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$Ca_3Na_4LiBe_4B_{10}O_{24}F$: A New Beryllium Borate with a Unique Beryl Borate ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ Layer Intrabridged by $[B_{12}O_{24}]$ Groups

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Supporting Information

ABSTRACT: A novel beryllium borate, $Ca_3Na_4LiBe_4B_{10}O_{24}F$, has been discovered. It possesses a unique ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layer composed of two opposite parallel $[Be_4B_4O_{12}F]_\infty$ layers bridged with $[B_{12}O_{24}]$ polyborates. The linkage of $[B_{12}O_{24}]$ to other structural units is first found in anhydrous borates. In the ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layer, multiple tunnels are arranged along different directions resided by the alkali and alkaline-earth cations. The compound remains stable in an ambient atmosphere from room temperature to the melting point at 830 °C and melts incongruently.

Exploration of new crystallines structure is of perpetual interest in solid-state chemistry because it often results in new properties that may open novel applications in materials science. Borates have attracted much attention owing to their rich structural varieties.[1] A B atom is either three- or four-coordinated with O atoms to form a BO_3 triangle or a BO_4 tetrahedron. These two basic units can further link together by sharing corners or edges and construct various fundamental building blocks (FBBs), such as B_2O_5, B_3O_6, B_3O_7, etc. Borates have given rise to a lot of important applications, including laser crystals, electrode materials, and catalytic agents.[2] For instance, BaB_2O_4 (BBO),[3] LiB_3O_5 (LBO),[4] and BiB_3O_6 (BIBO)[5] are widely used as nonlinear-optical materials.

In all borate FBBs, the $[B_{12}O_{24}]$ group was first observed in hydrous borates in which it is usually linked with hydroxyl groups.[6] This group is a circle polyborate constructed by six BO_4 tetrahedra and six BO_3 triangles through vertex linkages (Figure 1a). Each BO_4 tetrahedron contributes two terminated O atoms to connect with two neighboring BO_4 groups and shares the other two corners with the BO_3 triangles that reside on the external side of the 12-membered ring. Three BO_3 triangles incline upward and the other three downward to the ring and form a flower-petal shape. According to the scheme proposed by Christ and Clark,[1a] the polyanion in the $[B_{12}O_{24}]$ group can be described as 12: 6Δ + 6T, one of the maximum numbers in the crystal-chemical classification of known borates.

Recently, the $[B_{12}O_{24}]$ groups have also been discovered in three anhydrous borates: $Li_3KB_4O_8$, $LiNa_2Sr_8B_{12}O_{24}F_6Cl$,[7a] and $Li_3NaBaB_6O_{12}$.[7b] Interestingly, contrary to their hydrous cousins, these $[B_{12}O_{24}]$ groups are isolated without linking any other group to form a quasi-molecular-type structure. The irregular shape of isolated $[B_{12}O_{24}]$ groups in general reduces the size of the tunnels or/and cavities in the framework, which would impede the potential applications of the related borates, e.g., in electronics. The elimination of the dangling bonds on the nonbonding O atoms in the external vertexes of the BO_3 group in the $[B_{12}O_{24}]$ group is a key way to connect with other suit groups to form a 2D or 3D network.

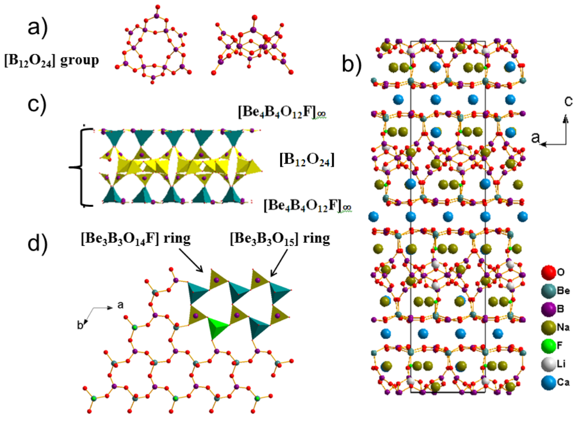

Figure 1. (a) Top and side views of a $[B_{12}O_{24}]$ group presented in borates. (b) Atomic arrangement of CNLBBF viewed along the *b* axis. The Ca, Na, Li, Be, B, O, and F atoms are shown as blue, yellow, gray, teal, violet, red, and green spheres, respectively. (c) Polyhedral view of the ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layer without the A-site cations. (d) $[Be_4B_4O_{12}F]_\infty$ layer extended in the *ab* plane. The B–O units, BeO_4 tetrahedra, and BeO_3F tetrahedra are represented by yellow, teal, and green polyhedra, respectively.

In previous studies, beryllium has been introduced into borate to eliminate the dangling bonds on BO_3 triangles.[8] In particular, Wang et al. have systematically investigated the M_2O–BeO–B_2O_3 (M is alkaline metal) ternary phase diagrams, and these outstanding researches led to the discovery of a series of new alkaline metal beryllium borates.[9] So far, quite a few beryllium borate compounds have been found, and some of them exhibit application advantages in the ultraviolet and deep-ultraviolet spectral regions.[10] In addition, the connection of the $[B_{12}O_{24}]$ group with other groups via a Be–O linkage can construct new beryl borate frameworks, which would enrich the borate structure chemistry.

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In this work, we incorporated Be atoms into the borate system and successfully synthesized a new beryllium borate, $Ca_3Na_4LiBe_4B_{10}O_{24}F$ (CNLBBF). This compound is the first anhydrous borate in which the $[B_{12}O_{24}]$ groups are connected to other groups to form a unique 2D ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layer. In the superlayer, multiple tunnels are arranged along different directions resided by the alkali and alkaline-earth cations.

CNLBBF was synthesized by a high-temperature solution reaction with a spontaneous nucleation technique, and the colorless and transparent single crystals were obtained from melting. The growth system was $Na_2CO_3/CaCO_3/LiF/BeO/B_2O_3$ with a molar ratio of 0.9:0.5:0.4:1:2. The single-crystal X-ray diffraction (XRD) data were collected and solved. The relative experimental methods and results are shown in Supporting Information section S1 and Tables S1−S4.

The structure of CNLBBF is shown in Figure 1b. It crystallizes in the trigonal space group of $R\bar{3}$, with $a = 9.3535(13)$ Å, $c = 38.053(8)$ Å, and $Z = 6$. In the symmetric unit, Na, Ca, Li, B, Be, O, and F atoms occupy two, three, one, four, two, eight, and one crystallographically unique positions, respectively. The infinite 2D ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layer is its main framework (Figure 1c). Each ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layer consists of two platelike infinite $[Be_4B_4O_{12}F]_\infty$ layers extended in the *ab* plane with opposite orientations to one another, bridged by polyborate $[B_{12}O_{24}]$ groups. The external vertexes of the BO_3 units in the $[B_{12}O_{24}]$ group connect with the $[Be_4B_4O_{12}F]_\infty$ layers to form the sandwichlike structure.

The $[Be_4B_4O_{12}F]_\infty$ layer in the *ab* plane is displayed in Figure 1d, which clearly shows the BO_3, BeO_4, and BeO_3F anionic groups with a molar ratio of 4:3:1. The triangle BO_3 groups are alternately connected with BeO_4 and BeO_3F groups to form $[Be_3B_3O_{15}]$ and $[Be_3B_3O_{14}F]$ 12-membered rings, respectively. These 12-membered rings further link together to form an infinite alveolate network perpendicular to the *c* axis. Although these 12-membered rings have been individually presented in other beryllium borates (e.g., the $[Be_3B_3O_{14}F]$ group in $NaCaBe_2B_2O_6F$[10f] and the $[Be_3B_3O_{15}]$ group in $Sr_2Be_2B_2O_7$[8b]), the assembly of both rings into one beryllium borate is first found.

The $[B_{12}O_{24}]$ groups connect the adjacent $[Be_4B_4O_{12}F]_\infty$ layers by sharing external vertexes of the BO_3 units with beryl oxide groups via a B−O−Be covalent bond. The $[B_{12}O_{24}]$ bridged units are much different from those in all other layer beryllium borates, where the relatively simple bridging units are usually presented, including BO_3, B_2O_5, and B_3O_6 groups.[11] Compared with these simple bridging groups, the $[B_{12}O_{24}]$ group is a complicated 3D polyhedron with irregular shape and results in a framework with 2D tunnels along the [100] and [110] directions. Because of the large size of the $[B_{12}O_{24}]$ group, the interlayer spacing in ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ is 9.23 Å. To our best knowledge, this is the largest interlayer spacing in all beryllium borates. As a comparison, the interlayer spacing in γ-$KBe_2B_3O_7$ with the $[B_3O_6]$ bridge group is 8.70 Å.[11]

Na and Ca atoms are located in the tunnels (Figure 2). For the three crystallographically sited Ca atoms, Ca(1), Ca(2), and Ca(3) are nine-, six-, and six-coordinated with O atoms, respectively, while for the two crystallographically sited Na atoms, Na(1) is coordinated with six O atoms and Na(2) is coordinated with five O and one F atoms, respectively. Na(1), Na(2), and Ca(3) cations are alternately located at the tunnels inside the ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layers. The Ca(2) and Ca(3) atoms reside in the interstices between the two neighboring layers. The ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ double layers are linked to one another through a Ca−O electrostatic force.

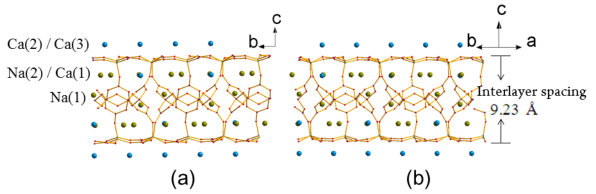

Figure 2. Beryl borate framework of the ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layer with Na and Ca atoms. The Ca and Na atoms are shown as blue and dark yellow. Views (a) along the *a* axis and (b) along the [110] direction.

In CNLBBF, the B−O bond distances of the BO_3 and BO_4 groups are in the ranges of 1.343(3)−1.386(2) and 1.448(3)−1.497(2) Å, respectively. The BeO_4 and BeO_3F groups with Be−O and Be−F distances range from 1.580(5) to 1.663(3) Å. The Ca−O bond distances range from 2.4050(14) to 2.6588(14) Å. The Na−O bond distances range from 2.2634(14) to 2.8926(16) Å, and the Na−F bond distance is 2.6542(9) Å. The Li−O bond distance is 2.065(2) Å, and the Li−F bond distance is 1.728(7) Å. All of the bond lengths are comparable to those of other reported compounds.

In addition, elemental analysis shows the presence of Ca, Na, Li, Be, and B atoms with a molar ratio of 3.1:3.7:1.0:4.0:9.6 in the title compound. This corresponds to the composition of the result determined by crystal structure and satisfies the overall charge balance of the compound. Thus, it was reasonable to define the chemical formula of the title compound.

The thermal behavior of CNLBBF was examined with a differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) thermobalance. The DSC curve shows that its melting point is about 830 °C. The TGA curve demonstrates that the compound remains stable in an ambient atmosphere varied from room temperature to 1150 °C without weight loss (Figure 3). After melting, the cooled solid remains were characterized by XRD, and it was found that the solid can be seen as an amorphous state with a weak BeO characteristic peak. The XRD results clearly reveal that this compound melts incongruently.

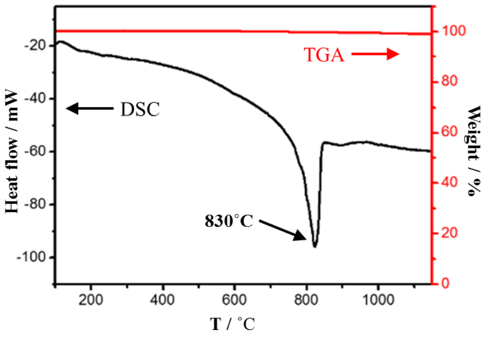

Figure 3. DSC/TGA curves of CNLBBF.

It is worth noting that the anhydrous $[B_{12}O_{24}]$ FBBs are very rare and are only found in the following three borates: $Li_3KB_4O_8$, $LiNa_2Sr_8B_{12}O_{24}F_6Cl$,[7a] and $Li_3NaBaB_6O_{12}$,[7b] considering the fact that there are thousands of anhydrous borates discovered up to now. In these three borates, the $[B_{12}O_{24}]$ groups are isolated without forming any covalent bonds with other FBBs. The isolated $[B_{12}O_{24}]$ polyborate is a wide-open ring and has the capability of capturing various small groups. For instance, various organic small molecules were reported to be captured by this ring in $Pb_6(Li_{0.65}Na_{0.19})[B_{12}O_{24}]I_{0.84}\cdot 0.168H_2O$.[6e] However, in the title compound, the plackets of the $[B_{12}O_{24}]$ ring are saturated by $[Be_4B_4O_{12}F]_\infty$ layers and form two small cavities per ring in the intralayer interstices. Because of the space limitation, in each cavity one Li atom is fixed, surrounded by one F and three O atoms. This location pattern of Li atoms is very different from that in all other anhydrous borates that contain the $[B_{12}O_{24}]$ group (Figure 4). In $LiNa_2Sr_8B_{12}O_{24}F_6Cl$, Li atoms are exactly placed in the central position of the $[B_{12}O_{24}]$ group. In $Li_3NaBaB_6O_{12}$, Li atoms are out of the $[B_{12}O_{24}]$ group and surround the group. In $Li_3KB_4O_8$, Li atoms adopt both above ways, placed in the central and outside surrounding positions. Interestingly, the above-mentioned anhydrous borates are all in the $R\bar{3}$ space group, implying that the local symmetry $\bar{3}$ of the $[B_{12}O_{24}]$ group would affect the overall symmetry of the crystal.

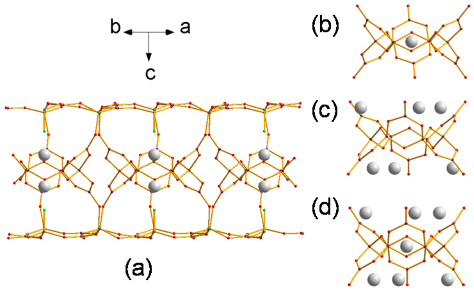

Figure 4. (a) Li atoms located in the ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layer and the location of Li cations with $[B_{12}O_{24}]$ polyborate in (b) $LiNa_2Sr_8B_{12}O_{24}F_6Cl$, (c) $Li_3NaBaB_6O_{12}$, and (d) $Li_3KB_4O_8$.

In conclusion, a new beryllium borate, CNLBBF, has been synthesized. In this compound, the main framework is a novel infinite 2D ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layer. The superlayer is composed of two neighboring infinite platelike $[Be_4B_4O_{12}F]_\infty$ layers bridged by $[B_{12}O_{24}]$ groups, which is first found in borates. Because the $[B_{12}O_{24}]$ group is a complicated polyhedron, the ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ layers have diverse 2D tunnels filled with Na and Ca atoms. Meanwhile, Li atoms are imprisoned in the cavities formed by $[B_{12}O_{24}]$ and beryl borate layers. In addition, the interlayer spacing in ${}^{2}_{\infty}[Be_8B_{16}O_{40}F_2]$ is as large as 9.23 Å, which is the largest interlayer spacing in beryllium borates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data file for CNLBBF (CCDC 931089), experimental methods, and tables and figures for crystal characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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