PKU-5: An Aluminoborate with Novel Octahedral Framework Topology

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Abstract: A new anhydrous aluminoborate $Al_4B_6O_{15}$ (PKU-5) has been synthesized in a boric acid flux in a closed system at 350 °C. PKU-5, which crystallizes in the space group $R3$ with the lattice constants $a=11.43398(9)$ and $c=6.48307(5)$ Å, consists of Al octahedra and triangularly coordinated boron. The Al octahedron adopts the (10,3)-a network, in which each octahedron shares three edges with the neighboring octahedra forming ten-membered-ring channels. The octahedral backbone in PKU-5 can be considered as a primary octahedral framework topology and, setting out from the structures of the aluminoborates (PKU-1 and PKU-5), we propose construction rules for the octahedral frameworks. There are two types of connections for edge-sharing octahedra in porous frameworks, *trans* and *cis* type, by which various microporous octahedral frameworks of different topologies can be constructed. The borate groups share oxygens with the Al octahedral frameworks forming two kinds of three-membered-ring units consisting of two octahedra and one triangle (2Al+B) and one octahedron and two triangles (Al+2B), respectively.

Keywords: aluminum · borates · microporous materials · structure elucidation

Introduction

Zeolites, in which tetrahedrally coordinated atoms are covalently linked into porous frameworks, are of interest for applications ranging from catalysis to adsorption and ion exchange and thus have been extensively studied.[1–7] In addition to aluminosilicates, many other systems, such as aluminophosphates and germanium oxides, were successfully synthesized with the zeolite structures. Recently intense research was focussed on synthesis of new materials with large open frameworks.[8–11] Beside the tetrahedral systems,[12] great efforts have been devoted to include nontetrahedral atoms. This strategy yielded a number of tetrahedra/octahedra mixed porous frameworks, such as ETS-4, ETS-10 and so forth.[13–16] Some of these phases have large openings up to 24-memebered ring (such as NTHU-1).[10,11] In these structures tetrahedra and octahedra share corners forming porous frameworks, and their structural principle is more or less similar to zeolites.

It is well known that octahedra may also share edges or faces forming extended structures. Such connections are often seen in condensed solid-state compounds; however, those connections are not common in the microporous structures. A typical example of purely octahedral porous frameworks is the todorokite family,[17–19] initially found as manganese oxide minerals in deep oceans. In these compounds the Mn octahedra share six edges forming rock salt blocks, which are further interconnected by sharing corners (rutile type connection) forming one-dimensional tunnel framework. The premeditated valance variation of the Mn^{IV} cations makes these octahedral molecular sieves attractive as redox catalysts and the materials used in batteries and chemical sensors. The natural-occurring wightmanite, $Mg_5O(OH)_5BO_3$,[20,21] also contains an octahedral framework with a one-dimensional tunnel structure. The BO_3 groups link to octahedra and compensate the negative charge of the framework. Recently, a microporous compound with 24-rings (VSB-5)[11] has been reported to contain octahedral framework in which the NiO_6 octahedra share faces, edges, and corners. This material contains Ni^{II} and Ni^{III} and exhibits interesting hydrogenation catalytic properties. These materials provide a way of accommodating the metal ions that can only be six-coordinate into microporous materials; this may bring new catalytic, electronic, and magnetic properties to microporous materials.

Lehmann et al.[22] studied aluminoborate system many years ago aimed at searching for compounds analogous to the aluminosilicate zeolites. They identified three com-

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pounds with B/Al ratios of 3:1, 2:1 and 2:3, but no further characterization was reported. Xu et al.[23–25] studied aluminoborate systems under hydrothermal synthesis and revealed a series aluminoborate phases. However the further study was obstructed by difficulty of growing crystals suitable for structure determination. Recently we carried systematic synthesis of polyborates by using boric acid as a flux.[26–28] By applying this synthesis method to the aluminoborate system, we obtained a novel aluminoborate $HAl_3B_6O_{12}(OH)_4$ (PKU-1).[29] The structure of PKU-1 consists of a microporous Al octahedral backbone with 18- and 10-rings. In this paper, we reported a novel anhydrous aluminoborates, $Al_4B_6O_{15}$ (PKU-5), whose backbone framework is constructed by solely three-connected edge-sharing octahedra. In addition, setting out from the known edge-sharing octahedral frameworks, we also proposed rules that govern the topologies of porous edge-sharing octahedral frameworks.

Results

Synthesis reaction: PKU-5 was initially obtained by decomposition of the partially Cr-substituted PKU-1 at 770 °C. Systematic synthetic studies revealed that PKU-5 can also be obtained by direct reaction of $AlCl_3$ with excess boric acid in closed system at 350 °C [Eq. (1)]:

$$4\,AlCl_3 + 6\,H_3BO_3 \xrightarrow{350\,^{\circ}C} Al_4B_6O_{15} + 3\,H_2O + 12\,HCl \tag{1}$$

The high reaction temperature is crucial to PKU-5. At lower temperatures (< 250 °C) other aluminoborates, such as PKU-1, were formed. PKU-5 is stable up to 800 °C. At 900 °C it transforms to a known condensed aluminoborate $Al_4B_2O_9$. SEM micrographs show that the crystal size of the PKU-5 sample obtained from boric acid flux (Figure 1a) is quite small with hexagonal-shaped planar morphology. Meanwhile the PKU-5 sample obtained by thermal decomposition retained the needle-shape morphology of the PKU-1 as shown in Figure 1b. The needles are not single crystals, but are composed of large number of small particles in size of about few nanometers.

Crystallographic characterization: Crystals of PKU-5 obtained from the boric acid flux are too small for single-crystal structure determination. The crystallographic study was therefore performed by an ab initio method using powder X-ray diffraction data. Selected 26 reflections were used as input to the powder diffraction indexing program TREOR90,[30] which produce a trigonal cell: $a = 11.43398(9)$ and $c = 6.48307(5)$ Å. The systematic absences narrow the possible space groups to $R\bar{3}m$, $R\bar{3}$, $R3m$, $R32$, and $R3$. The structure of PKU-5 was established in the space group $R3$ by using ab initio method in TOPAS.[31] All of the atoms could be readily located, and the structure was refined with Rietveld techniques. A six-term Chebyshev polynomial and a $1/2\theta$ term were used to model the background. The peak shapes were modeled with the pseudo-Voigt function. Soft restraints were applied to the thermal displacement parameters of the atoms. The final refinement converged to $Rp = 0.025$, $Rwp = 0.032$, and GOF = 1.83. Figure 2 illustrates the Rietveld fit of the diffraction pattern for the PKU-5 obtained from boric acid flux. The atomic parameters, the selected bond lengths and angles of the PKU-5 structure are listed in Tables 1 and 2. The PKU-5 sample was also examined with high-resolution transmission elctron microscopy (HRTEM) and electron diffraction (ED) (Figure 3). The

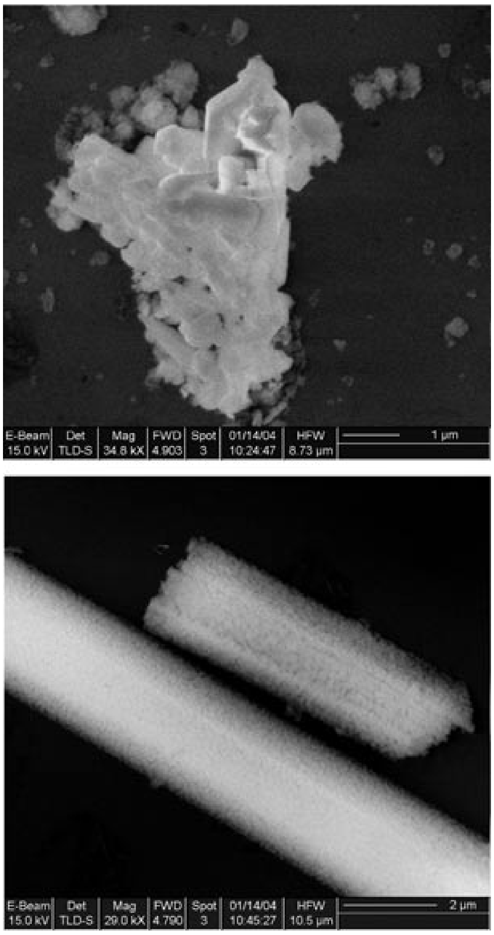

Figure 1. SEM micrographs of the PKU-5 samples synthesized a) from boric acid flux at 350 °C (bar = 1 µm) and b) by thermal decomposition of Cr-substituted PKU-1 at 770 °C (bar = 2 µm).

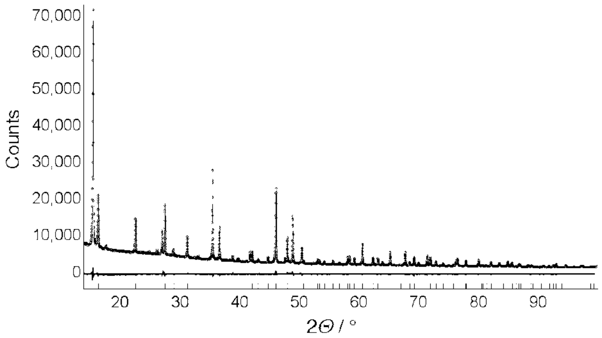

Figure 2. Rietveld fit to the powder X-ray diffraction pattern of $Al_4B_6O_{15}$ (PKU-5). The symbol ● represents observed pattern and the solid line is the calculated pattern; the marks below the diffraction patterns are the reflection positions and, the difference curve is also shown below the diffraction curves.

Table 1. Refined atomic parameters of $Al_4B_6O_{15}$ (PKU-5).[a]

site	*x*	*y*	*z*	B_{eq}
Al1	0	0	0	0.73(29)
Al2	0.97702(37)	0.23442(45)	0.9426(10)	0.80(27)
O1	0.79868(59)	0.62563(64)	0.0982(12)	0.45(32)
O2	0.80273(65)	0.49487(60)	0.8039(16)	0.44(29)
O3	0.82383(66)	0.43333(66)	0.1518(11)	0.40(30)
O4	0.70812(55)	0.49220(67)	0.4709(14)	0.40(31)
O5	0.93061(78)	0.31519(68)	0.7414(10)	0.40(35)
B1	0.7235(12)	0.5254(11)	0.6706(17)	0.80(36)
B2	0.8078(12)	0.5230(12)	0.0145(17)	0.80(32)

[a] Space group: *R*3 (No. 146); lattice constants: $a = 11.43398(9)$, $c = 6.48307(5)$ Å, $V = 734.017(13)$ Å^3; $\rho_{calcd} = 2.8015\,g\,cm^{-1}$, $Rp = 0.025$, $Rwp = 0.032$.

Table 2. Selected bond lengths [Å] and angles [°] in the structure of $Al_4B_6O_{15}$ (PKU-5).

Al1–O4 (×3)	1.860(8)	B1–O4	1.336(14)
Al1–O3 (×3)	1.967(6)	B1–O5	1.386(18)
Al2–O5	1.824(10)	B1–O2	1.416(17)
Al2–O1	1.859(8)	B2–O1	1.344(8)
Al2–O4	1.877(11)	B2–O2	1.397(10)
Al2–O5	1.877(9)	B2–O3	1.437(16)
Al2–O1	1.932(7)		
Al2–O3	1.936(10)		
O4-B1-O5	119.1(11)	O1-B2-O2	125.7(3)
O4-B1-O2	117.5(9)	O1-B2-O3	116.5(3)
O5-B1-O2	122.0(13)	O2-B2-O3	117.8(3)

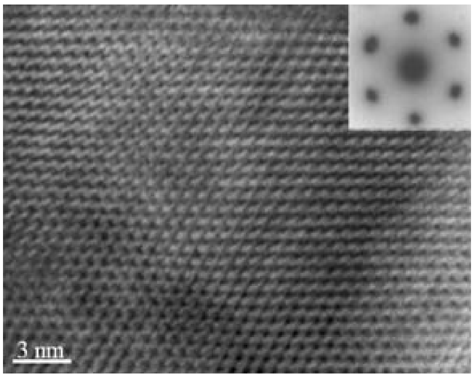

Figure 3. The high-resolution TEM image of PKU-5 in the [001] zone; The electron diffraction pattern (ED) is shown as an insert at the upper-right corner.

ED pattern exhibits typical threefold symmetry and the HRTEM shows an hexagonal pattern; these correspond to the crystal structure of PKU-5 reasonably well. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax:(+49) 7247-808-666; e-mail: crysdata@fiz.karlsuhe.de) on quoting the depository number CSD-413650.

The structure of PKU-5: The structure of PKU-5 can be considered as composed of Al atoms and B_2O_5 groups. The two boron atoms are all triangularly coordinated by oxygen atoms, with the B–O distances ranging from 1.336 to 1.437 Å, and share a corner forming the polyborate B_2O_5 group (Figure 4). The oxygen atoms, except the O2 that bridges the two triangular boron atoms, are all coordinated to the aluminum atoms in octahedral geometry. Thus an alternative way of describing the PKU-5 structure is to consider it as consisting of Al octahedral backbone $[Al_4O_{12}]$ and borate groups. The Al octahedra share edges forming the octahedral framework backbone, while the boron and O2 atoms can be considered as being attached on the surface of Al octahedral backbone to stabilize the framework. In Figure 5 we show the structure of PKU-5 projected along the *c* axis, in which the Al-octahedral framework is emphasized by polyhedra and the B_2O_5 borate groups are expressed with balls and sticks. The Al–O bond lengths in the structure range from 1.824 to 1.967 Å, which is typical for six-coordinate aluminum atoms.

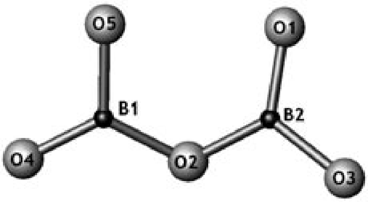

Figure 4. The B_2O_5 borate group in the PKU-5 structure.

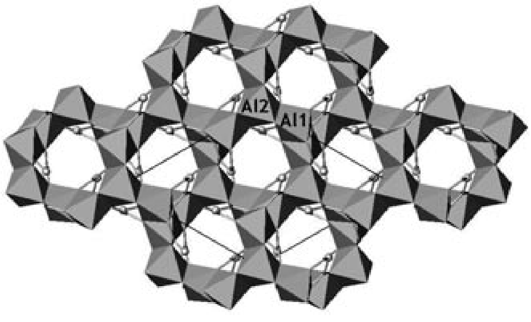

Figure 5. A projection of the structure of PKU-5 along the *c* axis. AlO_6 is expressed as octahedron in order to emphasize the framework backbone. The boron atoms and the oxygen atoms are expressed as dark and light balls, respectively.

The structure of PKU-5 contains two crystallographic independent aluminum atoms, Al1 (3a) and Al2 (9b). As far as the topology of the Al octahedral backbone is concerned, these aluminum atoms are identical, since all of the Al octahedra share three edges and act as triangular nodes. In fact the topology of the backbone framework of the PKU-5 structure is the three-connected chiral (10,3)-a network and could be described with pseudo cubic symmetry with $a_c \approx 7.9$ Å. In Figure 6 we show the skeletons of the octahedral framework projected close to the $(100)_c$ and $(111)_c$ directions of the cubic cell. Viewed down the $(100)_c$ (Figure 6a), the backbone of PKU-5 appears as octagonal-like tunnel formed by interconnection of fourfold helix chains. While along the $(111)_c$ direction, the backbone appears to trace out a honeycomb-like tunnels (Figure 6b) formed by threefold helix chains and three-connected octahedra. This three-

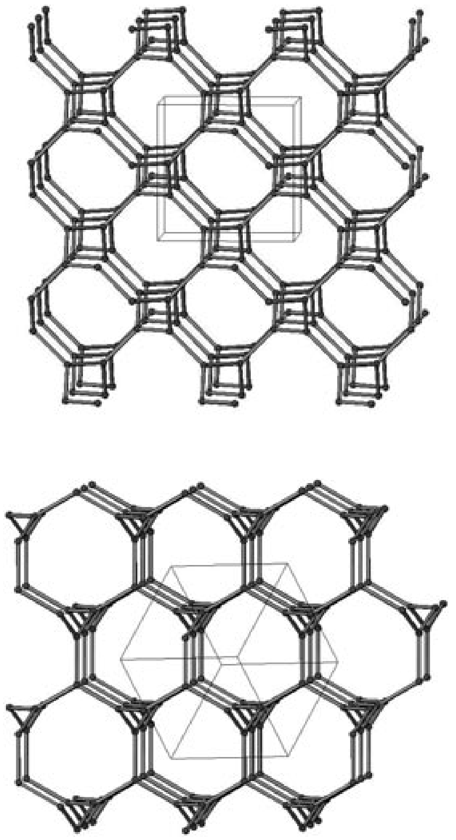

Figure 6. The octahedral backbone in PKU-5 projected close to a) $(1\,0\,0)_c$ and b) $(1\,1\,1)_c$ directions of the pseudo cubic cell.

connected chiral (10,3)-a network has been observed recently in nickel and cobalt benzenetricarboxylates.[32,35] The presence of the B_2O_5 groups compresses the backbone framework along the $(1\,1\,1)_c$ direction, hence the real structure only retains threefold symmetry. It is also worth noting that all of the octahedra share three independent edges and act as triangular-connected species in the PKU-5 structure. The backbone represents, therefore, a primary topology for the triangular-connected octahedral frameworks.

The backbone framework of PKU-5 carries high negative charge ($[Al_4O_{12}]^{12-}$) and is not stable without charge compensation. The borate groups are essential to compensate the negative charge of the octahedral framework. In the structure of PKU-5, the negative charge of the framework ($[Al_4O_{12}]^{12-}$) is compensated by the attached $[B_6O_3]^{12+}$ groups. In fact the linkage of octahedra and triangular borates is optimized in the PKU-5 structure by the fact that the oxygen atoms on the octahedral framework are all three-coordinated to boron and aluminum atoms. Meanwhile the presence of borate groups blocks partially the cavities of the framework. The fundamental octahedral ring in PKU-5 is a buckled ten-membered ring. As shown in Figure 7, the B_2O_5 groups block the ten-membered rings perpendicular to the c axis so that the effective cavity of PKU-5 is one-dimensional parallel to the c-axis (the calculated effective free-space is about 1.7 Å in diameter). The nitrogen adsorption experiment indicated that the free space of the PKU-5 structure is rather small (the BET surface area is about 48 $m^2\,g^{-1}$).

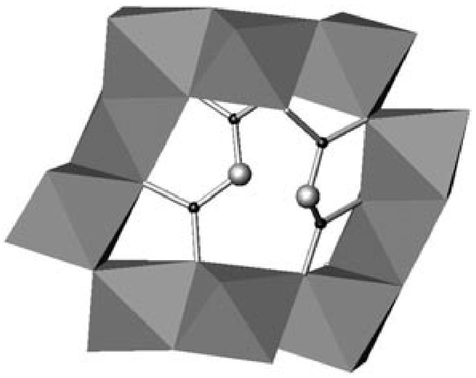

Figure 7. The ten-membered octahedra ring perpendicular to the c axis in the PKU-5 structure. The borate groups B_2O_5 block the channel completely.

Discussion

Unlike the tetrahedral frameworks, in which the tetrahedra are linked by means of sharing corners and variable T-O-T angle leads to diverse zeolite topologies, the edge-sharing connectivity of octahedra is much more rigid and thus only limited framework topologies are accessible. Restricting to the edge sharing, one can find that there are only two different kinds of connections for octahedra that can lead to three-dimensional porosity. We refer to these octahedra as *cis* and *trans* as shown in Figure 8. The *trans*-octahedron, featuring parallel sharing of the two opposite edges, may act as a girder in octahedral frameworks. The *cis*-octahedron, on the other hand, shares two edges and leaves two neighboring vertices free. These two free vertices can be further shared with additional octahedra, forming a planar triangular node (Al-Al-Al angle is close to 120°). Thus, the *cis*-octahedron may act as a node in octahedral framework. To construct an octahedral framework, one always needs the *cis*-octahedra, while the *trans*-octahedra can be used to enlarge

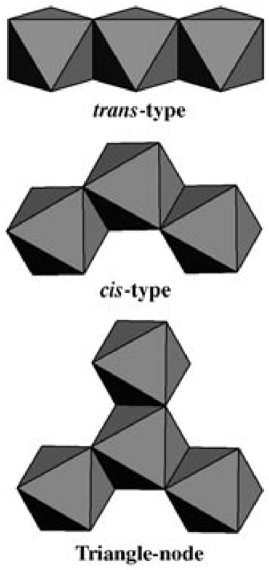

Figure 8. The *trans*- and *cis*-type connections of octahedra. The triangular node is a octahedral cluster consisting of four octahedra.

the cavity of the frameworks. Appropriate connection of these octahedral clusters may lead to various octahedral frameworks with three-dimensional tunnels. PKU-5 is an example that consists of only the *cis*-octahedra, in which each octahedron links to three neighboring octahedra forming a three-dimensional tunnel framework.

Figure 9 illustrates two examples of using the *trans*- and *cis*-octahedra to construct more complicated octahedral frameworks. Nickel glutarate[36] contains a large porous octahedral framework with 20-membered ring tunnels. The backbone framework in the nickel glutarate structure has identical topology as that in PKU-5, but with 20-membered rings and could be readily obtained by inserting a *trans*-octahedron between the triangular nodes in the PKU-5 framework. PKU-1 is also an aluminoborate ($HAl_3B_6O_{12}(OH)_4$) that contains porous Al-octahedral backbone with 10- and 18-membered windows.[29] It crystallizes in trigonal structure ($R\bar{3}$) with the lattice constants, $a = 22.0381(2)$ and $c = 7.0261(1)$ Å. PKU-1 contains threefold helix chains formed by the *cis*-type octahedra. The octahedral backbone is formed by interconnection of the *cis*-chains by *trans*-octahedra. The 18-membered windows are parallel to the c axis, while the 10-membered windows are along each of {100} directions. As can be seen in Figure 9, the octahedral framework of PKU-1 can be considered as replacing the triangle-nodes in PKU-5 with *trans*-octahedra and then rearranging the helix chains to maximize edge-sharing. Although the octahedral framework in PKU-1 has different topology from that in PKU-5 and nickel glutarate, it is also constructed by the *cis*- and *trans*-octahedra. It is woth noting that the structural principles of todorokite (also called OMS family) are different,[17–19] although they are also constructed with octahedra. The fundamental building units in todorokite are rock salt (111) blocks, which are linked through corner-sharing (rutile-type).

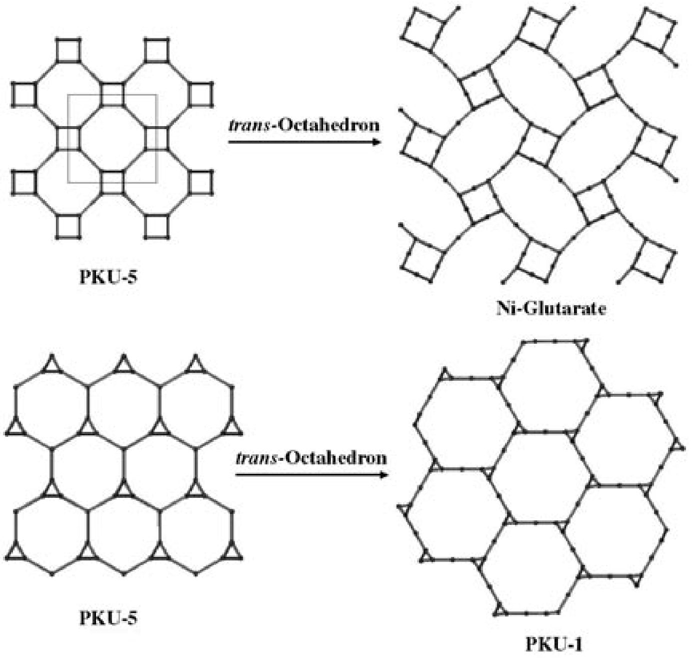

Figure 9. Construction of octahedral frameworks by *cis*- and *trans*-octahedra.

The borate groups in the structures of PKU-1 and PKU-5 are all present in triangular geometry. The preference of the triangular geometry could be understood from the three-membered ring units identified in these structures. In Figure 10, we show two types of fundamental three-membered rings, namely 2Al+B or Al+2B, respectively. The 2Al+B unit consists of two Al octahedra and one triangular borate BO_3, while the Al+2B unit is composed of one Al octahedron and a polyborate group B_2O_5. The linkage of the Al octahedra and borate groups in the structures of PKU-1 and PKU-5 is exclusively through these three-membered rings. The geometrical optimization of the three-membered rings is specially exemplified by PKU-5. PKU-5 is an anhydrous aluminoborate. The terminal oxygen atoms on the B_2O_5 group are all coordinated to Al atoms in a way that both of three-membered rings, 2Al+B and Al+2B, are formed around the B_2O_5 group.

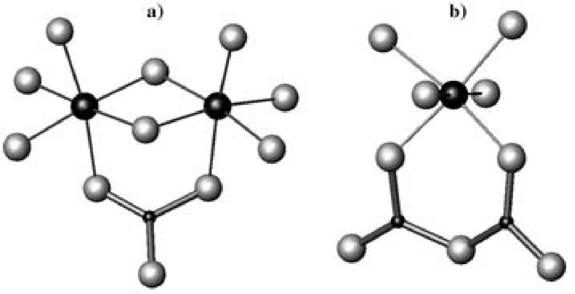

Figure 10. Three-member ring units in the structure of PKU-5: a) 2Al+B and b) Al +2B.

Conclusion

By carrying the reactions of aluminum salts in the boric acid flux, we identified a new aluminoborate, $Al_4B_6O_{15}$ (PKU-5), which contains a novel Al octahedral framework with the (10,3)-a network. Together with the previously reported PKU-1, we proposed rules that may be used to construct the structures of the aluminoborates. Firstly, all Al octahedra share edges in two different ways, that is, the *cis*- and *trans*-type connections, which can be used to construct various three-dimensional porous octahedral frameworks. The *cis*-octahedron is an essential component for the three-dimensional Al-octahedral frameworks, while the *trans*-octahedron can be used as a girder to enlarge the cavity. Secondly the triangular borate groups are preferentially in the triangle geometry, which share corners with Al octahedra forming three-membered ring units, 2Al+B and Al+2B. In addition, the borate groups are essential to compensate the negative charge of the Al octahedral frameworks.

Although the octahedral frameworks are three-dimensional in both PKU-5 and PKU-1, borate groups partially blocked the small tunnels (ten-membered ring), and thus the effective cavities are one-dimensional. To achieve effective three-dimensional cavity, one needs to design the octahedral frameworks with larger three-dimensional tunnels (>ten-membered ring). The backbone framework of nickel glutarate might be a suitable candidate for making effective three-dimensional porous aluminoborate, since it has three-dimensional 20-membered tunnels. Of course one could also use the structural principles established from the PKU-1 and PKU-5 to design other new topology for the octahedral frameworks.

Experimental Section

Synthesis of PKU-5: PKU-5 was synthesized by reaction of aluminum salts with boric acid in the boric acid flux. All starting materials used in this study were analytical grade and used as received without further purification. In a typical reaction a 50 cm^3 platinum autoclave was charged with $AlCl_3 \cdot 6H_2O$ (5 mmol), H_3BO_3 (50 mmol), and B_2O_3 (25 mmol). After being heated at 350 °C for 10 days, the solid was washed with distilled water until the residual H_3BO_3 was completely removed. The obtained product was a white powder (PKU-5). The impurity in the product is mainly another aluminoborate (PKU-6). Depending on the reaction time and temperatures, the quantity of the impurity varied from about 3–50 mol%, as estimated by powder X-ray diffraction. The sample used in the structure determination contained about 3 mol% PKU-6. PKU-5 could also be obtained by decomposition of the transition-metal-substituted PKU-1 samples. Transition-metal-substituted (about 20 atm%) PKU-1 (Cr-PKU-1 and Fe-PKU-1) were synthesized by using the boric acid flux method at 220 °C for 10 to 14 days. The transition metal nitrates were used as the starting materials. Decomposition of the Cr-substituted PKU-1 sample at about 770 °C in air for 24 h yielded an almost phase-pure product, whereas for the Fe-substituted PKU-1, $Al_4B_2O_9$ impurity was always present. The formula of PKU-5 established from structural analysis is $Al_4B_6O_{15}$, which agrees to the measured $B/Al = 1.45$ (by using ICP method). The IR spectrum indicates that the boron atoms in the compound are all triangularly coordinated (IR: $\tilde{\nu} = 1383$, 1318, 1275, 1231 cm^{-1}). The nitrogen adsorption isotherm measurement shows that the BET surface area of PKU-5 was only 48 m^{2}g^{-1}.

Analytical methods: The chemical analysis was carried out by ICP method on an ESCALAB2000 analyzer, which allowed us to determine the molar ratio of B/Al in the products. IR spectroscopy, with a Nicolet Magna-IR-750 series , was used to identify the coordination of boron atom in the structures. The electron diffraction pattern (ED) and HRTEM studies were performed on a Hitachi H-9000. The nitrogen gas sorption isotherm was measured using a Micromeretics ASAP 2010 V5.01 H on samples that had been vacuum degassed at 200 °C. Powder X-ray diffraction data were collected at room temperature on a Bruker D8 diffractometer with a curved germanium primary monochromator ($Cu_{K\alpha 1}$ $\lambda = 1.5406$ Å). Tube voltage and current were 50 kV and 40 mA, respectively. The transmission mode was used and the sample was monitored on a planar plastic film. The diffraction pattern was recorded with PSD detector with step scan size/time of 0.0144 (2θ)/30 s. The structure was solved and refined by using software package TOPAS.[31]

Acknowledgement

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