''\ \langle b''\Delta c''\mathrm{T}\rangle^8 + \ldots$] that contains the detailed information for points (iii) to (v) above.

3.1. Number of borate polyhedra and clusters in the FBB

Here, b and c represent the number of $B\varphi_3$ triangles and $B\varphi_4$ tetrahedra in each cluster, while m is the number of the identical clusters connecting directly in the FBB.

3.2. Linkage between borate polyhedra in the FBB

Simple linkage: + denotes that two groups link together by sharing an O atom. When reflecting the linkage of simple Δ and T, + is removed. For example, Δ + T + T is abbreviated as Δ2T.

As mentioned above, there are 17 borates whose FBB is composed of two separate parts, which was not included in previous descriptors. Herein, this relationship between two parts can simply be described using '&'. For example, the descriptor of $Li_3Eu_2(BO_3)_3$ (ICSD 2106) is 3: [2Δ & Δ], which indicates that this FBB has two unconnected parts: a branched unit (2Δ) and a single unit (Δ). [$Li_3Eu_2(BO_3)_3$ is classified into branched borates since the branched unit (2Δ) is dominant in the structure of borate polyanions.]

Complex linkage: In some cases, the borate polyhedron may be connected to more than two other polyhedra or clusters. Each polyhedron or cluster that is separately connected to the central borate polyhedron is listed with the symbol | |; the central borate polyhedron is laid before (or behind) the symbol | |; the sequence of these polyhedra or clusters is not

important. Taking $Cr_2BP_3O_{12}$ (ICSD 409459) as an example, regardless of the types of the tetrahedra, the descriptor of this structure (Fig. 4*a*) can be written as 4: [Δ 3|T|] (simplified from 4: [Δ |T|T|T|]), which indicates that it contains three BO_4 (PO_4) tetrahedra connected to a central BO_3 triangle. Another example is $Mg_3B_7O_{13}Cl$. At high temperature this crystal structure has cubic symmetry (Burns & Carpenter, 1996), which consists of a network of corner-sharing BO_4 tetrahedra (ICSD 22009). The FBB of this structure is 4: ∞^3[O 4|T|] (simplified from 4: ∞^3[O |T|T|T|T|]), indicating that four BO_4 tetrahedra are simultaneously connected to the central O atom (Fig. 4*b*; Sueno *et al.*, 1973; Grice *et al.*, 1999).

In some synthetic borates (Huppertz & von der Eltz, 2002; Emme & Huppertz, 2003), two BO_4 tetrahedra can be connected by two O atoms, whose topological structure can be described by a symbol of the linear configuration of two edge-shared tetrahedra (Huppertz, 2003). In the current algebraic description, TT is introduced to describe such a case. For example, the descriptor of $Dy_4B_6O_{15}$ is written as 6: ∞^1 [2T + TT + 2T] (Fig. 4*c*).

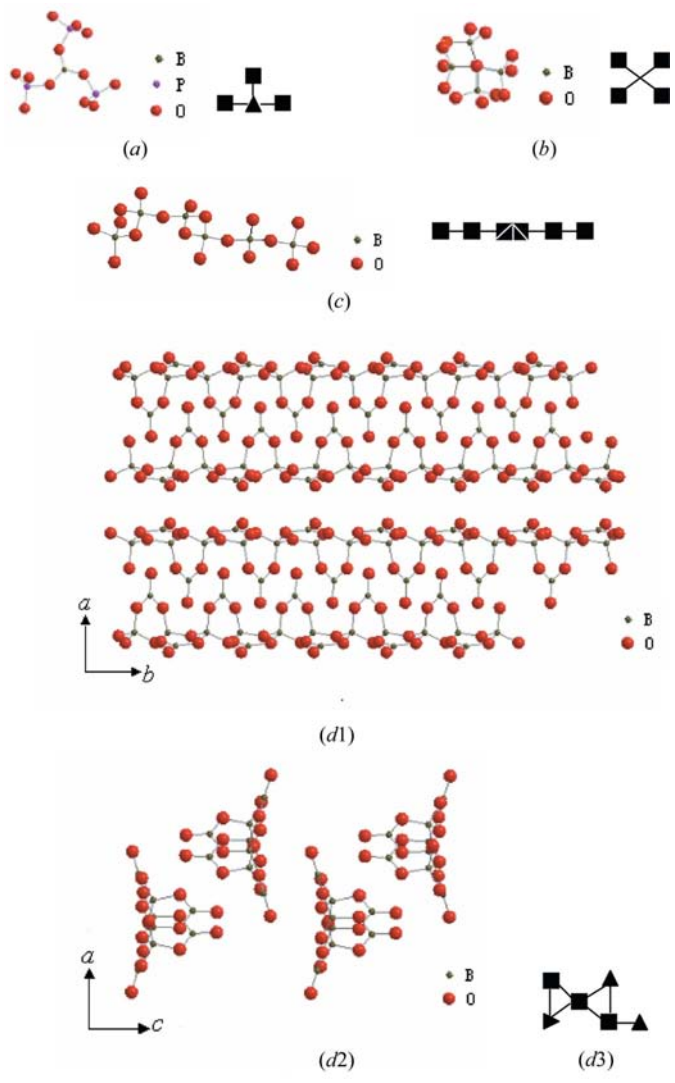


Figure 4
Structures and topologies of FBBs in some borates: (*a*) branched FBB in $Cr_2BP_3O_{12}$; (*b*) branched FBB in β-$Mg_3B_7O_{13}Cl$; (*c*) normal-ring FBB (B_2O_2 ring) in $Dy_4B_6O_{15}$; (*d*) infinite '8'-shaped-ring chain of the poly anion (*d*1 and *d*2) and corresponding FBB topology (*d*3) of $AgBO_2$ (all Ag atoms are omitted for clarity).

3.3. Different rings in the FBB

Different symbols are used to express various rings in order to simplify the algebraic description. In general, the symbol ⟨⟩ represents a ring structure and the type of ring is indicated by a superscript on ⟨⟩ (see Table 6 for details).

4. Results and discussion

Classifying all FBBs into six types and assigning them by easily grasped topological notation is effective in the study of borates, allowing us to describe and understand borate structures. For example, '8'-shaped-ring FBBs mostly simplify the previous descriptions (two B_3O_x rings sharing a BO_4 tetrahedron; x = 7, 8, 9). A big-bridge-ring FBB is reminiscent of the appearance of a complicated structure, as shown in Type 4 in Table 3. Due to the flexible definition of a topological structure, any FBB of borates (including new and undiscovered ones) can be assigned to one of the current six topological types. Furthermore, if the framework of the FBB remains unchanged, the substitution of Bφ_3 for Bφ_4 (or Bφ_4 for Bφ_3) could not change the topological type of FBB. Therefore, the current topological classification of FBBs is tolerant for a variety of borates and thus can be applied to the analysis and classifcation of the FBBs of new borates.

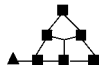
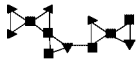
4.1. Comparison of several descriptions of borates

Several compounds are selected as examples (Table 7) to compare the descriptions proposed by Burns *et al.* (1995) (**A**), Touboul *et al.* (2003) (**B**), and our present work (**C**), respectively.

Comparison of **A** and **C**: **A** particularly emphasizes the topological structure of FBBs, which however does not give any information on the linkages between the FBBs in the borate structure. Therefore, $Ca_2B_3O_4(OH)_4Cl$, $CaB_3O_4(OH)_3H_2O$ and $CaB_3O_5(OH)$ (having the same FBB but different linkages) cannot be differentiated by **A**, as listed in Table 7. Also, **A** cannot describe the linkages between '8'-shaped-ring FBBs in $CaNaB_5O_6(OH)_6(H_2O)_5$ (isolated), $CaNaB_5O_7(OH)_4(H_2O)_3$ (chains) and $Na_3B_5O_8(OH)_2H_2O$ (sheets), respectively, while **C** can differentiate them by ∞^r (r = 1, 2 for chains and sheets; when the FBB is isolated, ∞^r is omitted). Furthermore, when describing the complex structure of FBBs such as $NaCa_2B_9O_{14}(OH)_4(H_2O)_2$ and $Na_6B_{13}O_{22.5}$ in Table 7, **A** always seems complicated, while **C** seems simpler with $\langle\rangle^h$ and $\langle\rangle^8$ indicating the different structure of the groups.

Comparison of **B** and **C**: although **B** can describe the linkages of the FBBs in borate structures by ∞^r, it cannot clearly reflect the inside topological structures of FBBs. For example, **B** cannot distinguish the normal-ring FBBs in $LnB_6O_9(OH)_3$ and big-bridge-ring FBBs in $Na_3VB_6O_{13}$ (both of their FBBs are described as [(6: 3Δ+3T)] by **B**), while **C**

Table 6
Different clusters and corresponding symbols in the current description.

Ring	Symbol	Example	Topological structure of FBB	Linkages between the FBBs	Descriptor by the current work	ICSD No. or reference
Normal-ring	$\langle\rangle$	$CaB_3O_4(OH)_3(H_2O)$		Chain	3: ∞^1 [$\langle\Delta 2T\rangle$]	22193
Bridge-rings: Bridge-ring	$\langle\rangle^b$	$(NH_4)_2B_4O_5(OH)_4(H_2O)_2$		Isolate	4: [$\langle 2\Delta 2T\rangle^b$]	100400
Double-bridge-ring	$\langle\rangle^{2b}$	β-$Dy_2B_4O_9$		Chain	8: ∞^1[Δ + $\langle 6T\rangle^{2b}$ + Δ]	412659 (Huppertz *et al.*, 2003)
6-Bridge-ring	$\langle\rangle^{6b}$	$Ag_6B_{12}O_{18}(OH)_6(H_2O)_3$		Isolate	12: [$\langle 6\Delta 6T\rangle^{6b}$]	67217
Big-bridge-ring	$\langle\rangle^{B}$	$Mg_3B_7O_{13}Cl$		Network	7: ∞^3 [$\langle 6T\rangle^{B}$ + Δ]	42495
'8'-Shaped-rings: '8'-Shaped-ring	$\langle\rangle^{8}$	$Ca_2B_5O_9Br$		Network	5: ∞^3 [$\langle 2\Delta 3T\rangle^{8}$]	18001
Double-'8'-shaped-ring	$\langle\rangle^{2-8}$	β-$Tl_2B_4O_7$		Network	12: ∞^3 [$\langle 2\Delta 3T\rangle^{8}$ + $\langle 4\Delta 3T\rangle^{2-8}$]	93745
Infinite-'8'-shaped-ring	$\langle\rangle^{n-8}$	$AgBO_2$		Chain (infinite-'8'-shaped-ring chain)†	5: ∞^1[$\langle 2\Delta 3T\rangle^{n-8}$ + Δ]	15510

† Infinite-'8'-shaped-ring chain is in fact the 'hinge-structure', which was first introduced by Sleight (1998). Here $\langle\rangle^{n-8}$ is introduced, where $\langle\rangle^{8}$ expresses the '8'-shaped-ring FBB and *n* indicates the infinite '8'-shaped chain. The configurations of $AgBO_2$ are given in Fig. 4(*d*).

gives different formulae to differentiate them, as shown in Table 7. Another example is the differentiation of $Na_5B_2P_3O_{13}$ and $CuLuB_4O_{10}$. The bridge-ring FBB in $Na_5B_2P_3O_{13}$ and the normal-ring FBB in $CuLuB_4O_{10}$ are easily differentiated by $\langle\rangle^b$ and $\langle\rangle$ in **C**, while **B** seems unclear. In the example $CaB_3O_5(OH)$, **B** only indicates that its FBB consists of two BO_3 triangles and four BO_4 tetrahedra, while **C** can involve not only the information obtained by **B** but also can reflect the inside double-bridge-ring structure by $\langle\rangle^{2b}$.

Furthermore, there are many borates (see Table S5 and S5′ of the supplementary material) having a similar structure to β-CaB_2O_4 and $TlB_2O_3(OH)H_2O$ (in Table 7) that cannot be described completely by **A** and **B**. In **C** $\langle\rangle^{n-8}$ is introduced, where $\langle\rangle^{8}$ still expresses the '8'-shaped-ring FBB and *n* indicates the infinite '8'-shaped helical chain (Fig. 4*d*). From the comparison it can be observed that our algebraic description includes more information about the linkages between the borate polyanions and reflects the inside structure of the FBBs more simply and directly.

4.2. Comparison of several borate classifications

Among the borate classifications available, both Xie (1964) and Grice *et al.* (1999) classified borates according to the polymerization of polyanions in the crystal structure (*i.e.* isolated, infinite line, layer and network). From their viewpoint, many compounds consisting of the same FBB groups but having different degrees of polymerization belong to different classes. For instance, the following compounds consist of the same $\langle 4\Delta T\rangle^8$ '8'-shaped-ring FBB: $CaNa_3B_5O_{10}$ (isolated rings, ICSD 61165), α-CsB_5O_8 (layer of rings, ICSD 93841) and KB_5O_8 (network of rings, ICSD 2712). However, since their FBBs have different polymerization types they are classified into isolated polyhedra, infinite layer and network polyhedra, respectively. However, on the basis of our classification, $CaNa_3B_5O_{10}$, α-CsB_5O_8 and KB_5O_8 can be classified into the same type: '8'-shaped-ring borates. The subsequent subdivisions of these compounds are '8'-shaped-ring isolated borates, '8'-shaped-ring layer borates and '8'-shaped-ring network borates, respectively.

Strunz (1997) classified *ca* 150 borates based on the number of B atoms in the repeating unit of the borate anions (mono-, di-, tri-, tetra-, penta-, hexa-, heptaborates and further megaborates). In this case, $Li_2B_4O_7$ (FBB: $\langle 2\Delta 2T\rangle^b$, ICSD 23876), α-LnB_5O_9 (FBB: $\langle 2\Delta 2T\rangle^b$ +Δ; Ln = Pr $\rightarrow$ Eu; Li *et al.*, 2002, 2003) and $CdLaB_5O_{10}$ (FBB: $\langle 2\Delta 3T\rangle^8$, ICSD 59246) can be classified into tetraborate, pentaborate, respectively, *i.e.* α-LnB_5O_9 is classified in the same class as $CdLaB_5O_{10}$. However, from their FBBs it is easy to see that α-LnB_5O_9 is more similar to $Li_2B_4O_7$. According to our classification, $Li_2B_4O_7$ and α-

LnB_5O_9 belong to bridge-ring borates, while $CdLaB_5O_{10}$ belongs to '8'-shaped-ring borates. Other examples are $LiBa_2B_5O_{10}$ (FBB: $\Delta+\langle 2\Delta 2T\rangle^b+\Delta$; ICSD 71875), $CaNa_3B_5O_{10}$ (FBB: $\langle 4\Delta T\rangle^8$; ICSD 61165) and $LaMgB_5O_{10}$ (FBB: $\langle 2\Delta 3T\rangle^8$; ICSD 23386). All of them are considered as pentaborates according to Strunz's classification. Actually, the FBB of $LiBa_2B_5O_{10}$ belongs to bridge-ring FBBs and the FBBs of the other two belong to '8'-shaped-ring FBBs. Therefore, it is more reasonable to classify them into bridge-ring borate and '8'-shaped-ring borate, respectively.

The current classification, which can reflect the inside topological structure of FBBs directly, is better balanced and more reasonable (comparing Fig. S7 to Fig. S8 in the supplemetary data). Additionally, it is interesting to note that the complexity of borate FBBs is not related to the type of FBB. For example, in $Cs_3B_7O_{12}$ (Nowogrocki *et al.*, 2003) the largest FBB 63: ∞^2 $[\langle 4\Delta 3T\rangle^{2-8}+10\langle 3\Delta 2T\rangle^8+\langle 2\Delta 3T\rangle^8+T]$ exists, which is just an '8'-shaped-ring FBB, while in α-NaB_3O_5 (Krogh-Moe, 1974) it has a simple but combined-ring FBB, 9: ∞^3 $[\langle 4\Delta T\rangle^8+\langle 2\Delta 2T\rangle^b]$.

4.3. Some useful information included in the current borate classification

The vast amounts of structural data in our current borate classification are propitious to synthesize new borates; meanwhile, the new borates can enrich the current classification system. According to our classification results, two simple figures are formed (Figs. 5 and 6). On the one hand, it is evident that single Δ or T borates are in the majority among all anhydrous borates (Fig. 5). Further analysis shows that most single Δ or T borates are transition-metal and multi-metal borates (Table S1). This phenomenon may be attributed to the different valence states and coordination abilities of various cations. Cations with a higher valence state (such as transition metals) have a stronger coordination ability and can form rather rigid coordinate bonds with the O atoms in both BO_3 and BO_4 (Leonyuk, 1997). These high-valence cations usually establish the basic framework of the structure, therefore, in this case the anionic stability is of secondary importance. Owing to the weakening tendency of polymerization, these borates often have structures with isolated BO_3 triangles and BO_4 tetrahedra. This statistical law offers a guideline that using transition metals to synthesize new borates with a single BO_3 or BO_4 group has a greater chance of success.

On the other hand, the distribution of hydrated borates seems well balanced in each group (Fig. 6) and most of the polyanions tend to be isolated in crystal structure (Table S8). This phenomenon may originate from the steric hindrance of water molecules in solution and the crystal lattice. More statistical results (see the tables in the supplementary data) indicate that the FBBs of alkaline borates, pseudo-alkaline borates and alkaline-earth metal borates tend to present complex structures, which gives a clue as to how to synthesize new borates with complex FBBs.

Borate minerals as well as synthetic borates have been included in the current classification. Take the case of four boracite-group minerals: $Mg_3B_7O_{13}Cl$ (boracite), $(Mg_xFe_{1-x})_3B_7O_{13}Cl$ (trembathite), $(Fe_xMg_{1-x})_3B_7O_{13}Cl$ (congolite) and $(Fe_xMg_{1-x})_3B_7O_{13}Cl$ (ericaite). At low temperature, all the FBBs of these compounds are big-bridge-ring (see the fourth one in Type 4 of Table 3) and connect together to form a network (Burns & Carpenter, 1996; Grice *et al.*, 1999). Therefore, their low-temperature phases can be classified into bridge-ring network borates. However, at high temperature these borate polyanions were converted into another complex network structure (Sueno *et al.*, 1973; Grice *et al.*, 1999). As expected, their high-temperature phases have the same FBB, given as 4: ∞^3[O 4|T|] (Fig. 4*b*), and thus are classified into branched-network borates. Therefore, under the same conditions, borate minerals may prefer to form an identical framework of borate polyanions, which will be classified into the same category according to the current classification.

Previous work has shown the contribution of different anions to the SHG properties of borates using the chemical-

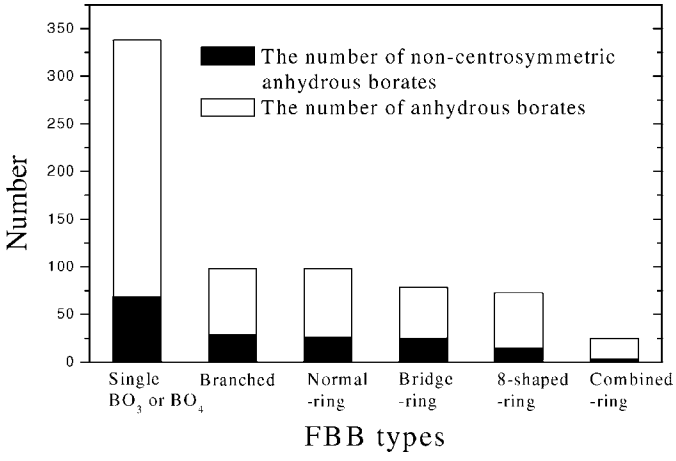


Figure 5
Distributions of anhydrous and non-centrosymmetric anhydrous borates in each type of classification (see Table S7 of the supplementary data for details).

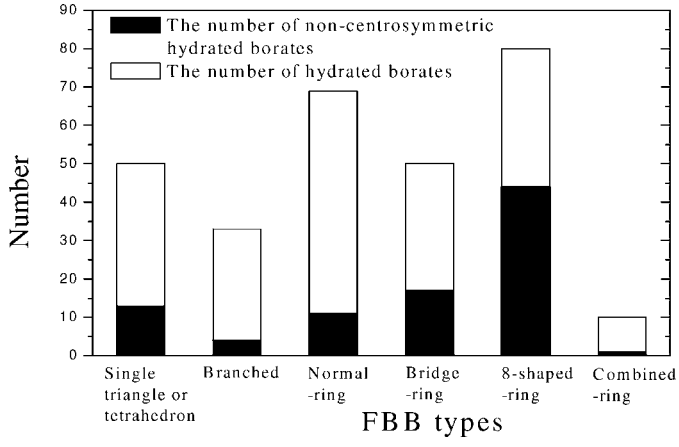
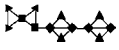


Figure 6
Distributions of hydrated and non-centrosymmetric hydrated borates in each type of classification (see Table S8 of the supplementary data for details).

Table 7
Structural units of some borates and the comparison of some available descriptors.

Chemical formula	FBB (topology)	Polymerization of FBB	Descriptors			ICSD No. or reference
			A	**C**	**B**	
$Ca_2B_3O_4(OH)_4Cl$		Isolate	$\Delta 2\square$: $\langle\Delta 2\square\rangle$	3: $[\langle\Delta 2T\rangle]$	3: $[(3\text{:}\ \Delta + 2T)]$	200074
$CaB_3O_4(OH)_3H_2O$		Chain	$\Delta 2\square$: $\langle\Delta 2\square\rangle$	3: $\infty^1[\langle\Delta 2T\rangle]$	3: $\infty^1[(3\text{:}\ \Delta + 2T)]$	22193
$CaB_3O_5(OH)$		Layer	$\Delta 2\square$: $\langle\Delta 2\square\rangle$	3: $\infty^2[\langle\Delta 2T\rangle]$	3: $\infty^2[(3\text{:}\ \Delta + 2T)]$	22192
$CaNaB_5O_6(OH)_6(H_2O)_5$		Isolate	$2\Delta 3\square\square$: $\langle\Delta 2\square\rangle$–$\langle\Delta 2\square\rangle$	5: $[\langle 2\Delta 3T\rangle^8]$	5: $[(5\text{:}\ 2\Delta + 3T)]$	100565
$CaNaB_5O_7(OH)_4(H_2O)_3$		Chain	$2\Delta 3\square$: $\langle\Delta 2\square\rangle$–$\langle\Delta 2\square\rangle$	5: $\infty^1[\langle 2\Delta 3T\rangle^8]$	5: $\infty^1[(5\text{:}\ 2\Delta + 3T)]$	35245
$Na_3B_5O_8(OH)_2H_2O$		Layer	$2\Delta 3\square$: $\langle\Delta 2\square\rangle$–$\langle\Delta 2\square\rangle$	5: $\infty^2[\langle 2\Delta 3T\rangle^8]$	5: $\infty^2[(5\text{:}\ 2\Delta + 3T)]$	1308
$NaCa_2B_9O_{14}(OH)_4(H_2O)_2$		Layer	$4\Delta 5\square$: $\langle\Delta 2\square\rangle$–$\langle\Delta 2\square\rangle$–$\langle\Delta 2\square\rangle$ = $\langle\Delta 2\square\rangle$	9: $\infty^2[\langle 2\Delta 3T\rangle^8$ + $\langle 2\Delta 2T\rangle^b]$	9: $\infty^2[(5\text{:}\ 3\Delta + 2T)$ + $(4\text{:}\ 2\Delta + 2T)]$	39758
$Na_6B_{13}O_{22.5}$		Network	$7\Delta 6\square$: $\langle 2\Delta\square\rangle$–$\langle\Delta 2\square\rangle\langle\Delta 2\square\rangle$ = $\langle\Delta 2\square\ \rangle\langle\Delta 2\square\rangle$ = $\langle\Delta 2\square\rangle$	13: $\infty^2[\langle 3\Delta 2T\rangle^8$ + $2\langle 2\Delta 2T\rangle^b]$	13: $\infty^2[(5\text{:}\ 3\Delta + 2T)$ + $(4\text{:}\ 2\Delta + 2T)$ + $(4\text{:}\ 2\Delta + 2T)]$	Penin *et al.* (2005)
$LnB_6O_9(OH)_3$ (Ln = Sm → Lu)		Network	$3\Delta 3\square$: $\langle\Delta\square\Delta\square\Delta\square>$	6: $\infty^3[\langle 3\Delta 3T\rangle]$	6: $\infty^3[(6\text{:}\ 3\Delta + 3T)]$	Li *et al.* (2002)
$Na_3VB_6O_{13}(VO_4$ is ignored)		Layer	$3\Delta 3\square$: $[O]\langle\Delta 2\square\rangle\|\langle\Delta 2\|\rangle\|\langle\Delta 2\square\rangle$	6: $\infty^2[\langle 3\Delta 3T\rangle^B]$	6: $\infty^2[(6\text{:}\ 3\Delta + 3T)]$	280184
$Na_5B_2P_3O_{13}$ (PO_4 is treated as BO_4)		Chain	$5\square$: $\langle 3\square\rangle$ = $\langle 3\square\rangle\square$	5: $\infty^1[\langle 4T\rangle^b + T]$	5: $\infty^1[(4\text{:}\ 4T) + T]$	401178
$CuLuB_4O_{10}$		Layer	$4\square$: $\langle 4\square\rangle$	4: $\infty^2[\langle 4T\rangle]$	4: $\infty^2[(4\text{:}\ 4T)]$	401709
$CaB_3O_5(OH)$		Layer	$2\Delta 4\square$: $\langle\Delta 2\square\rangle$ = $\langle 4\square\rangle$ = $\langle\Delta 2\square\rangle$	6: $\infty^2[\langle 2\Delta 4T\rangle^{2b}]$	6: $\infty^2[(6\text{:}\ 2\Delta + 4T)]$	14254
β-CaB_2O_4		Chain (infinite '8'-shaped-ring chain)	$3\Delta 3\square$: $\langle\Delta 2\square\rangle$–$\langle\Delta 2\square\rangle\Delta$	6: $\infty^2[\langle 2\Delta 3T\rangle^{n-8} + \Delta]$	6: $\infty^1[(6\text{:}\ 2\Delta + 3T)$ + $(1\text{:}\ \Delta)]$	20097
$TlB_2O_3(OH)H_2O$		Chain (infinite '8'-shaped-ring chain)	$3\Delta 3\square$: $\langle\Delta 2\square\rangle$–$\langle\Delta 2\square\rangle\Delta$	6: $\infty^2[\langle 2\Delta 3T\rangle^{n-8} + \Delta]$	6: $\infty^1[(6\text{:}\ 2\Delta + 3T)$ + $(1\text{:}\ \Delta)]$	100670

bond method and anion group theory (Xue *et al.*, 2000; Xue & Zhang, 1997; Chen *et al.*, 1999), respectively. The single BO_3 and B_3O_6 normal-ring contribute most to their large SHG. From Figs. 3 and 4 it can be observed that non-centrosymmetric borates make up a reasonable fraction in all borates. Therefore, our classification tables (in the supplementary material) can assist people to effectively search for novel borates with better SHG properties.

5. Conclusions

A structural classification of well defined topologies such as normal-, bridge-, '8'-shaped- and combined-ring FBBs as well as branched FBBs has been demonstrated. All the borates available can be classified hierarchically according to their topological structure and the polymerization of the FBBs in their crystallographic frame. Our systematic borate classification (including 545 anhydrous borates and 296 hydrated borates, as shown in Fig. 7) is the most comprehensive borate classification and provides new insight into the structural differences between various borates. In our proposed classification, all identical FBBs can be classified into the same type. In addition, an algebraic description was also proposed to describe a variety of topologically unique constructions of FBBs and their polymerizations in borate structures. Our results show that this algebraic description is much simpler and more convenient to describe FBB topologies in borate chemistry.

The study of inorganic borates and borate minerals is an active field for general scientists. The number of new structural

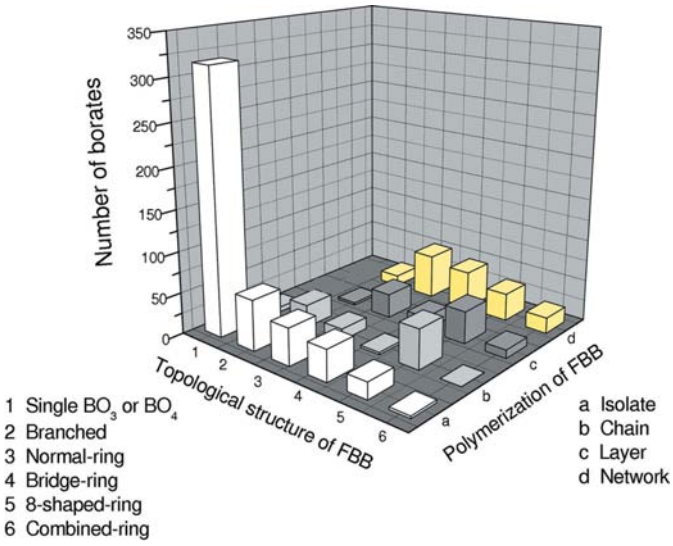


Figure 7
Final distributions of borate classification according to our proposed classification schemes for the topological structure and polymerization of FBBs of borates (more details are given in the supplementary data).

types and novel applications continues to grow. Our current work has effectively classified hundreds of borates and discussed their topological structures, which has shown some useful statistical information for the design and search of novel borate structures. The present study, to some degree, offers help in understanding and classifying all the borates available and those yet to be available.

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