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A New Cesium Pentaborate with New $B_{10}O_{19}$ Building Blocks

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Supporting Information

ABSTRACT: A new polymorph of CsB_5O_8 has been synthesized. Its crystal structure was determined from single-crystal X-ray diffraction spectroscopy. The new polymorph of CsB_5O_8 with new $B_{10}O_{19}$ building blocks containing helical chains has been synthesized. The relation and differences of tunnels contained in all of the CsB_5O_8 polymorphs are discussed to show the exciting diversity of cesium pentaborate.

The crystal chemistry of borates and the structural systems of its basis differ from those of silicates, phosphates, sulfates, carbonates, nitrates, and organometallic complexes because anionic radicals in the borate class can be both boron tetrahedra and triangles.[1] The BO_3 and BO_4 groups comprise an exciting structural chemistry with a great variety of connection and arrangement patterns.[2] The phase transition of BaB_2O_4 may be the best illustration that different arrangement patterns of B−O groups significantly influence the crystal structures, leading to compounds with interesting and useful properties.[3] In the low-temperature phase β-BaB_2O_4, the B_3O_6 anionic groups arrange parallel in the same layer and rotate a little in different layers. Also, β-BaB_2O_4 is the most frequently used nonlinear-optical (NLO) material.[4] However, in the high-temperature phase α-BaB_2O_4, the B_3O_6 groups are mutually symmetrically arranged. These make α-BaB_2O_4 crystallize in the centrosymmetric space group, but it has a large birefringence.[5] The diverse structural possibilities for metal borate are one of the reasons for the research focus, and they have been widely used in phosphors, glass, and nonlinear optics.[6] In addition, some borates contain structures similar to organic compounds or nanomaterials. For example, in $NaBeB_3O_6$, three BO_3 triangles and two BeO_4 tetrahedra share their vertexes to form a nearly coplanar double six-membered ring $[Be_2B_3O_{11}]^{9-}$, which is similar to a naphthalene molecule.[7] In our recent research, $Na_{11}B_{21}O_{36}Cl_2$ and $Na_{11}B_{21}O_{36}Br_2$ with a graphene-like borate double layer are reported.[8] In the paper, cesium pentaborate with 2_1 helical chains, which is known as the basic structure of DNA, has been synthesized. The M_2O−B_2O_3 (M = Rb, Cs) systems have been investigated to search for a new compound. In the end, a new phase of CsB_5O_8 (δ-CsB_5O_8) has been synthesized. In 2002, $Cs[B_5O_6(OH)_4]\cdot 2H_2O$ was synthesized; the compound has the same formula form and fundamental building blocks (FBBs) as $KB_5O_8\cdot 4H_2O$, which was the first NLO borate.[9,10] In that paper, they dehydrated $Cs[B_5O_6(OH)_4]\cdot 2H_2O$ and obtained four different powder X-ray diffraction (PXRD) patterns of CsB_5O_8. (The structure of the fourth CsB_5O_8 modification is unknown, and no PXRD pattern is given in the paper.) In the following research, they reported two phases of the four types of CsB_5O_8 (α and γ) and summarized the entire crystal structure of MB_5O_8 (M = Rb, Cs) to give an overall description.[11] In 2007, Bubnova et al. determined the crystal structure of β-CsB_5O_8 from PXRD data using synchrotron radiation.[12] In this communication, we will report the crystal structure of δ-CsB_5O_8 for the first time. The synthesis of the title compound adds a new member to the family of alkali pentaborates and enriches the structure chemistry. Although all of the phases of MB_5O_8 contain B_5O_{10} units, each phase of CsB_5O_8 (α, β, γ, and δ) contains its own unique enclosing tunnels in the structure. We deem that it is very important and interesting to study the polymorphism in CsB_5O_8 as well as its structure transformation. Understanding the crystallographic architecture of these four polymorphs may provide new insight into controlling the B−O structure change among polymorphisms.

Polycrystalline samples of δ-CsB_5O_8 were synthesized by a traditional solid-state reaction technique with a stoichiometric mixture of Cs_2CO_3 and H_3BO_3 powders. The mixtures were heated in air between 420 and 600 °C. The room temperature PXRD patterns of the mixtures obtained at different temperatures are shown in Figure S1 in the Supporting Information (SI). There is no δ-CsB_5O_8 phase when the temperature is below 500 °C. When the reaction temperature dwells at 530 °C for 24 h, the PXRD pattern mostly resembles the pattern of the δ-CsB_5O_8 phase. However, there are some weak peaks, which are labeled by black symbols, corresponding to the patterns of α-CsB_5O_8 (PDF No. 51-1612) and β-CsB_5O_8 (PDF No. 51-1613). Then higher reaction temperatures lead to the disappearance of δ-CsB_5O_8. To ensure suitable reaction conditions, a series of reactions were carried out at 530 °C with different reaction times from 24 to 72 h (Figure S2 in the SI). When the reaction time was about 36 h, the δ-CsB_5O_8 phase disappeared. So, it is difficult to synthesize the pure phase of δ-CsB_5O_8 owing to the existence of three other phases of CsB_5O_8. When different raw reagent ratios are considered, such as superfluous H_3BO_3 or Cs_2CO_3, the pure phase of δ-CsB_5O_8 has not been obtained either.

Crystals of δ-CsB_5O_8 are grown by a spontaneous crystallization method. The title compounds crystallize in the space group *Pccn* (No. 56) of the orthorhombic system. There are three unique Cs atoms, 10 unique B atoms, and 16 unique O

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atoms in the asymmetric unit. The B−O bond lengths are normal in a BO_3 triangle and a BO_4 tetrahedron.[13] There are three types of Cs ions. The Cs1 atoms are coordinated by 8 O atoms, while Cs2 and Cs3 are in the 10-coordinate environment (Figure S3 in the SI). The inductively coupled plasma (see in the SI) and bond valence calculation in Table S1 in the SI also confirm that the formula and crystal structure of the title compound are correct.

The structure of δ-CsB_5O_8 features a 3D framework composed of CsO_n ($n = 8, 10$) polyhedra and the new FBB $B_{10}O_{19}$ (Figure 1c), which consists of eight BO_3 and two BO_4 units. According to the scheme proposed by Burns et al. and summarized by Touboul et al.,[14] the $B_{10}O_{19}$ building block can be classified as $\{10{:}\infty^3[(5{:}4\Delta + T) + 2(2.5{:}2\Delta + 0.5T)]\}$. To the best of our knowledge, it has not been reported previously in any anhydrous and hydrated borates. The $B_{10}O_{19}$ units connect with each other to form the two special 2_1 helical chains[15] containing tunnels in the [010] direction, with Cs^+ ions filling in the space to balance the charge. The cesium pentaborate with 2_1 helical chains, which is known as the basic structure of DNA, has been reported.[16,17]

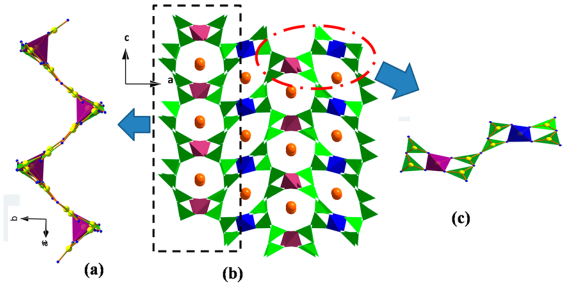

Figure 1. (a) Wave-layer structure composed of one type of B_5O_{10} in δ-CsB_5O_8. (b) Polyhedral representation of δ-CsB_5O_8 along the [010] direction. (c) FBB $B_{10}O_{19}$. Color code: BO_3, green; BO_4, purple.

By the comparison of the structures of δ-CsB_5O_8, α-CsB_5O_8, β-CsB_5O_8, and γ-CsB_5O_8, the four polymorphs all contain enclosing tunnels in the boron−oxygen anionic radical (Figures 2 and S4, S5, and S6 in the SI). However, the FBBs of δ-CsB_5O_8 are different from those in α-CsB_5O_8, β-CsB_5O_8, and γ-CsB_5O_8. In δ-CsB_5O_8, two different kinds of BO_4 groups make the FBB be $B_{10}O_{19}$, while the FBBs are B_5O_{10} in α-CsB_5O_8, β-CsB_5O_8, and γ-CsB_5O_8.

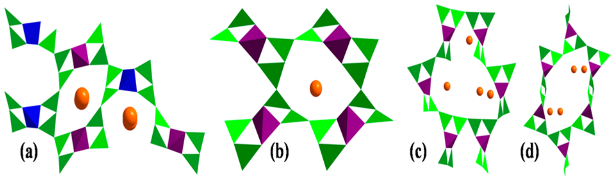

Figure 2. Enclosed tunnels of the polymorphs of (a) δ-CsB_5O_8, (b) α-CsB_5O_8, (c) β-CsB_5O_8, and (d) γ-CsB_5O_8.

All of the tunnels of different polymorphs are diverse in size and composition. At first glance, the compositions of the tunnels of α-CsB_5O_8 and δ-CsB_5O_8 are identical: two BO_4 and eight BO_3. However, the tunnels in α-CsB_5O_8 are formed by connecting four B_5O_{10}. The tunnels of δ-CsB_5O_8 consist of three $B_{10}O_{19}$. Furthermore, the tunnels are all closed in α-CsB_5O_8 but 50% open in δ-CsB_5O_8. In the aspect of arrangement, the tunnels are different from $-BO_4(BO_3)_4BO_4(BO_3)_4-$ in δ-CsB_5O_8 to $-BO_4(BO_3)_2BO_4(BO_3)_6-$ in α-CsB_5O_8. In δ-CsB_5O_8, the enclosed tunnels are almost the same as the ones in α-CsB_5O_8 (see Figures 1 and S4 in the SI). Although all of the B_5O_{10} groups are connected through the four corner O atoms, the B_5O_{10} groups are diverse in the B−O bond lengths and angles in the $B_{10}O_{19}$ group. The existence of different B_5O_{10} groups may be the reason why the two structures differ from a layer structure in α-CsB_5O_8 to a 3D framework in δ-CsB_5O_8. This makes us believe that $B_{10}O_{19}$, which differs from the connection of two B_5O_{10} groups, is a new FBB. Enclosed tunnels also exist in the 3D frameworks of β-CsB_5O_8 and γ-CsB_5O_8. Both tunnels are composed of six B_5O_{10} units.

From the structure of view, the differences of the B−O bond lengths and angles in each B_5O_{10} and the connecting angle between B_5O_{10} groups may be the primary cause of the abundant crystal chemistry. Because of this, the tunnel of the α phase can grow into the tunnels of β and γ by twisting the connected B_5O_{10} groups (the gray and red ones shown in Figure S7 in the SI). The twisted B_5O_{10} groups break the original tunnels and form new tunnels. In addition, the phase transition among polymorphs of α-CsB_5O_8, β-CsB_5O_8, and γ-CsB_5O_8 has been demonstrated by Penin et al.[13,14] In the paper, the structure of δ-CsB_5O_8 can be transformed into α-CsB_5O_8 also via the transition state of γ-CsB_5O_8 by twisting the connected B_5O_{10} groups (the gray and red ones shown in Figure S8 in the SI). The phenomenon can be observed from the solid-state synthesis (Figure S1 in the SI); the mixture turns into α-CsB_5O_8 when the temperature dwells at 600 °C. The main difference between the polymorphs lies in the bond lengths and angles. So, we calculated the bond strain index (BSI) and global instability index (GII) values (Table 1) to compare their structural strains. The results show that α-CsB_5O_8 is the most stable phase in both methods. The values of BSI of β-CsB_5O_8 and γ-CsB_5O_8 are the larger ones, which demonstrates that a larger tunnel makes a larger bond strain.

Table 1. BSI and GII Values of CsB_5O_8

	BSI	GII
α-CsB_5O_8	0.036	0.059
β-CsB_5O	0.061	0.142
γ-CsB_5O_8	0.085	0.162
δ-CsB_5O_8	0.054	0.154

In conclusion, a new polymorph, δ-CsB_5O_8, crystallizing in the orthorhombic space group *Pccn* was obtained. The 3D network consists of 2_1 helical chains and enclosed tunnels with three types of Cs^+ ions filling in the space to balance the charge. To the best of our knowledge, the FBB $B_{10}O_{19}$ has not been reported previously in any anhydrous and hydrated borates. The relation and difference of the tunnels contained in all of the CsB_5O_8 polymorphs are discussed to show the exciting diversity of CsB_5O_8. The BSI and GII values are calculated to compare their strains and stability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystallographic information files in CIF format, selected bond lengths and angles, and figures of PXRD and crystal structures. 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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