



**M₂Ca₃B₁₆O₂₈ (M = Rb, Cs): a structure analogous to SBBO
with three-dimensional open-framework layers**

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ARTICLE

$M_2Ca_3B_{16}O_{28}$ (M = Rb, Cs): a structure analogous to SBBO with three-dimensional open-framework layers

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Two isostructural alkali calcium borates, $M_2Ca_3B_{16}O_{28}$ (M = Rb, Cs) have been successfully synthesized by the flux method. The two compounds crystallize in the monoclinic space group $C2/c$ (No. 15) and feature a three-dimensional open-framework layer. The M^+ (M = Rb, Cs) cations occupy the in-layer three-dimensional micro-pores, and the Ca^{2+} cations bridge the layers to form the three-dimensional network. Based on the structure analysis, it is found that $M_2Ca_3B_{16}O_{28}$ (M = Rb, Cs) compounds have the similar structure with that of the $Sr_2Be_2B_2O_7$. In addition, spectroscopic properties and first-principles calculations have been carried out on the title compounds.

Introduction

Borates have become a research focus in the chemistry and material field owing to their abundant structure types and excellent physical properties ranging from nonlinear optical (NLO), ferroelectric, piezoelectric to semiconducting behaviors.¹⁻³ In the Periodic Table of Elements, boron is the second cycle III group element, and the outer electronic structure is $2s^22p^1$. The atomic orbitals are hybridized to planar sp^2 or three-dimensional sp^3 structures. Accordingly, the boron atoms adopt triangular BO_3 or tetrahedral BO_4 oxygen coordination in the borate crystals. These building units are connected with each other via sharing corners or edges to form some different B_xO_y fundamental building blocks (FBBs). For example, the B_3O_6 FBB of the β - BaB_2O_4 is made up of three BO_3 building units sharing three vertex oxygen atoms, the $B_{18}O_{36}$ FBB of $Sr_8MgB_{18}O_{36}$ is composed of six B_3O_7 (consisted of two BO_3 and one BO_4 building units) sharing six oxygen atom, and the $B_{11}O_{24}$ FBB of the $Ba_4B_{11}O_{20}F$ is the condensation of five BO_3 and six BO_4 building units sharing oxygen atoms.⁴⁻⁶ These FBBs are responsible for the functional properties of borates.

Over the past decades, continuous intensive studies have resulted in the development of various commercial NLO materials, such as β - BaB_2O_4 (BBO) and LiB_3O_5 , which are applicable for the generation of coherent light from ultraviolet region to near-infrared region. However, there is still lack of commercially available NLO materials for the generation of deep-ultraviolet (wavelength below 200nm) coherent light. $KBe_2BO_3F_2$ (KBBF) makes researchers' eyes turn to the beryllium borates, because the terminal O atoms can be eliminated. That makes the transmission range extend to the

deep UV region.⁷ Nevertheless, the layered growth habit of KBBF limits its application prospect. In 1995, Chen et al first report the excellent linear and nonlinear optical properties (moderate birefringence, large second harmonic generation effect and short cut-off edge) of $Sr_2Be_2B_2O_7$ (SBBO), which overcome the layered growth habit of KBBF.⁸ Thereafter, a series of beryllium borate compounds were explored, such as $Na_2CsBe_6B_5O_{15}$, $NaCaBe_2B_2O_6F$, $Na_3Sr_3Be_3B_3O_9F_4$, $NaBeB_3O_6$ and $ABe_2B_3O_7$ (A = K, Rb).⁹⁻¹² They all exhibit exciting optical properties. However, the toxicity of beryllium remains an obstacle for the practical applications of these compounds. In recent years, using the TO_4 (T = Zn, Al, or B) tetrahedra to substitute the BeO_4 tetrahedra has been taken into account to overcome the toxicity of beryllium borates. They lead to a variety of beryllium-free compounds, such as $Cs_3Zn_6B_9O_{21}$, $Rb_3Al_3B_3O_{10}F$, and $M_2Cd_3B_{16}O_{28}$ (M = Rb, Cs).¹³⁻¹⁵ In them, $Cs_3Zn_6B_9O_{21}$ consists of the targeted $[Zn_2BO_3O_2]_{\infty}$ layers with adjacent layers connected by $[B_3O_6]$ groups, $Rb_3Al_3B_3O_{10}F$ features a framework structure consisting of alveolate $[Al_3(BO_3)_3OF]_{\infty}$ layers tightly bound via Al–O and Al–F bridged bonds, with the in-layer $[BO_3]$ groups in nearly coplanar and aligned arrangement. Moreover, another beryllium-free borate, $Li_4Sr(BO_3)_2$, have been reported. Its structure features $[SrBO_3]_{\infty}$ layers bridged by NLO-active $[BO_3]$ groups.¹⁶

In this study, we intend to use the BO_4 tetrahedra to replace the BeO_4 tetrahedra exploring new compounds, and successful synthesis $M_2Ca_3B_{16}O_{28}$ (M = Rb, Cs). To the best of our knowledge, $M_2Ca_3B_{16}O_{28}$ (M = Rb, Cs) are the first compounds in the M–Ca–B–O (M = Rb, Cs) systems. Before them, no compounds have been reported in the systems. The crystal structures of $M_2Ca_3B_{16}O_{28}$ (M = Rb, Cs) feature a three-

dimensional (3D) open-framework layer. The M^+ ($M = \text{Rb}, \text{Cs}$) cations occupy the in-layer 3D micro-pores, and the Ca^{2+} cations bridge the layers to form the 3D network. The detailed structure comparison between $\text{M}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and SBBO was carried out in this report. In addition, spectroscopic properties and first-principles calculations have been carried out on title compounds.

Experimental

Reagents

Rb_2CO_3 (Xinjiang Research institute of Nonferrous Metals, 99.5%), Cs_2CO_3 (Xinjiang Research institute of Nonferrous Metals, 99.0%), CaCl_2 (Tianjin BaiShi Chemical Co., Ltd., 96.0%), CaO (Tianjin JiZhun Chemical Co., Ltd., 98.0%), H_3BO_3 (Tianjin BaiShi Chemical Co., Ltd., 99.5%), B_2O_3 (Chengdu KeLong Chemical Co., Ltd., 98.0%), PbO (Tianjin BaiShi Chemical Reagent Co., Ltd., 99.0%) are used as received.

Crystal growth

The single crystals of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ were grown from the high-temperature solutions. The solution was prepared in a platinum crucible by melting a mixture of Rb_2CO_3 , CaCl_2 , H_3BO_3 and PbO at ratios of 1:1:14:5. The mixture was melt into a transparent and clear solution in a programmable temperature electric furnace at 750 °C. The homogenized solution was then cooled rapidly. During the process of cooling, a platinum wire was intermittently dipped into the solution to try the initial crystallization temperature. When the temperature was decreased to 610 °C, there were some small crystals generating on the surface of solution. Then the solution was further cooled to 550 °C at a rate of 2.5 °C/h. Finally, it was allowed to cool to room temperature by powering off the furnace. Thus, some clear, millimeter size, colorless lamellate crystals were got. Some high quality crystals were selected for the property characterization. Similarly, the single crystals of $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ are also obtained in the similar way.

The powders samples of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ can't be synthesized by solid reaction, they were obtained by grinding the millimeter size lamellate crystals selected from the product of spontaneous crystallization, and the impurity on the surface of the crystals was washed away with water.

Powder X-ray diffraction

The powder X-ray diffraction (XRD) data of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ were carried out on a Bruker D8 ADVANCE X-ray diffractometer equipped with a diffracted beam monochromator set for $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The 2θ range was 10–70° with a scan step width of 0.02° and a fixed counting time of 1 s per step. The experimental XRD pattern of the polycrystalline powder is in good agreement with the calculated one derived from the single-crystal data, excepting for an additional peak (figure 1).

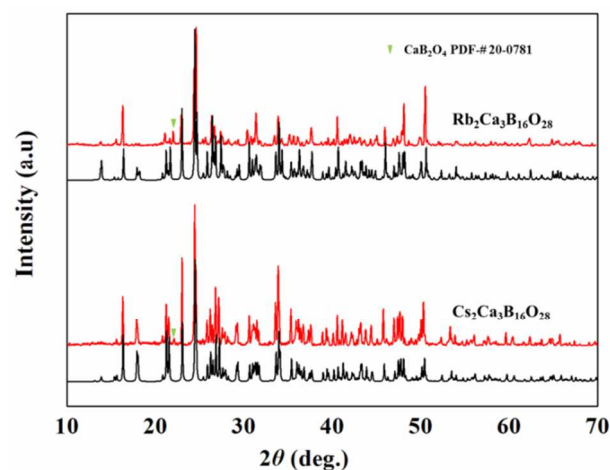


Figure 1 Experimental and calculated X-ray diffraction patterns of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$. The red curves are experimental patterns; the black ones are calculated patterns.

Structure determination

The single crystals of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ with dimensions 0.138 mm × 0.115 mm × 0.019 mm and 0.122 mm × 0.096 mm × 0.028 mm were selected for the structure determination, respectively. Their crystal structures were determined by single-crystal X-ray diffraction on a Bruker SMART APEX II CCD diffractometer at 296(2) K using monochromatic $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), and integrated with the SAINT program.¹⁷ Numerical absorption corrections were carried out using the SCALE program for an area detector. All calculations were performed with programs from the SHELXTL crystallographic software package.¹⁸ All atoms were refined using full matrix least-squares techniques, final least-squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The structure was checked for missing symmetry elements with PLATON.¹⁹ Crystal data and structure refinement information are summarized in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters of the title compounds are listed in Table S1 in the Supporting Information. Selected interatomic distances and angles are given in Table S2 in the Supporting Information.

IR spectroscopy

The infrared spectrum was recorded on a Shimadzu Affinity-1 Fourier transform infrared spectrometer in the 400–4000 cm^{-1} range, the sample was mixed thoroughly with dried KBr.

Transmittance spectroscopy

Transmittance spectral data of the $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ crystals were obtained at room temperature with a Shimadzu SolidSpec-3700DUV spectrophotometer. Data were collected in the wavelength range of 190–3300 nm.

Table 1 Crystal data and structure refinements for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$.

Empirical formula	$\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$	$\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group, Z	$C2/c$, 4	
Formula weight	912.14	1007.02
a (Å)	21.64(2)	21.703(7)
b (Å)	7.731(9)	7.717(3)
c (Å)	13.399(15)	13.456(5)
β	91.701(14)°	91.095(4)°
Volume (Å ³)	2240(4)	2253.2(13)
Density (Mg/m ³)	2.704	2.969
Theta range for data collection	2.80–27.24°	2.80–27.47°
R(int)	0.0451	0.0428
Goodness-of-fit on F ²	1.066	1.108
Final R indices	R1 = 0.0424,	R1 = 0.0493,
$[\text{F}_o^2 > 2\sigma(\text{F}_o^2)]^a$	wR2 = 0.1035	wR2 = 0.1074
R indices (all data) ^a	R1 = 0.0595,	R1 = 0.0694,
	wR2 = 0.1127	wR2 = 0.1193
Extinction coefficient	0.00061(4)	0.00207(7)
Largest diff. peak and hole (e ⁻ Å ⁻³)	0.765 and -1.520	1.888 and -3.670

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Differential thermal analysis

The thermal behaviors of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ were carried out on a NETZSCH STA 449C simultaneous analyzer under flowing nitrogen gas. The sample was enclosed in Pt crucibles and heated from room temperature to 1000 °C at a rate of 10 °C·min⁻¹.

Numerical calculation details

To investigate a deep structure-property, the electronic structures were calculated using density functional theory (DFT) implemented in the CASTEP package.²⁰ The exchange-correlation potential was calculated using the Perdew–Burke–Ernzerhof (PBE) function within the generalized Gradient Approximation (GGA) scheme.²¹ For the purpose of achieving energy convergence, the plane-wave energy cutoff was set at 800.0 eV within the Norm-conserving pseudopotential. And the numerical integration of the Brillouin zone was performed using a $2 \times 2 \times 1$ Monkhorst–Pack scheme k-point grid sampling for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$.²² The following orbital electrons were treated as valence electrons, B $2s^2 2p^1$, O $2s^2 2p^4$, Ca $3s^2 3p^6 4s^2$, Rb $4s^2 4p^6 5s^1$ and Cs $5s^2 5p^6 6s^1$. Other parameters used in the calculations were set by the default values of the CASTEP code.

Results and discussion

Structure description

$\text{M}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ (M = Rb, Cs) crystallize in the monoclinic space group $C2/c$, with $a = 21.64(2)$ Å, $b = 7.731(9)$ Å, $c = 13.399(15)$ Å, $\beta = 91.701(14)^\circ$, $Z = 4$ for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $a = 21.703(7)$ Å, $b = 7.717(3)$ Å, $c = 13.456(5)$ Å, $\beta = 91.095(4)^\circ$, $Z = 4$ for $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$. Because $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ are isostructural, only the structure of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ will be discussed in detail. In the asymmetric, there are one unique Rb atom, two unique Ca atoms, eight unique B atoms and fourteen unique O atoms. The B atoms adopt two coordination models of the planar BO_3 triangle (B1, B2, B3 and B4) and the BO_4 tetrahedron (B5, B6, B7 and B8), which condense into a boat-shaped fundamental building block (FBB) $[\text{B}_8\text{O}_{18}]$ group (Figure 2a), which can be written as $8:2[3:(\Delta+2\text{T})+(1:\Delta)]$ according to the definition given by Burns et al.²³ Further, the boat-shaped $[\text{B}_8\text{O}_{18}]$ FBB connects with six neighboring analogues to form a 2D $[\text{B}_8\text{O}_{15}]_\infty$ layer in the bc plane (Figure 2b). Seen along the b -axis, the $[\text{B}_8\text{O}_{15}]_\infty$ layer is exhibited as the part circled by the dotted blue line in Figure 2c. Two face-to-face 2D $[\text{B}_8\text{O}_{15}]_\infty$ layers are further bridged by corner-sharing O8 atoms to give the 3D open-framework $[\text{B}_8\text{O}_{14}]_\infty$ layers (Figure 2c). Interestingly, the Rb^+ cations fill the in-layer 3D holes, while the Ca^{2+} cations bridge the 3D open-framework layers to form the 3D network of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ (Figure 2d).

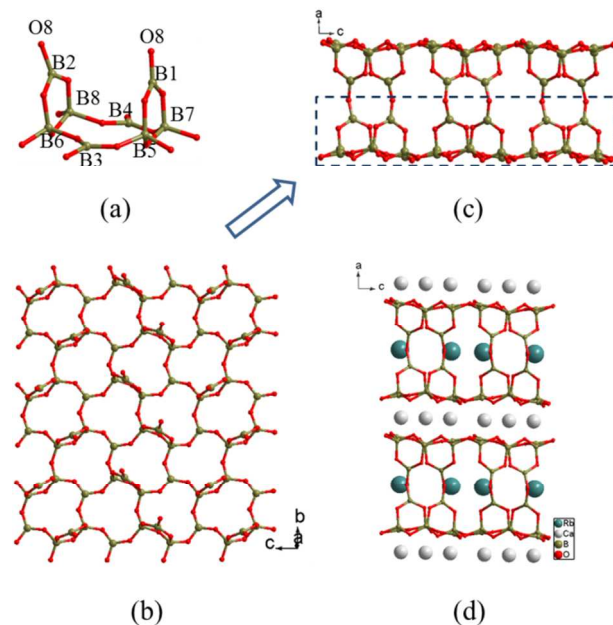


Figure 2 (a) The $[\text{B}_8\text{O}_{18}]$ group (b) The 2D $[\text{B}_8\text{O}_{15}]_\infty$ layer in the bc plane (c) the 3D open-framework $[\text{B}_8\text{O}_{14}]_\infty$ layers (d) the 3D network of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$

The Rb atom are connected with seven O atoms to form RbO_7 polyhedron and the bond length range are 2.894(4)–3.462(4) Å, and two RbO_7 polyhedra share four O atoms to form a dimer (figure S1a in the supporting information). The Ca1 and Ca2 atoms are both surrounded by eight O atoms to form Ca1O_8 and Ca2O_8 polyhedra (figure S1b in the supporting

information) and the bond length range are 2.279(3)–2.948(4) Å. The ratio of Ca1O_8 and Ca2O_8 is 1:2, and one Ca1O_8 polyhedron share O atoms with two Ca2O_8 polyhedra share O atoms to form a V-shape, which are linked end-to-end to form a chain along the b axis. The adjacent chains are antiparallel in the bc plane (figure S1c in the supporting information). However, the RbO_7 polyhedron and the CaO_8 polyhedra are not share the oxygen atom. For the B–O units, the B–O bond lengths range from 1.335(6) to 1.504(5) Å. All the bond lengths are also consistent with those observed in other compounds.²⁴⁻²⁵

In the structure of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$, B–O units determine the basic architecture of frame, and the Rb and Ca atoms maintain the charge balances. The results of bond valence calculations (Table S1 in the Supporting Information) indicate that the Rb, Ca, B and O atoms are in oxidation states of +1, +2, +3 and -2, respectively. These data demonstrate once again that the structure is correct.

$\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ has a similar stoichiometry to $(\alpha\text{-CaB}_4\text{O}_7)_4$ and $(\text{Rb}_2\text{B}_4\text{O}_7)_4$, and from the formula, $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ seems to be the compound in which two Rb atoms substitute one Ca atom of $(\alpha\text{-CaB}_4\text{O}_7)_4$ or three Ca atoms substitute six Rb atoms of $(\text{Rb}_2\text{B}_4\text{O}_7)_4$.²⁶⁻²⁷ Coincidentally, the FBBs of $(\alpha\text{-CaB}_4\text{O}_7)_4$ and $(\text{Rb}_2\text{B}_4\text{O}_7)_4$ are also $[\text{B}_8\text{O}_{18}]$ group, however, the three compounds all exhibit different connect mode. In $(\alpha\text{-CaB}_4\text{O}_7)_4$, the $[\text{B}_8\text{O}_{18}]$ group is composed of one $[\text{B}_3\text{O}_7]$ group and one $[\text{B}_4\text{O}_9]$ group bridged by one $[\text{BO}_4]$ group and can be written as $8\cdot[4:(2\text{T}+2\Delta)+1\cdot\text{T}+3:(\text{T}+2\Delta)]$ (figure S2a in the supporting information). While in $(\text{Rb}_2\text{B}_4\text{O}_7)_4$, the $[\text{B}_8\text{O}_{18}]$ group can be seen as one $[\text{B}_3\text{O}_8]$ group and one $[\text{B}_4\text{O}_9]$ group bridged by one $[\text{BO}_3]$ group, which can be written as $8\cdot[4:(2\text{T}+2\Delta)+1\cdot\Delta+3:(2\text{T}+\Delta)]$ (Figure S2b in the supporting information).

Comparing the structures with SBBO

What is interesting is that the framework of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ is similar to that of SBBO. In the asymmetric unit of SBBO, there are two unique Sr atoms, one unique Be atom, one unique B atom and two unique O atoms. Both B and Be atoms have only one kind of coordination environment, the planar BO_3 triangle and the BeO_4 tetrahedron, respectively. Three BO_3 triangles and three BeO_4 tetrahedra share six O atoms to form the cricoid $[\text{Be}_3\text{B}_3\text{O}_{15}]$ unit. Similar to $\text{M}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$, the cricoid $[\text{Be}_3\text{B}_3\text{O}_{15}]$ unit was connected with six neighboring analogues to form a 2D layer in the ab plane (Figure 3a). Two face-to-face 2D layers are further bridged by corner-sharing O2 atoms to give 3D open-framework layers. Interestingly, Sr1 cations are located in the porous layers, while Sr2 cations are found in the interlayers (Figure 3b).

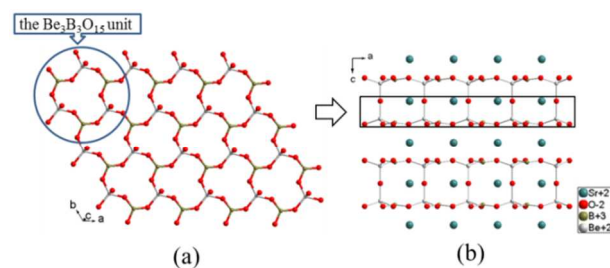


Figure 3 (a) The 2D $[\text{Be}_3\text{B}_3\text{O}_{15}]_\infty$ layer in the ab plane (b) The 3D network of SBBO.

Compounds like $\text{Na}_2\text{Ti}_2\text{B}_{10}\text{O}_{17}$, $\text{M}_2\text{Cs}_2\text{B}_{10}\text{O}_{17}$ ($\text{M} = \text{Na}, \text{K}$), and $\text{Na}_2\text{B}_{10}\text{O}_{17}\cdot\text{H}_2\text{O}$ (the four compounds are isostructural) also contain a 3D open-framework layer.²⁸⁻³⁰ And the framework of the four compounds is different from that of the title compounds. In the structure of $\text{Na}_2\text{Cs}_2\text{B}_{10}\text{O}_{17}$, the $[\text{B}_5\text{O}_{11}]$ group, consisting of three $[\text{BO}_3]$ and two $[\text{BO}_4]$, looks like a “∞”-shaped ring (Figure 4a). In Figure 4b, we can see that each $[\text{B}_5\text{O}_{11}]$ group is linked with four analogues around it to form a 2D $[\text{B}_5\text{O}_9]_\infty$ layer. Two adjacent layers link with each other through sharing bridging O atoms to form a 3D open-framework (Figure 4c). Apparently, seen along the b -axis, the adjacent frameworks do not link with each other directly (Figure 4d).

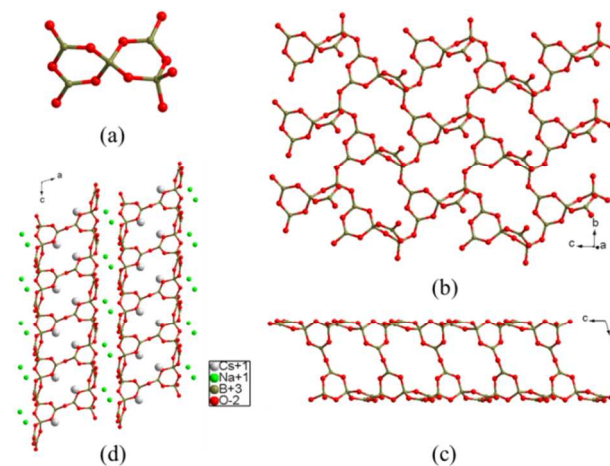


Figure 4 (a) The $[\text{B}_5\text{O}_{11}]$ group (b) The 2D $[\text{B}_5\text{O}_9]_\infty$ layer (c) The 3D open-framework layer (d) The 3D network of $\text{Na}_2\text{Cs}_2\text{B}_{10}\text{O}_{17}$.

IR measurement

In order to further specify the coordination of boron in the FBBs, the infrared spectrum was measured (Figure S3 in the Supporting Information). The strong peaks at 1396, 1316, 1142 and 1120 cm^{-1} are attributed to the asymmetric stretching of BO_3 and BO_4 , respectively.³¹ The peaks at 914 and 722 cm^{-1} are attributed to the symmetric stretching of BO_3 and BO_4 , respectively. The 635 cm^{-1} peaks belong to the out of plane bending of BO_3 . The peaks at 545 and 519 cm^{-1} are attributed to

the bending of BO_3 and BO_4 . Those further confirm the existence of BO_3 triangles and BO_4 tetrahedra, and are consistent with the results obtained from the single-crystal X-ray structural analysis.

Transmittance spectroscopy

Transmittance spectroscopy data of the title compounds are exhibited in Figure S4 in the Supporting Information. It can be noticed that the cut-off edge is about 242 nm for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and 234 nm for $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$. According to the relationship between energy and wavelength ($E = hc/\lambda$), the experimental energy gap of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ are 5.12 eV and 5.30 eV, respectively.

TG and DSC analysis

The TG and DSC curves of polycrystalline samples of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ are shown in Figure S5 in the Supporting Information. The curves show that the two compounds exhibit one endothermic peak and no weight loss upon heating to 1000 °C. In order to further confirm the thermal behavior of $\text{M}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ ($M = \text{Rb}, \text{Cs}$), the stoichiometric powder mixture of M_2CO_3 ($M = \text{Rb}, \text{Cs}$), CaO and B_2O_3 are placed into a platinum crucible and heated to 1000°C, then slowly cooled to room temperature. Analysis of the powder XRD pattern of the solidified melt reveals that the main phase of the solid product is CaB_2O_4 (Figure S6 in the Supporting Information).

Band structures, density of states and optical properties

The band structures of $\text{M}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ ($M = \text{Rb}, \text{Cs}$) are presented in Figure S7 in the Supporting Information. Both of two compounds belong to indirect band-gap compounds. The extrapolated experimental optical gaps (5.12 eV for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and 5.30 eV for $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$) are in good agreement with the calculated values (5.05 eV for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and 5.28 eV for $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$).

The calculated partial density of states (PDOS) of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ are shown in the Figure 5. It is clear that near the Fermi surface (energy region varying from -10 to 0 eV), 2p orbitals of O atoms are the main contributor for the top of valance bands. At the bottom of the conduction bands, the main occupants are Rb 5s orbitals for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and Cs 6s orbitals for $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$. Accordingly, the absorption spectrum near the UV-Visible cut-off wavelength can be assigned as the charge transfers from O 2p orbitals to the Rb 5s orbitals for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and Cs 6s orbitals for $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$.

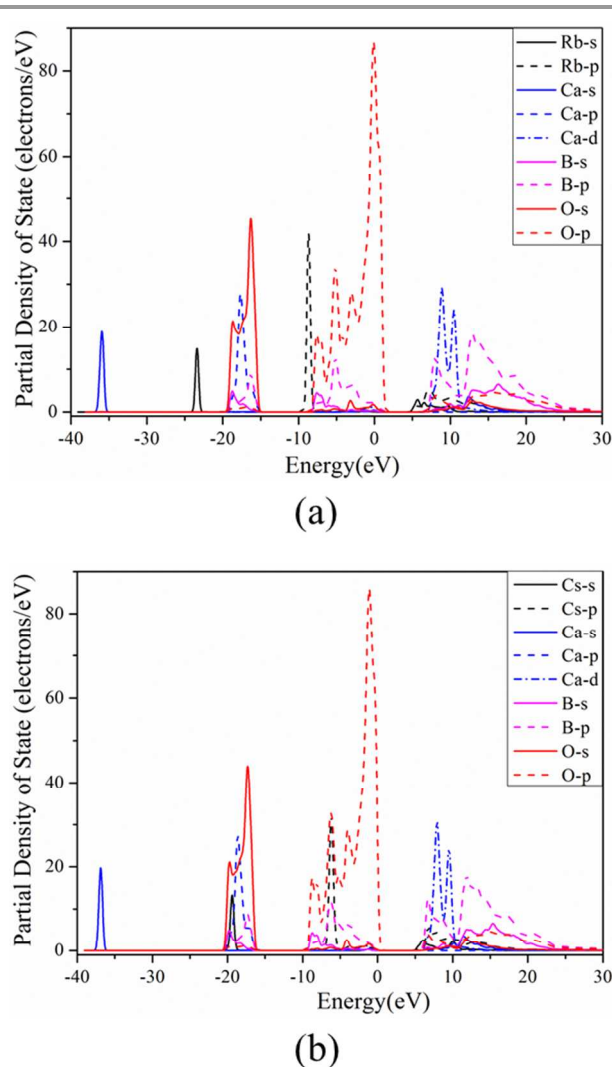


Figure 5 PDOS of $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ (a) and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ (b).

Conclusion

In conclusion, two new alkali calcium borates, $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$, have been discovered and single crystals have been grown by the high temperature solution method for the first time. The crystal structures feature a 3D open-framework layer, and the M^+ ($M = \text{Rb}, \text{Cs}$) cations occupy the in-layer 3D micro-pores, while the Ca^{2+} cations fill in the interlayer. The structure analysis shows that the structures of title compounds are similar to that of SBBO. The first principles calculations show that the calculated band gaps (5.05 eV for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and 5.28 eV for $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$) agree well with the experimental ones (5.12 and 5.30 eV). And the PDOS calculations show that the interaction between s orbitals of cations (Cs 6s for $\text{Cs}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$ and Rb 5s for $\text{Rb}_2\text{Ca}_3\text{B}_{16}\text{O}_{28}$) and O 2p orbitals dominated the band gaps of two compounds.

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Notes and references

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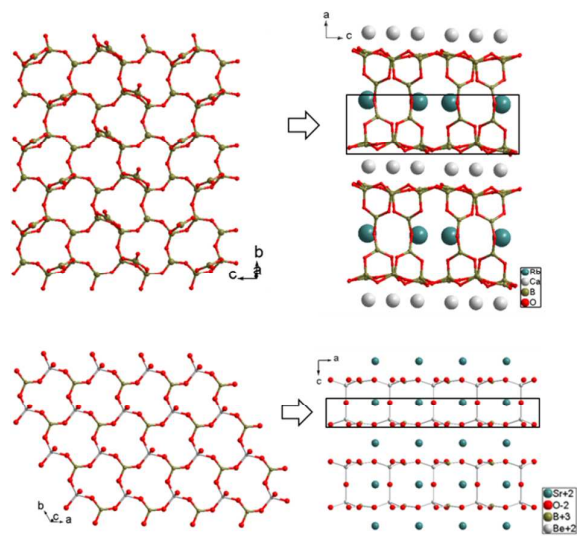
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† Electronic supplementary information (ESI) available: IR and transmittance spectra, final refined atomic positions and isotropic thermal parameters, selected bond distances and angles and first-principles calculations in $M_2Ca_3B_{16}O_{28}$ ($M = Rb, Cs$). CCDC 1420732 for $Rb_2Ca_3B_{16}O_{28}$ and CCDC 1420733 for $Cs_2Ca_3B_{16}O_{28}$. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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Table of contents

Manuscript title: $M_2Ca_3B_{16}O_{28}$ ($M = Rb, Cs$): a structure analogous to SBBO with three-dimensional open-framework layers



The structure comparison between $M_2Ca_3B_{16}O_{28}$ ($M = Rb, Cs$) and $Sr_2Be_2B_2O_7$.