DOI: 10.1002/ejic.201100270

Oxo Boron Clusters and Their Open Frameworks

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Dedicated to Professor John D. Corbett on the occasion of his 85th birthday

Keywords: Microporous materials / Open frameworks / Borates / Clusters / Structure elucidation

This review article briefly summarizes the recent research advances in the field of crystalline oxo boron clusters and their open frameworks. By using different amine molecules and transition metal complexes or inorganic ions as the charge-balancing agents, different oxo boron clusters, such as $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^{2-}$, $[B_5O_6(OH)_4]^-$, $[B_7O_9(OH)_5]^{2-}$, $[B_8O_{10}(OH)_6]^{2-}$, $[B_9O_{12}(OH)_6]^{3-}$, and $[B_{14}O_{20}(OH)_6]^{4-}$ polyanions, have been successfully isolated and structurally characterized. These polyborate anions may act as the main building blocks to create new open-framework compounds with layered and three-dimensional structures. Odd ring channels and helical channels are noteworthy in open-framework borate structures. Besides their traditional zeolitic properties, open-framework borates exhibit interesting optical properties including photoluminescence and second harmonic generation, suggesting their potential applications in catalysis, nonlinear optics, display and lighting devices.

1. Introduction

Crystalline microporous materials with regular pore structures have found widespread applications in catalysis, separation, ion-exchange, and gas storage.[1–3] Aluminosilicate zeolites are the most notable microporous inorganic solids with pore size below 20 Å.[4] Of fundamental interest in this research is to synthesize new zeolitic materials, because the utility of these materials is intimately related to their compositions and framework topologies. During the past years, considerable efforts have been made in synthesizing non-aluminosilicate-based open-framework materials, such as metal phosphates, phosphites, arsenates, and germanates.[5–8] In contrast to zeolites constructed from corner-sharing MO_4 tetrahedra, the presence of MO_5 and MO_6 polyhedra in these open structures is noteworthy. As a result, the largest pore size increases from an 18-membered ring (18 MR) in zeolites to 30 MR in open-framework germanates.[9]

Boron is of current interest as a framework building element for several reasons. First, boron can be coordinated by three or four oxygen atoms to form a BO_3 triangle or a BO_4 tetrahedron. The triangular geometry of BO_3 is unique in zeolite chemistry, and it can be further coordinated by a nitrogen atom because of the electron-deficient character of boron. Second, the ability of boron to form different cluster aggregates offers a new approach to construct open-framework structures from cluster building units. The diverse borate clusters and rich connection modes between these oxoanions indicate that a large number of framework structures can be potentially accessed. Furthermore, many borate compounds, such as β-BaB_2O_4 (BBO), LiB_3O_5 (LBO), $CsLiB_6O_{10}$, and $Sr_2Be_2B_2O_7$, are transparent and have high nonlinear optical coefficients.[10–13] It is expected that open-framework materials from oxo boron clusters can integrate the uniform porosity of zeolites with the extraordinary optical properties of metal borates.

Several approaches have been developed for the synthesis of metal borates. The traditional method is based on high-temperature solid-state reaction.[14] It is well known that microporous inorganic solids are metastable phases, and they are thermodynamically unstable. Thus, high-temperature reaction conditions usually result in the formation of dense phases. Another approach is the utilization of the molten boric acid flux method. It is well known that boric acid melts at about 171 °C, and it does preserve some desirable requirements as a reaction medium for metal borates. Some rare earth polyborates have been successfully prepared under flux conditions.[15,16] Recently, hydro/solvothermal reaction has been extensively studied to prepare new oxo boron clusters and open-framework metal borates. The reaction temperature is usually below 200 °C and enables the use of amine molecules as the reactants, which will decompose at elevated temperature. In addition, the reduced viscosity of the solvent under hydro/solvothermal

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conditions enhances the solubility of the reactant and promotes the growth of good quality single crystal. By tuning the reaction variables, such as temperature, pH, reactant source and type, solvent, and structure-directing agent, different metastable kinetic phases rather than thermodynamic phases can be obtained under solution-mediated conditions.

In this review we describe the recent advances in the synthesis of open-framework boron oxides and metal borates constructed from polyborate anions. As the important intermediates of open-framework structures, oxo boron clusters in isolated forms will be briefly introduced. Dense-phase borates, extended borate structures without pores, and different types of open-framework boron-containing solids, such as phosphate-rich borophosphates, will be excluded in this scope.[17] Besides the rich structural chemistry of borate compounds, the interesting zeolitic and optical properties of open-framework borates, such as microporosity, ion exchange, catalysis, photoluminescence, and second harmonic generation, will be presented.

2. Oxo Boron Clusters

The complicated structures of open-framework borates usually consist of oxo boron clusters as their building units. It has been proposed that the high-dimensional framework structures are likely to be formed through a progressive build-up process from low-dimensional structures.[18] From the viewpoint of structural chemistry, the elucidation of the structures of oxo boron clusters may help to understand how open-framework borates are formed and enable the synthesis of new microporous materials with designed architectures and properties.

So far, a variety of oxo boron clusters have been found in isolated forms, such as $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^{2-}$, $[B_5O_6(OH)_4]^-$, $[B_7O_9(OH)_5]^{2-}$, $[B_8O_{10}(OH)_6]^{2-}$, $[B_9O_{12}(OH)_6]^{3-}$, and $[B_{14}O_{20}(OH)_6]^{4-}$.[19] These polyborate anions usually consist of corner-sharing BO_3 triangles and BO_4 tetrahedra. Three types of cations can serve as the charge-balancing agents in their structures: inorganic cations, protonated amines, and transition metal complexes.

As shown in Figure 1a, the $[B_3O_3(OH)_4]^-$ cluster consists of one $BO_2(OH)_2$ tetrahedron and two $BO_2(OH)$ triangles, which are connected with each other to form a ring structure by sharing corner oxygen atoms.[20] The core of the cluster is a planar benzene-like B_3O_3 ring. According to the classification of polyborate anions by Heller, Christ, and Clark, the shorthand notation for this oxo boron cluster is "3:2Δ+1T, isolated", where the specified number is the number of boron atoms in the isolate cluster, and the symbols Δ and T mean triangle and tetrahedron, respectively.[21,22]

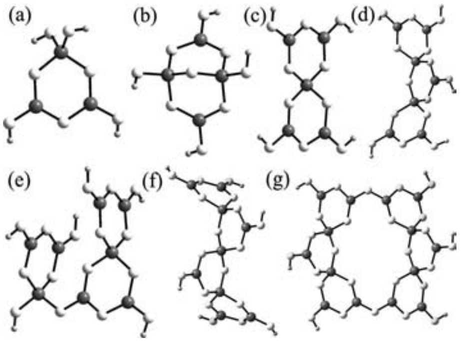

Figure 1. A view of the oxo boron clusters containing different boron atoms: (a) $[B_3O_3(OH)_4]^-$, (b) $[B_4O_5(OH)_4]^{2-}$, (c) $[B_5O_6(OH)_4]^-$, (d) $[B_7O_9(OH)_5]^{2-}$, (e) $[B_8O_{10}(OH)_6]^{2-}$, (f) $[B_9O_{12}(OH)_6]^{3-}$, (g) $[B_{14}O_{20}(OH)_6]^{4-}$.

The $[B_4O_5(OH)_4]^{2-}$ cluster consists of two $BO_2(OH)_2$ tetrahedra and two $BO_2(OH)$ triangles, as shown in Figure 1b.[23] Each $BO_2(OH)_2$ tetrahedron shares a corner oxygen atom with the other $BO_2(OH)_2$ tetrahedron and two corner oxygen atoms with the two $BO_2(OH)$ triangles. Each $BO_2(OH)$ triangle shares two corner oxygen atoms with the two $BO_2(OH)_2$ tetrahedra. The shorthand notation for this tetraborate is "4:2Δ+2T, isolated".

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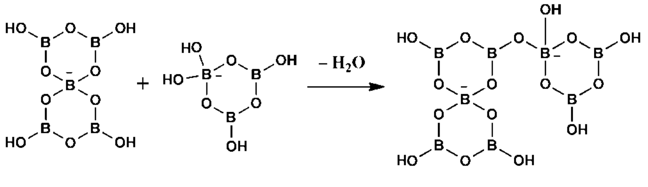
Guo-Yu Yang graduated from Jilin University in 1988, and received his M.S. and Ph.D. from the Department of Chemistry, Jilin University in 1991 and 1998, respectively. In 1991, he joined Jilin University. From 1998 to 2001, he did his postdoctoral work at University of Notre Dame and Stockholm University. He moved to Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, in 2001 as a full professor in chemistry. His research interest is focused on porous and nonlinear optical materials built by oxo cluster units, cluster-organic frameworks, and oxo cluster chemistry including transition metal, main group, and lanthanide clusters.

The $[B_5O_6(OH)_4]^-$ cluster consists of one BO_4 tetrahedron and four $BO_2(OH)$ triangles, as shown in Figure 1c.[24–26] The pentaborate cluster is characteristic of two B_3O_3 rings which are perpendicular to one another. The BO_4 tetrahedron is located at the center of the cluster and shares four corner oxygen atoms with the four $BO_2(OH)$ triangles. Each $BO_2(OH)$ triangle shares two corner oxygen atoms with one BO_4 tetrahedron and one $BO_2(OH)$ triangle. The shorthand notation is "5:4Δ+1T, isolated".

The $[B_7O_9(OH)_5]^{2-}$ cluster is composed of two BO_4 tetrahedra and five $BO_2(OH)$ triangles, as shown in Figure 1d.[27,28] In addition to the five OH groups, three B_3O_3 rings linked by two common BO_4 tetrahedra are apparent in this heptaborate cluster. Two types of B_3O_3 rings, one containing two $BO_2(OH)$ triangles and one BO_4 tetrahedron (2Δ+1T) and the other having one $BO_2(OH)$ triangle and two BO_4 tetrahedra (Δ+2T), are present in the cluster. Its shorthand notation is "7:5Δ+2T, isolated".

The $[B_8O_{10}(OH)_6]^{2-}$ cluster is composed of two BO_4 tetrahedra and six $BO_2(OH)$ triangles, as shown in Figure 1e.[29] Similar to the $[B_7O_9(OH)_5]^{2-}$ cluster, the octaborate anion also contains three B_3O_3 rings. Two B_3O_3 rings are linked together by a tetrahedrally coordinated B atom, and the third ring is linked to the two fused B_3O_3 rings through an oxygen atom. An instructive way to view the structure involves two oxo boron clusters, $[B_3O_3(OH)_4]^-$ and $[B_5O_6(OH)_4]^-$, which are condensed together by eliminating a water molecule from their hydroxy groups, as shown in Scheme 1. The shorthand notation of this octaborate anion is "8:6Δ+2T, isolated".



Scheme 1. Possible pathway for the formation of the $[B_8O_{10}(OH)_6]^{2-}$ cluster by eliminating a water molecule from the $[B_3O_3(OH)_4]^-$ and $[B_5O_6(OH)_4]^-$ anions.

The $[B_9O_{12}(OH)_6]^{3-}$ cluster is composed of three BO_4 tetrahedra and six $BO_2(OH)$ triangles, as shown in Figure 1f.[30] There are four B_3O_3 rings (the inner two are "Δ+2T"-type rings and the outer two are "2Δ+T"-type rings) in the nonaborate cluster. The structure can be regarded as the extended analogue of the $[B_7O_9(OH)_5]^{2-}$ cluster by adding an inner "Δ+2T"-type B_3O_3 ring. Its shorthand notation is "9:6Δ+3T, isolated". By adding the "Δ+2T"-type B_3O_3 rings, larger polyborates constructed from B_3O_3 rings may be produced, such as $[B_{11}O_{15}(OH)_7]^{4-}$, $[B_{13}O_{18}(OH)_8]^{5-}$,···, $[B_{2n+3}O_{3n+3}(OH)_{n+3}]^{n-}$ ($n \geq 1$).

The $[B_{14}O_{20}(OH)_6]^{4-}$ cluster has a ring aperture. It is composed of four BO_4 tetrahedra and ten $BO_2(OH)$ triangles, as shown in Figure 1g.[31–33] The structure has an 8 MR window with the dimensions 5.4 × 7.7 Å delimited by four BO_4 tetrahedra and four BO_3 triangles. It can be conceptually constructed from two $[B_7O_9(OH)_5]^{2-}$ clusters by a dehydration process involving four hydroxy groups. It is worthy to note that isolated oxo boron clusters having more than six boron atoms are rare. The successful isolation of large borate clusters is of great interest to synthetic chemists.

3. Open-Framework Boron Oxides

Oxo boron clusters consist of active hydroxy groups, which may act as the main building blocks to construct various extended structures by condensation reactions with the elimination of water molecules under suitable synthetic conditions. Low-dimensional structures are usually generated during the polymeric processes. Examples include one-dimensional chain-like structures of $(H_21,3\text{-dap})[B_8O_{11}(OH)_4]\cdot H_2O$, $K_4B_{10}O_{15}(OH)_4$ and $KB_5O_7(OH)_2\cdot H_2O$, and two-dimensional layered structures of $(H_2en)[B_5O_8(OH)]$, $(H_2en)[B_6O_9(OH)_2]$, $[Cu(en)_2][B_7O_{13}H_3]$, $Na_4[B_{10}O_{16}(OH)_2]\cdot 4H_2O$, and $Pb[B_8O_{11}(OH)_4]$.[34–41] Recently, three open-framework boron oxides, $(H_2en)_2(Hen)_2B_{16}O_{27}$, $B_6O_9(en)$, and $B_6O_9(en)_2@H_2enCl_2$, were prepared under solvothermal conditions.[42,43] As shown in Figure 2a, $(H_2en)_2(Hen)_2B_{16}O_{27}$ has a three-dimensional inorganic framework accommodating organic cations. The complicated structure is built up by two borate layers from different oxo boron

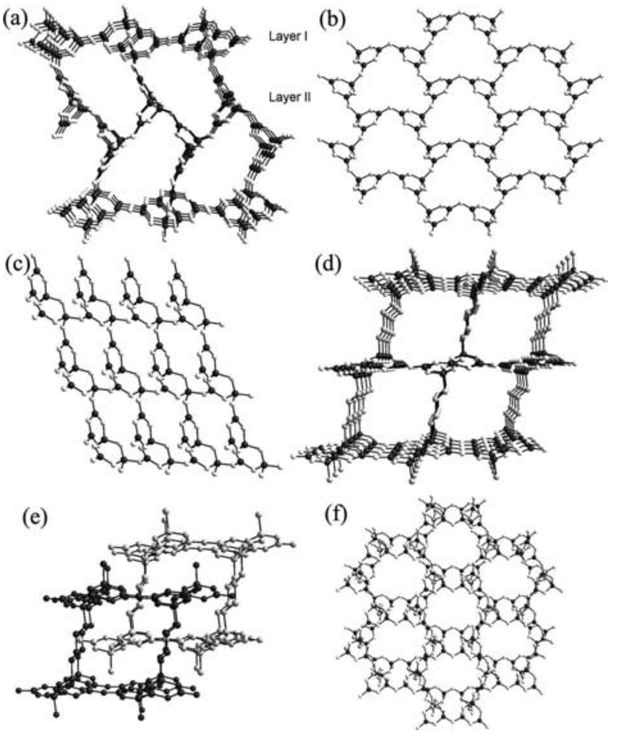


Figure 2. (a) The three-dimensional structure of $(H_2en)_2(Hen)_2B_{16}O_{27}$ consists of two types of borate layers. (b) The type I borate layer has a 6^3 network with a cyclic B_3O_7 cluster as the building unit. (c) The type II borate layer has a 4^4 grid network with a B_5O_{11} cluster as the building unit. (d) The borate layers in $B_6O_9(en)$ are pillared by en ligands to form an organic–inorganic hybrid framework. (e) $B_6O_9(en)$ has a twofold interpenetrating framework. (f) The structure of $B_6O_9(en)_2@H_2enCl_2$ has 12-ring channels along the [001] direction.

clusters. The type I borate layer is constructed from cyclic B_3O_7 clusters and has large 12 MR windows (Figure 2b). Each B_3O_7 cluster connects with three such building units, giving rise to the layered structure with a 6^3 network. The type II borate layer is constructed from B_5O_{11} clusters, as shown in Figure 2c. Each B_5O_{11} cluster shares four corner oxygen atoms with four adjacent B_5O_{11} clusters, which results in the formation of a 4^4 grid network. The two different borate layers alternate strictly along the [010] direction, and they are connected together by common oxygen atoms. Viewed along the [001] direction, large 13-ring channels delimited by six BO_4 tetrahedra and seven BO_3 triangles are apparent in the structure. The presence of two different oxo boron clusters in the crystalline framework is noteworthy. Different from $(H_2en)_2(Hen)_2B_{16}O_{27}$ with an anionic inorganic framework, $B_6O_9(en)$ has a neutral hybrid framework with borate layers pillared by en ligands (Figure 2d). The borate layer is parallel to the *ab* plane and has large 12 MR windows delimited by four BO_3N tetrahedra and eight BO_3 triangles. The network is similar to the borate layer found in $(H_2en)_2(Hen)_2B_{16}O_{27}$. When the layered structures are stacked along the [001] direction in an eclipsed mode and are further bridged by en molecules, the three-dimensional structure of $B_6O_9(en)$ is formed. The presence of B–en–B linkages in the structure is noteworthy. Although the pillared layered structure seems to have large voids, it is interpenetrated by an identical framework, thus precluding the presence of large cavities (Figure 2e). The noninterpenetrating structure, $B_6O_9(en)_2@H_2enCl_2$, built from the same borate layers and en ligands, is formed by incorporating diprotonated en cations and chloride anions as the extraframework species. The compound has large 12-ring channels along the [001] direction (Figure 2f).

It is of great interest to examine the roles of en molecules in the formation of the three open-framework boron oxide structures. In $(H_2en)_2(Hen)_2B_{16}O_{27}$, the organic molecules reside in the channels of the inorganic framework and act as the structure-directing agents to induce the formation of the specific open structure. In addition, the organic molecules are protonated to balance the negative charge of the inorganic framework. In $B_6O_9(en)$, the organic molecules directly connect to the boron atoms through strong covalent B–N bonds. They serve as bridging ligands to link borate layers into a three-dimensional framework. In the instance of $B_6O_9(en)_2@H_2enCl_2$, the organic species play multiple functions (i.e. structure-directing, charge-balancing, and structure-building).

4. Open-Framework Germanium Borates

Among microporous and open-framework inorganic solids, zeolites are of particular interest due to their diverse structures and many industrial applications. To imitate the chemical composition of zeolites that contain both tetravalent Si^{4+} and trivalent Al^{3+} ions, one effective synthetic strategy to produce borate-rich open frameworks is the use of tetravalent cations (e.g. Ge^{4+}) as linking centers to join together oxo boron clusters. Early attempts to prepare open-framework B–Ge–O compounds resulted in the formation of several germanate-rich frameworks.[44–49] The first borate-rich framework in this system is $K_2[Ge(B_4O_9)]\cdot 2H_2O$ (FJ-16), which was made under solvothermal conditions by using $K_2B_4O_5(OH)_4\cdot 2H_2O$ as boron source.[50] As shown in Figure 3a, this compound has an open-framework structure containing B_4O_9 clusters. In its three-dimensional framework, each B_4O_9 cluster uses all four terminal O atoms to bind to four Ge atoms, which in turn coordinate to four B_4O_9 clusters. If each B_4O_9 cluster and Ge atom are considered as 4-connected node in the network, the framework of FJ-16 can be reduced into a diamond topology (Figure 3b). Viewed along the [100] direction, the structure has medium-size 10-ring channels, where K^+ cations and water molecules reside. Careful analysis of the structure indicates that the 10-ring channels combine two pairs of helical chains with opposite handedness. Intersecting the 10-ring channels are two sets of 9-ring channels running along the [001] and the [110] directions.

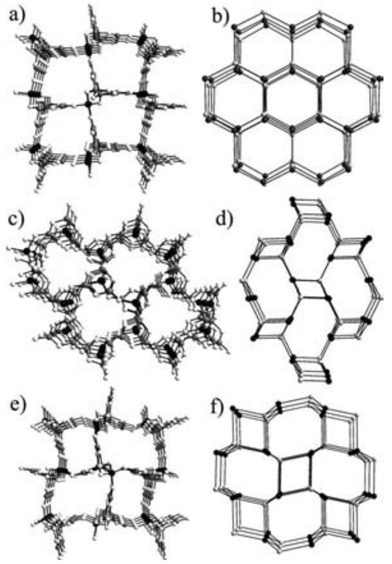


Figure 3. (a) Ball-and-stick representation of the structure of FJ-16 with 10-ring channels and (b) a diamond topology. (c) Ball-and-stick representation of the structure of CsB_3GeO_7 with 8-ring channels and (d) an ABW topology. (e) Ball-and-stick representation of the structure of FJ-18 with 8-/12-ring channels and (f) a CrB_4 topology.

The development of new synthetic techniques is very important to prepare novel microporous materials with unprecedented framework topologies and physical properties. For example, a low-temperature flux approach has been used by Zhao and co-workers to prepare a new germanium borate, $K_4[B_8Ge_2O_{17}(OH)_2]$.[51] In this flux approach, $K_2B_4O_5(OH)_4\cdot 2H_2O$ serves as both flux and reagent without the addition of any liquid solvents like water or alcohols. The compound has a unique double-layered structure containing intersecting channels along three directions: 8-ring channels along the [010] and the [110] directions, and 9-ring channels along the [101] direction. Different from FJ-16 with a 4-connected framework, the compound has a

(3,4)-connected framework. One corner of the B_4O_9 cluster is occupied by a terminal OH group, thus each B_4O_9 cluster acts as a three-coordinate ligand to connect three adjacent Ge atoms. Each Ge atom links three B_4O_9 clusters and one Ge atom through a μ(2) oxygen atom in the layered structure. The structure can be regarded as an intermediate of FJ-16. The successful isolation of $K_4[B_8Ge_2O_{17}(OH)_2]$ is a significant discovery, because it sheds some light on how an open structure is formed.

High-temperature solid-state reaction has also been used in the synthesis of open-framework germanium borate. The reaction of $CsCO_3$, GeO_2, and H_3BO_3 at 640 °C for seven days yields a new open-framework germanium borate, CsB_3GeO_7.[52] The compound has a three-dimensional structure with cyclic B_3O_7 clusters bridged by Ge atoms (Figure 3c). Viewed along the [100] and [001] directions, the structure has 8-ring channels and 10-ring channels, respectively. Because both the B_3O_7 cluster and the Ge atom act as 4-connected nodes, the anionic framework of CsB_3GeO_7 can be described as a 4-connected zeolitic network with ABW topology (Figure 3d). The replacement of $CsCO_3$ by $RbCO_3$ under similar synthetic conditions has resulted in the formation of three germanium borates, namely, $RbGeB_3O_7$, $Rb_2GeB_4O_9$, and $Rb_4Ge_3B_6O_{17}$.[53] $RbGeB_3O_7$ is isostructural with CsB_3GeO_7. The structure of $Rb_2GeB_4O_9$ shows a three-dimensional framework with B_4O_9 clusters connected by GeO_4 tetrahedra through corner sharing. It has a diamond topology if the B_4O_9 clusters and GeO_4 tetrahedra are regarded as 4-conneced nodes. $Rb_4Ge_3B_6O_{17}$ has a novel framework composed of B_3O_8 clusters, Ge_2O_7 dimers, and GeO_4 tetrahedra. The connectivity of B_3O_8 clusters and Ge_2O_7 dimers gives rise to a double-layered network parallel to the *ab* plane. Neighboring double layers are further linked by GeO_4 tetrahedra to create a three-dimensional structure. Viewed along the [010] direction, it seems that the structure has 8- and 9-ring channels. In fact, the structure does not have 8- and 9-ring windows along the [010] direction. The actual channels are helical along the [010] direction. Also interesting are two alkaline-earth germanium borates, $Ba_3[Ge_2B_7O_{16}(OH)_2](OH)(H_2O)$ and $Ba_3Ge_2B_6O_{16}$, which are obtained by different synthetic methods.[54] $Ba_3Ge_2B_6O_{16}$ was synthesized by high-temperature solid-state reaction of $BaCO_3$, GeO_2, and H_3BO_3 at 800 °C for four days. It has a thick layered structure constructed from circular B_6O_{16} units and GeO_4 tetrahedra. By reacting the same starting materials under hydrothermal conditions, a hydrated germanium borate phase with three-dimensional structure, $Ba_3[Ge_2B_7O_{16}(OH)_2](OH)(H_2O)$, was obtained as a result.

In addition to inorganic-cation-templated germanium borates, two organically templated B–Ge–O compounds containing oxo boron clusters have also been made under solvothermal conditions. The first example is $(H_2en)[Ge(B_4O_9)]$ (FJ-18), which contains ethylenediamine as the structure-directing agent.[55] The compound has a three-dimensional structure constructed from 4-connected B_4O_9 clusters and Ge atoms (Figure 3e). The two building units are strictly alternate in the network, giving rise to a 4-connected zeolitic structure with CrB_4 topology (Figure 3f). Viewed along the [100] direction, the structure has two kinds of channels: 12-ring and 8-ring. Two kinds of 9-ring channels running along the [010] and the [001] directions intersect with the 12-/8-ring channels to form four 9-ring windows perpendicular to each one of the 12- and 8-ring channels. It should be noted that the 12-ring channel found in FJ-18 is the largest one in borate-rich B–Ge–O system. The other organically templated germanium borate, $(CH_3NH_3)_2[Ge(B_4O_9)]$, was prepared by using methylamine as the structure-directing agent.[56] It has a three-dimensional structure constructed from strictly alternating B_4O_9 clusters and Ge atoms. If the B_4O_9 clusters and Ge atoms are considered as 4-connected nodes, this framework can be regarded as a diamond topology as found in FJ-16. Compared with FJ-16, this compound has a different pore aperture and channel orientation due to the presence of different extraframework cations.

5. Open-Framework Aluminum and Gallium Borates

Aluminum has long been a focus of research in the synthesis of new microporous materials since the discovery of natural zeolites containing aluminum as one of the main framework elements.[57,58] Different from the boron atom that exists in BO_3 or BO_4 form, aluminum can be surrounded by four, five, or even six oxygen atoms to form AlO_4, AlO_5, and AlO_6 polyhedra. By incorporating Al-centered polyhedra into borate frameworks, a large number of new open-framework structures can be potentially accessed. In the early 1970s, this synthetic strategy gave rise to three aluminum borates with B/Al ratios of 3:1, 2:1, and 2:3.[59] After that, several microporous aluminum borates were prepared under hydrothermal conditions in acidic medium.[60–65] However, the structures of these compounds remain unknown because of the lack of suitable single crystals for X-ray structural characterization.

Good quality single crystals of open-framework aluminum borates can be obtained in basic medium under solvothermal conditions. By using a mixture of pyridine and water as the solvent, a new three-dimensional open-framework aluminum borate, $(H_2teta)_2(Al_2B_{10}O_{20})\cdot 0.25H_2O$ (QD-3), was prepared in the presence of an organic structure-directing agent.[66] Its structure is constructed from B_5O_{10} clusters and Al atoms. Each B_5O_{10} cluster is linked with four Al atoms through the corner oxygen atoms and vice versa, so there is no Al–O–Al connection in the structure. Viewed along the [010] direction, the structure has very large 14-ring channels with a pore diameter of 12.8 × 7.5 Å. Under similar synthetic conditions, $[CH_3NH_2(CH_2)_3NH_3][AlB_5O_{10}]$ (QD-2) was made by using *N*-cyclohexyl-1,3-diaminopropane as the structure-directing agent.[67] The large amine molecules are unstable and decompose to form $CH_3NH_2(CH_2)_3NH_3^{2+}$ cations under the solvothermal conditions, which act as the real structure-directing agents. The connection between B_5O_{10} clusters and

Al atoms gives rise to a three-dimensional structure containing multidirectional helical channels along the [100], [010], and [001] directions. Viewed along the [110] direction, the structure has unusual 11-ring channels delimited by three AlO_4 tetrahedra, two BO_4 tetrahedra, and six BO_3 triangles. Although the structures of QD-2 and QD-3 are constructed from the same building units, their structures are completely different. QD-2 exhibits a diamond topology if B_5O_{10} clusters and Al atoms are regarded as 4-connected nodes. Such framework topology is often found in open-framework aluminum borates, because it can be generated by several different amine molecules.[68] QD-3 has a zeolitic ABW topology. Compared with CsB_3GeO_7 possessing the same ABW framework lattice, QD-3 exhibits larger pore size due to the presence of larger B_5O_{10} building units than the B_3O_7 cyclic unit in CsB_3GeO_7.

To systematically study the effect of different structure-directing agents on the structures of aluminum borates, Yang and co-workers reported a series of crystalline open structures in this system under solvothermal conditions.[69] As shown in Figure 4a, $[Al(B_4O_9)\ (BO)]\cdot H_2en$ and $[Al(B_4O_9)(BO)]\cdot H_21,3\text{-dap}$ have the same open-framework structures constructed from AlB_5O_{13} clusters. Such a building block contains a B_4O_9 unit, a BO, group and an Al atom. The presence of a μ_3-O in the building unit is noteworthy. Each AlB_5O_{13} cluster connects to six neighbors to form a three-dimensional structure with a pcu topology (Figure 4b). Viewed along the [100], [010], [001], and [011] directions, the structure has intersecting 10-, 9-, 9-, and 9-ring channels, respectively.

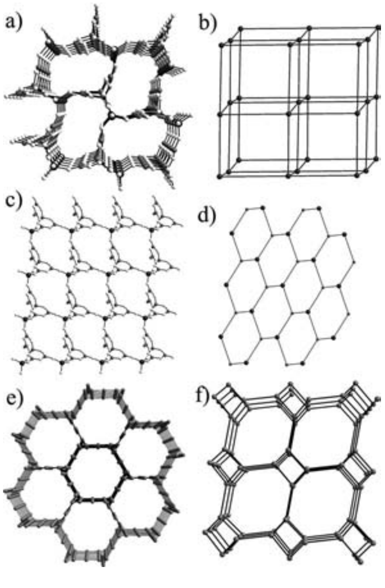


Figure 4. (a) The three-dimensional structure of $[Al(B_4O_9)(BO)]\cdot H_2en$ has 10-ring channels along the [100] direction and (b) a pcu topology. (c) The layered structure of $[Zn(deta)_2][Al(OH)(B_5O_9F)]$ has 11-ring windows and (d) a 6^3 network. (e) A view of the structure of PKU-1 containing 18 octahedral-atom channels. (f) The octahedral backbone of PKU-5 has a chiral (10,3)-a network.

Also interesting are two isomorphous open-framework aluminum borates templated by methylamine.[70] They have a diamond topology with the same formula: $(Hma)(H_2O)_2[Al(B_5O_{10})]$. By using dab as the structure-directing agent, an open-framework structure, $Al[B_5O_{10}]\cdot H_2dab\cdot 2H_2O$, was prepared; it has a CrB_4 topology constructed from 4-connected B_5O_{10} clusters and Al atoms. Along the [100] direction, two parallel channels with 12 MR and 8 MR coexist in the structure. Along the [010], [101], and [110] directions, the structure has partially overlapping odd 11-ring channels in the three directions. Compared with QD-2 and QD-3, which contain only one-dimensional 11-ring channels, the presence of intersecting 11-ring channels in the structure is noteworthy. Inorganic cations, such as K^+ and NH_4^+, have also been used in the synthesis of two open-framework aluminum borates, $K_2[AlB_5\ O_{10}]\cdot 4H_2O$ and $(NH_4)_2[AlB_5O_{10}]\cdot 4H_2O$. The two compounds are isomorphous and have three-dimensional structures with a diamond topology. The third class of structure-directing agents used in the solvothermal reactions is transition metal complexes. Based on the host–guest symmetry-matching concept, the employment of transition metal complexes as templating agents is promising for the synthesis of new open-framework compounds, because these templating agents have unique spatial configurations, various charges, different flexibilities, and hydrogen-bonding sites. Furthermore, the chiral nature of chiral metal complexes can be imprinted into the inorganic frameworks through hydrogen-bonding interactions. The first example of aluminum borate templated by a transition metal complex is $[Zn(deta)_2][Al\ (OH)(B_5O_9F)]$.[71] As shown in Figure 4c, this compound has a layered structure constructed from corner-sharing $AlO_3(OH)$ tetrahedra and B_5O_9F clusters. The compound has a 3-connected framework with a 6^3 topology (Figure 4d). It should be noted that the pentaborate cluster $[B_5O_{10-n}X_n]^{(5-n)-}$ (X = OH, F; n = 0–4) has several linkage modes. In $[M(deta)_2][B_5O_6(OH)_4]_2$ (M = Zn, Co), the $[B_5O_6(OH)_4]^-$ cluster exist in an isolated form as a result of the presence of four terminal OH groups.[72] In $B_5O_7(OH)_3Zn(tren)$, $[B_5O_7(OH)_3]$ acts as a monodentate ligand and makes one B–O–Zn connection to the adjacent Zn(tren) complex.[73] In $[Ag(py)_2][B_{10}O_{14}(OH)_4]$, the pentaborate cluster serves as a bridging ligand and connects two adjacent pentaborate clusters via *trans*-bridging oxygen atoms to form a chain-like structure.[74] In QD-2 and QD-3, the pentaborate clusters are fully deprotonated and serve as 4-connected ligands. In the case of $[Zn(deta)_2][Al(OH)(B_5O_9F)]$, the terminal F atom occupies one corner of the B_5O_9F cluster, as a result, the B_5O_9F cluster only makes three B–O–Al connections to adjacent Al atoms. Three-dimensional aluminum borates have also been prepared by the use of transition metal complexes as templating agents.[75] $[M(deta)_2][AlB_6O_{11}(OH)]$ (M = Co, Ni, Cd, Zn) have three-dimensional structures with two types of regular 11- and 13-ring channels along the [010] and [100] directions, respectively. Despite the presence of a terminal OH group, the $B_6O_{11}(OH)$ cluster condensed from the B_5O_{10} cluster and the $BO_2(OH)$ triangle acts as a new type of 4-connected building unit. A diamond topology can be produced if both $B_6O_{11}(OH)$ clusters and Al atoms are regarded as 4-connected nodes. $[M(en)_3][AlB_7O_{12}(OH)_2]\cdot(H_2O)_{0.25}$ (M = Co, Ni) is composed of linear $B_4O_6(OH)_2$ tetramers, crab-like B_6O_{12} clusters, and Al atoms. The alternating connection between crab-like B_6O_{12} clusters and Al atoms creates a layered structure parallel to the *ab* plane. These layers are stacked along the [001] direction in an ABAB sequence and are further pillared by linear $B_4O_6(OH)_2$ tetramers to lead to the formation of a three-dimensional structure. It has large, 15-ring channels running along the [110] and the [1–10] directions. To the best of our knowledge, the 15-ring channels are the largest odd-numbered-ring channels known in crystalline porous materials. Viewed along the [100] direction, it appears that the compound has elliptical 16-ring channels. In fact, the 16-ring channels are not closed. They are enclosed by two intertwined helices of the same handedness.

Recently, the boric acid flux method has been adopted by Lin and co-workers to prepare several aluminum borates (denoted as PKU-*n*).[76–79] Among these compounds, $HAl_3B_6O_{12}(OH)_4$ (PKU-1) and $Al_4B_6O_{15}$ (PKU-5) have porous octahedral frameworks containing edge-sharing AlO_6 octahedra. The largest pore sizes in the two compounds are delimited by 18 MR for PKU-1 (Figure 4e) and 10 MR for PKU-5. Interestingly, all borate groups in both structures are present in triangular geometry. For PKU-1, there are two kinds of borate groups: $BO_2(OH)$ and dimeric $B_2O_4(OH)$. The $B_2O_4(OH)$ groups are attached to the walls of 10-ring channels and almost block the channels along the [100] direction. $BO_2(OH)$ groups reside within the 18-ring channels and narrow these channels along the [001] direction. For anhydrous PKU-5, the terminal oxygen atoms on the dimeric B_2O_5 group are all coordinated to aluminum atoms. Two B_2O_5 groups block its 10-ring window completely. Since all AlO_6 octahedra share three edges and they actually act as triangular nodes, the topology of the octahedral backbone of PKU-5 is the three-connected chiral (10,3)-a network (Figure 4f). Also interesting is $HAl_2B_3O_8$ (PKU-6), which has a mixed square-pyramidal/triangular framework that contains AlO_5 square pyramids and BO_3 triangles. The linkage of edge-sharing AlO_5 square pyramids in the structure creates one-dimensional chains, which are interconnected by linear B_3O_7 units to form an open-framework network. The structure has one-dimensional 8-ring channels along the [010] direction, which is delimited by four BO_3 triangles and four AlO_5 square pyramids. Different from PKU-1, PKU-5 and PKU-6 with neutral frameworks, $[H_{18}Al_7B_{12}O_{36}]Cl_3$ (PKU-8) has an unusual cationic framework. The structure of PKU-8 consists of two building units: $[Al_7O_{24}]$ clusters and $[B_{12}O_{30}]$ rings. Each $[B_{12}O_{30}]$ ring is linked with six $[Al_7O_{24}]$ clusters through common oxygen atoms and vice versa, just like Na and Cl in the rock salt structure. A remarkable structural feature of PKU-8 is the presence of a large 12 × 8.6 Å ellipsoidal cage. The Cl^- ions are accommodated within the ellipsoidal cage, in which the disordered Cl^- ions are located.

From the viewpoint of crystal chemistry, open-framework gallium borates might be easily prepared as the structural analogues of aluminum borates. Surprisingly few studies have been reported on the synthesis of open-framework gallium borates. $K_2[GaB_5O_{10}]\cdot 4H_2O$ represents the first open-framework gallium borate with a chiral network.[80] The structure has odd 11-ring channels along the [110] direction and is closely related to the aluminum borate $K_2Al[B_5O_{10}]\cdot 4H_2O$.[69] $Ba_4Ga_2B_8O_{18}Cl_2\cdot NaCl$ has a three-dimensional open-framework structure having tunnels filled with Ba^{2+}, Cl^- ions and NaCl molecules.[81] The open framework is produced by linking B_4O_9 clusters with tetrahedrally coordinated gallium atoms. An intriguing feature of the structure is its resemblance to that of the mineral hilgardite. One of the main differences between the two structures is the oxo boron cluster, which is B_5O_{12} in hilgardite, as compared to B_4O_9 in the open-framework gallium borate. In 4-connected metal borate structures, B_4O_9 clusters are usually linked with tetravalent Ge ions to produce a net charge of –2 for the stoichiometry of $[MB_4O_9]$. When trivalent metal ions (i.e. Al^{3+} and Ga^{3+}) are used in the synthetic system, they are usually linked with relatively low-charged B_5O_{10} clusters to satisfy the local charge balance. The network based on the linkages of B_4O_9 clusters and Ga atoms is highly charged, and this charge should be balanced by highly charged guest species, such as alkaline earth Ba^{2+} cations, according to the host–guest charge-matching concept.[82,83]

6. Open-Framework Transition Metal Borates and Related Materials

Transition metals are attractive framework-building elements for several reasons. First, transition metals have flexible coordination environments. They can be coordinated by four, five, and six oxygen atoms to form extended structures in the forms MO_4, MO_5, and MO_6. Second, transition metals can be incorporated into inorganic frameworks in different valence states. For example, vanadium in trivalent, tetravalent, or pentavalent state has been found in vanadium oxide and vanadium phosphate compounds.[84,85] Furthermore, microporous compounds containing d-block elements may possess catalytic, magnetic, and photochemical properties. Despite extensive studies on open-framework metal phosphates, a limited number of transition metal borates with open frameworks are known. Harrison and co-workers reported a three-dimensional zinc borate, $Zn_4O(BO_3)_2$, built up from "fused", vertex-sharing ZnO_4 tetrahedra and BO_3 triangles. This compound has small channels with a diameter of 3.5 Å, which run along the crystallographic [100], [010], and [001] directions.[86] Rao and co-workers reported hydrothermal synthesis of a new open-framework zinc borate, $Zn(H_2O)B_2O_4\cdot xH_2O$.[87] Two cyclic building units, a Zn_3O_9 cluster and a $B_{12}O_{24}$ cluster, are involved in the framework structure. Each Zn_3O_9 cluster connects with four adjacent $B_{12}O_{24}$ clusters, and each $B_{12}O_{24}$ cluster connects with eight Zn_3O_9 clusters. The two different building units are connected in such a way that they give rise to a three-dimensional structure with 8-ring channels along the [211] direction, as shown in Figure 5a. Lately, the efforts to make open-framework zinc borates by using organic amines as the structure-directing agents resulted in the formation of four organic–inorganic hybrid frameworks under solvothermal conditions: Zn(1,2-dap)($B_4O_8H_2$), Zn(1,3-dap)($B_4O_8H_2$)·H_2O, Zn(appip)($B_5O_{10}H_3$)·H_2O, and Zn_2(1,3-dap)$_2$($B_8O_{15}H_2$).[88] Zn(1,2-dap)($B_4O_8H_2$) has a one-dimensional structure formed by the linkage of $B_4O_7(OH)_2$ clusters and Zn(1,2-dap) fragments. Each $B_4O_7(OH)_2$ cluster shares two corner oxygen atoms with an adjacent tetrameric unit, forming a chain-like structure. Zn(1,2-dap) fragments are attached to the borate chain through Zn–O bonds and compensate the negative charge of the borate chain. Zn(1,3-dap) ($B_4O_8H_2$)·H_2O and Zn(appip)($B_5O_{10}H_3$)·H_2O have layered structures with borate chains linked by zinc complexes. Zn_2(1,3-dap)$_2$ ($B_8O_{15}H_2$) has a three-dimensional structure. Each B_4O_8(OH) cluster shares three corner oxygen atoms with an adjacent tetrameric unit, forming a layered structure with 12 MR windows. The borate layers are linked by Zn(1,3-dap) fragments through Zn–O bonds to form a three-dimensional hybrid framework.

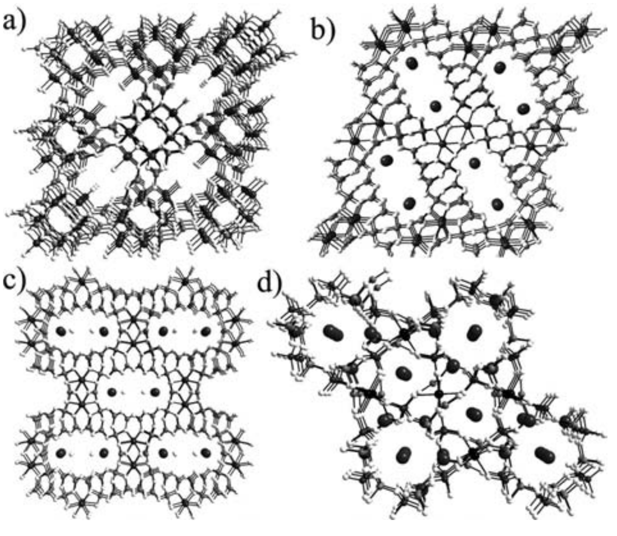


Figure 5. (a) The three-dimensional structure of Zn(H_2O)-B_2O_4·xH_2O has 8-ring channels along the [211] direction. (b) The three-dimensional structure of $Na_2Co_2B_{12}O_{21}$ has 12-ring channels along the [001] direction. (c) The three-dimensional structure of $MCuB_7O_{12}$·nH_2O has 14-ring channels along the [010] direction. (d) The three-dimensional structure of $Na_2[MB_3P_2O_{11}(OH)]$·$0.67H_2O$ has 12- and 6-ring channels along the [001] direction.

By reaction of CoB_4O_7 and borax at high temperature, a new cobalt borate, $Na_2Co_2B_{12}O_{21}$, with a tunnel structure templated by Na^+ cations was prepared and characterized.[89] Three borate building blocks, BO_3 triangles, B_3O_7 and B_4O_9 clusters, are observed in the structure. The BO_3 triangles act as bridging ligands between B_3O_7 and B_4O_9 clusters. Each B_3O_7 cluster shares four corner oxygen atoms with two B_3O_7 clusters, one BO_3 triangle, and one B_4O_9 cluster. Each B_4O_9 cluster shares four corner oxygen atoms with two B_3O_7 clusters and two BO_3 triangles. The connectivity between these building units creates a three-dimensional borate structure with 10- and 12-ring channels along the [010] direction. The octahedrally coordinated cobalt ions are encapsulated in the 10-ring channels through strong Co–O bonds, leaving the 12-ring channels occupied by extraframework Na^+ ions (Figure 5b). The cross-sectional dimensions of the elliptic 12-ring channel are 4.5 × 8.8 Å (atom to atom).

Recently, a new three-dimensional open-framework copper borate, $MCuB_7O_{12}$·nH_2O (M = Na, K), was prepared by the boric acid flux method.[90] At first glance, it seems that the compound has a similar structure with $Na_2Co_2B_{12}O_{21}$. Careful analysis of the two structures indicates that the two compounds are constructed from different borate building units and they have different pore sizes. $MCuB_7O_{12}$·nH_2O contains two types of borate building blocks, BO_3 triangles and B_3O_7 clusters. Each B_3O_7 cluster shares three corner oxygen atoms with three adjacent B_3O_7 clusters, forming a layered structure parallel to the *ab* plane. The borate layers are further linked by BO_3 triangles to give rise to a three-dimensional borate framework with 10-ring and 14-ring channels along the [010] direction. The 10-ring channels are occupied by octahedrally coordinated Cu ions, and the 14-ring channels are occupied by alkaline metal cations and water molecules (Figure 5c). The 14-ring channel, delimited by four BO_4 tetrahedra and ten BO_3 triangles, has dimensions of 7.3 × 9.5 Å (calculated from the oxygen-to-oxygen distance across the window). After the removal of water molecules by heating the sample up to 300 °C, the framework structure remains stable.

The use of borate and phosphate groups in the construction of open-framework structures leads to the synthesis of a large number of new compounds.[91–94] Interestingly, most three-dimensional borophosphate structures are phosphate-rich with B/P ratios not larger than 1. Borate-rich borophosphates usually have one-dimensional chain structures.[95] $Na_2[MB_3P_2O_{11}$ (OH)]·$0.67H_2O$ (M = Mg, Mn, Fe, Co, Ni, Cu, Zn) are a series of borate-rich borophosphates with open frameworks.[96] They are isostructural to each other and consist of MO_6 octahedra, PO_4 tetrahedra, and B_3O_7(OH) clusters. Viewed along the [001] direction, two kinds of channels can be found as shown in Figure 5d. One is the large 12-ring channel delimited by six BO_4 tetrahedra and six PO_4 tetrahedra. The other is small 6-ring channel formed by three MO_6 octahedra and three PO_4 tetrahedra. Another borophosphate framework with a B/P ratio of 3:2 is $Na_5(H_3O)[M^{II}_3\{B_3O_3(OH)\}_3(PO_4)_6]$·$2H_2O$ (M^{II} = Mn, Co, Ni) (denoted as MBPO-CJ25).[97] The three compounds possess isostructural three-dimensional open-framework structures with 12-ring channels running along the [010] directions. The connectivity of strictly alternating MO_6 octahedra and PO_4 tetrahedra produces layered networks with the famous Kagomé topology. The metal phosphate layers are parallel to the *ab* plane and they are further linked by B_3O_7(OH) clusters to give rise to a three-dimensional structure. The structure exhibits high thermal stability and it can be kept intact upon calcination at 550 °C for M = Ni.

7. Open-Framework Actinide Borates

Open-framework actinide-containing compounds exhibit diverse structures due to the high coordination numbers and the variety of coordination geometries adopted by actinide elements. During the past years, a large number of actinide-containing compounds with layered and three-dimensional structures have been prepared under hydrothermal conditions.[98–100] These materials are typically based on an anionic framework in which the charge is balanced by extraframework cations that are located in the free space surrounded by the anionic portions. For example, $Li[(UO_2)B_5O_9]\cdot H_2O$ (LiUBO-1) has an anionic three-dimensional framework based on uranyl borate sheets linked by BO_3 triangles.[101] The uranyl borate sheet can be understood as a polyborate layer within 9-ring windows encapsulating linear uranyl groups, UO_2^{2+}. As a result, the uranium atom has a rare hexagonal bipyramidal coordination environment, UO_8. The adjacent uranyl borate layers are further linked by BO_3 triangles to form a three-dimensional structure with open cages. The lithium cations are located between two neighboring BO_3 triangles in the structure, and H_2O molecules reside in the open cages. In an effort to understand the crystallized portions of vitrified nuclear waste, a three-dimensional open-framework thorium borate, $[ThB_5O_6(OH)_6][BO(OH)_2]\cdot 2.5H_2O$ (NDTB-1) was prepared and characterized.[102] This compound has an unusual cationic framework in which water molecules and borate anions reside within its large channels running along the [110] direction. Its structure consists of twelve-coordinated Th^{4+} ions, BO_3 triangles, and BO_4 tetrahedra. The borate units are polymerized and form $B_{10}O_{24}$ (4Δ+6T) clusters that bridge between the Th^{4+} ions to form a supertetrahedral framework.

8. Selected Properties of Open-Framework Borates

Microporosity is one of the most common properties for open-framework inorganic solids. For example, the nitrogen adsorption isotherm of an open-framework aluminum borate, PKU-1, indicates that this compound is a characteristic microporous material with a high BET surface area of $340\ m^2 g^{-1}$. It exhibits a maximum uptake of about $71.4\ cm^3$ of nitrogen per gram of sample. In comparison, PKU-5 has a smaller pore size and its free space is rather small (the BET surface area is about $48\ m^2 g^{-1}$). The microporous nature of PKU-1 indicates that this material may be a good heterogeneous catalyst for the selective oxidation of styrene. To improve the acidity and redox properties, a considerable amount of Cr can be incorporated into the framework of PKU-1.[103] The Cr-PKU-1 catalyst shows significant catalytic activity (conversion 53.7%) and styrene epoxide selectivity (40.2%) under mild conditions.

Open-framework borates usually contain extraframework cations in their channels, which may be exchanged by other cations under certain conditions. For example, an open-framework cobalt borate, $Na_2Co_2B_{12}O_{21}$, contains mobile Na^+ cations in its 12-ring channels. By heating the crystalline sample of $Na_2Co_2B_{12}O_{21}$ in a large excess of molten $LiNO_3$ at 280 °C for four days, all Na^+ cations can be exchanged by Li^+ ions. Interestingly, only 45 to 65% of inorganic cations (i.e. Na^+ or K^+ ions) in the 14-ring channels of $MCuB_7\ O_{12}\cdot nH_2O$ can be exchanged by smaller Li^+ ions in a similar ion-exchange process, despite the larger channel sizes of $MCuB_7O_{12}\cdot nH_2O$ relative to $Na_2Co_2B_{12}O_{21}$. Recently, an open-framework thorium borate NDTB-1 with a cationic framework was successfully isolated. Interestingly, the borate anions within its channels can be exchanged by some colored anions, such as MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, ReO_4^-, and TcO_4^-. When as-synthesized crystals of NDTB-1 are immersed in a diluted solution of TcO_4^- for 36 h, they can uptake about 72% of the radioactive anions.

Transition metal compounds with the Kagomé topology are of current interest for their magnetic properties such as geometric magnetic frustration. For the open-framework structure of MBPO-CJ25, the presence of a metal phosphate layer with Kagomé structure is noteworthy. The temperature dependence of the magnetic susceptibilities of these compounds were measured in the temperature range 4–300 K with an applied field of 1000 Oe. The susceptibility obeys the Curie–Weiss rule [$\chi_m = C/(T - \theta)$] over the measured temperature range. The negative Weiss constants for these compounds imply a weak antiferromagnetic interaction between the metal centers. Although concentrated Kagomé networks exhibit spin frustration, the absence of spin frustration in this structure may be attributed to the larger distance between the adjacent metal atoms.[97]

Photoluminescence of open-framework borates has also been examined at room temperature. Three-dimensional open-framework aluminum borates usually exhibit blue fluorescence emission centered at about 490 nm. It is noteworthy that the photoluminescence of $(H_2en)_2(Hen)_2B_{16}O_{27}$ can be modified from blue to white by a simple heat-treatment process. After heat treatment of the organically templated borate at 250 °C, the sample displays a broad visible photoluminescent spectrum that appears white to the eye. It has an external photoluminescent quantum yield of about 14.3%. Since no metal activator ions exist in the sample, the self-activating photoluminescence may originate from structural defects caused by heat treatment.

Open-framework borates with noncentrosymmetric structures may have interesting second-order nonlinear optical properties. Second harmonic generation (SHG) measurements, carried out on the powder samples by the Kurtz-Perry method at room temperature, reveal that open-framework aluminum borates templated by organic or inorganic cations, such as $[Al(B_4O_9)(BO)]\cdot H_2en$, $[Al(B_4O_9)(BO)]\cdot H_2dap$, $K_2[AlB_5O_{10}]\cdot 4H_2O$; and $(NH_4)_2[AlB_5O_{10}]\cdot 4H_2O$, display a moderate to strong SHG response that is about 2.0 times that of KDP (KH_2PO_4) powder, whereas the SHG signals for aluminum borates templated by transition metal complexes are relative weak and are about 0.1–1.7 times that of KDP powder. For example, the intensity of the green light (frequency-doubled output: λ = 532 nm) produced by the powder sample of $[Zn(deta)_2][Al(OH)(B_5O_9F)]$ exhibits an SHG efficiency that is approximately 0.1 times that of KDP powder.

9. Conclusions

A number of crystalline open-framework boron oxides and metal borates have been synthesized and structurally characterized. These borate-based structures frequently contain four-connected oxo boron clusters, such as B_3O_7, B_4O_9, and B_5O_{10} polyanions, as their building units. Oxo boron clusters can be organized into three-dimensional zeolitic frameworks by metal ions or through common oxygen atoms. Despite the fact that even-numbered-ring channels dominate in zeolite structures, the presence of large odd-numbered-ring channels in aluminum borate frameworks is noteworthy. Also interesting is the appearance of helical channels in open-framework borate systems. By using different structure-directing agents with various size and shape, the pore apertures of open-framework borates can be effectively modulated. In addition, the use of two types of amines as the structure-directing agents may favor the formation of different framework structures.[104] The coexistence of different oxo boron clusters in the same crystalline framework provides another exciting possibility to tune the framework structures. It should be possible to combine oxo boron clusters with other oxo anions, such as oxo germanium clusters, to produce novel microporous materials. By adopting new synthetic strategies, such as the fluoride route and the ionothermal method, new open-framework metal borates may be synthesized in the near future.

The synthesis of new open-framework borate materials is an exciting and promising field. The main challenge of this research is to synthesize new microporous materials with desired structures and functionalities by design, because little is known about their crystallization mechanisms. The use of various techniques, such as in situ NMR, energy-dispersive X-ray diffraction, and small-angle X-ray scattering, may help to understand the formation processes of open-framework structures. In addition, computational methods exhibit great potential in contributing toward the synthesis of target structures with specific channels.[105]

Acknowledgments

We thank the National Natural Science Foundation of China (Z.-E. L., grant 20801037; G.-Y. Y., grants 20725101, 50872133, 20821061), and the National Program on Key Basic Research Project (973 Program, grant 2011CB932504) for supporting this work.

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Received: March 18, 2011