Ba₄M(CO₃)₂(BO₃)₂ (M=Ba, Sr): two borate-carbonates synthesized by open high temperature solution method

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ABSTRACT Two borate-carbonates Ba₄M(CO₃)₂(BO₃)₂ (M = Ba, Sr) have been successfully synthesized in the open air representing the first examples of borate-carbonate complex. Their structures were determined by single crystal X-ray diffraction and they both crystallize in same space group, *Pnma*. Their structures feature a Ba/Sr-based three dimensional framework composed of the BaO₈ polyhedra (the SrO₈ polyhedra), isolated BO₃ and CO₃ triangles. Detailed structure analysis shows that the intergrowth of [Ba₃(BO₃)₂]/[Ba₂Sr(BO₃)₂] and [BaCO₃] layers favors the formation of these two borate-carbonates. In addition, their syntheses, spectroscopic properties and thermal behaviors were investigated.

Keywords: borate-carbonates, open air, intergrowth

INTRODUCTION

Inorganic functional materials are becoming more and more important due to the diversity of structures and their wide range of applications [1–9]. In the recent years, borate attracts more attention owing to the ability of the B atoms that can form the BO₃ triangles or the BO₄ tetrahedra. Polymerization of these B–O groups can construct one dimensional (1D) chains, 2D layers, and 3D networks [10–17]. Such various structure configurations make the structure chemistry of borates virtually unsurpassed. Borate materials have been reported for many applications, such as birefringence, piezoelectric, pyroelectric, and nonlinear optics [18–21]. However, they still cannot satisfy the requirements of our life. Therefore, scientists made more investigations and claimed that many potential optical materials can be obtained. Kniep and Halasyamani [22–26] reported a series of borophosphates that include exciting structural chemistry with a great variety of connection patterns and variable extension of the an-

ionic partial structures. Besides, several borogermanates with abundant structure types activated by the flexible coordination geometries of the Ge and B atoms have been reported by Mao's and Yang's groups [27–29]. Very recently, Pan *et al.* [30–35] designed and synthesized a series of fluorooxoborates, which are ideal systems for searching ultraviolet (UV) and deep UV nonlinear optical (NLO) materials with excellent optical performances. And also by replacing the BeO₄ units by B–O/F basic blocks, some issues, such as toxicity of raw materials and layering tendency in KBe₂BO₃F₂ (KBBF) family have been avoided [30–35]. The synthesis of these materials with different anionic groups not only helps us explore new compounds, but also enriches the structural chemistry of borates.

Analogous to the BO₃ triangles, the CO₃ groups possess a similar planar triangle, which are also beneficial for good optical properties, such as moderate birefringence or bulk NLO coefficients with the coparallel alignment [36–40]. For example, CaCO₃ has a large birefringence since the coparallel alignments of the CO₃ groups lead to the large anisotropic polarizability [41]. For series of alkali-alkaline earth metal carbonate fluoride, ABO₃F (A = K, Rb, Cs; B = Ca, Sr, Ba), the coplanar and parallel arrangements of the CO₃ groups lead to a large second-harmonic generation (SHG) response [42]. Thus, combining the BO₃ groups and the CO₃ groups in one compound may be a good strategy to obtain new compounds with special crystal structure or good optical property. Through our investigation based on Inorganic Crystal Structure Database (ICSD) (Table S1), there are only 5 anhydrous borate-carbonates. For example, Sr₂CuO₂-(CO₃)_{1-x}(BO₃)_x (synthesized in a flowing mixed gas of O₂ and CO₂ atmosphere using solid state reaction) [43], Ca₄Mn₃O₃(BO₃)₃CO₃ (a mineral called gaudefroyite,

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Figure 1 Experimental and calculated XRD patterns of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$. The red curve is the calculated pattern; the black one is the experimental one.

presumably formed in geologic high-temperature and high-pressure conditions [44] and $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$ have been synthesized [45]. We notice that these compounds (3/5) are synthesized under hydrothermal conditions or a geologic or geologic-like environment (similar to hydrothermal reaction). Only two anhydrous compounds, $\text{Sr}_2\text{CuO}_2(\text{CO}_3)_{0.85}(\text{BO}_3)_{0.15}$ and $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$ were synthesized by the high-temperature solid-state reaction/solution method. However, $\text{Sr}_2\text{CuO}_2(\text{CO}_3)_{0.85}(\text{BO}_3)_{0.15}$ was synthesized under a CO_2 atmosphere. In fact, only $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$ was synthesized by the high-temperature solution method in air. The less borate-carbonates synthesized by the high-temperature solution method in air can be attributed to their difficult formation process. First, the borate-carbonates need to completely dissociate their ‘parent’ salt, and then the different cations or anions further reconstruct to form the new crystal structure. However, according to Pauling’s rules, each kind of cation’s coordination polyhedra and anion’s groups in crystal structure have their own periodic arrangement and symmetry. This makes their coexistence difficult. For borate-carbonates, they are not like the complex salts that consist of cations and halogen anions. It is easy for them to adjust halogen position to meet the requirement of the periodicity and symmetry of the whole crystal structure [46–49]. However for the complex salts that one or more kinds of the cations connect with two or more anion groups, the mixed anion groups are some large acid radical anions. It is more difficult to mix them in a periodic arrangement with the specific symmetry of crystal. Thus, for synthesizing them, a higher temperature condition is often needed to provide enough energy to re-arrange the large acid radical anions in the periodic and symmetric style. However, it is worth

noting that for borate-carbonate, carbonate often decomposes before forming complex salts at high temperature condition.

In current work, we successfully synthesized $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$) by a high-temperature solution method in air. Moreover, the reason why two borate-carbonates can be synthesized by the high temperature solution method in air is discussed based on the structure analysis. In addition, since the pure phase of $\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$ were not obtained, the $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ compound were subjected to comprehensively experimental characterizations.

EXPERIMENTAL SECTION

Reagents

BaCO_3 (Tianjin Baishi Chemical Reagent Co., Ltd., 99.8%), $\text{Ba}(\text{NO}_3)_2$ (Beijing Chemical Industry Co., Ltd., 99.5%), SrCO_3 (Tianjin Baishi Chemical Reagent Co., Ltd., 99.8%), Na_2CO_3 (Beijing Chemical Co., Ltd., 99.5%), and H_3BO_3 (Beijing Chemical Industry Co., Ltd., 99.5%) were used as received.

Syntheses

Single crystals of $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$) were grown by a high temperature solution method. The molar ratio of stoichiometric $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$) with Na_2CO_3 is 1:4, respectively. The mixtures were put into a corundum crucible and heated up to 820°C and held at this temperature for 12 h. Then the mixtures were cooled to 700°C at a rate of 3°C h^{-1} and quenched to room temperature. The colorless small crystals of $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$) were obtained.

Polycrystalline samples were prepared by high temperature solid-state reactions with stoichiometric starting reagents of analytical purity in air, $\text{Ba}(\text{NO}_3)_2$, BaCO_3 , SrCO_3 and H_3BO_3 powders. We considered that the carbonates are prone to decompose at high temperature, especially in borate mixture. Polycrystalline $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$) were prepared using two step solid-state reactions. Initially, the pure $\text{Ba}_3(\text{BO}_3)_2$ powder was obtained by calcining the mixture of $\text{Ba}(\text{NO}_3)_2$ and H_3BO_3 at a molar ratio of 3:2 at 900°C for 48 h. Then the synthesized polycrystalline $\text{Ba}_3(\text{BO}_3)_2$ powder was further mixed with BaCO_3 at a molar ratio of 1:2 for $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{Ba}_3(\text{BO}_3)_2:\text{BaCO}_3:\text{SrCO}_3 = 1:1:1$ for $\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$) and the mixtures were heated to 880°C for $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ (900°C for $\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$) with a series of grinding. Polycrystalline $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ was synthesized (Fig. 1). Unfortunately, we did not obtain the

Table 1 Crystal data and structure refinement for $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ (M = Ba, Sr)

Empirical formula	$\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$	$\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group, Z	<i>Pnma</i> , 4	
Formula weight	924.34	874.62
Unit cell dimensions	$a = 7.923(2)$ Å	$a = 7.731(6)$ Å
	$b = 17.508(5)$ Å	$b = 17.349(4)$ Å
	$c = 9.144(3)$ Å	$c = 9.048(7)$ Å
Absorption coefficient	15.352 mm^{-1}	17.214 mm^{-1}
Crystal size(mm ³)	0.23×0.16×0.09	0.11×0.11×0.08
Theta range for data collection	2.33° to 27.44°	2.35° to 27.47°
Limiting indices	$-9 \leq h \leq 10, -22 \leq k \leq 21, -10 \leq l \leq 11$	$-8 \leq h \leq 10, -21 \leq k \leq 22, -10 \leq l \leq 11$
Reflections collected/unique	7221/1497 [<i>R</i> (int) = 0.0250]	6787/1435 [<i>R</i> (int) = 0.0397]
Completeness to theta	99.9%	99.7%
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1497/0/104	1435/0/105
Goodness-of-fit on F^2	1.090	1.039
Final <i>R</i> indices [$F_o^2 > 2\sigma(F_o^2)$] ^a	$R_1 = 0.0294$ $wR_2 = 0.0724$	$R_1 = 0.0257$ $wR_2 = 0.0591$
<i>R</i> indices (all data) ^a	$R_1 = 0.0317$ $wR_2 = 0.0736$	$R_1 = 0.0350$ $wR_2 = 0.0625$
Extinction coefficient	0.00041(9)	0.000450(9)
Largest diff. peak and hole (e Å ⁻³)	1.639 and -2.966	1.035 and -1.021

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

pure phase of $\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$ by the solid state reaction due to lower decomposition temperature of SrCO_3 than that of BaCO_3 , which makes SrCO_3 decompose into SrO before forming $\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$.

X-ray crystallographic studies

The single crystals of $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ (M = Ba, Sr) were selected for the structure determination. Their crystal structures were determined by single-crystal X-ray diffraction on an APEX II CCD diffractometer with monochromatic Mo K α radiation ($\lambda = 0.71073$ Å) at 296(2) K and integrated with the SAINT program. Numerical absorption corrections were carried out using the SCALE program for area detector [50]. All calculations were performed with programs from the SHELXTL crystallographic software package [51]. All atoms were refined using full matrix least-squares techniques, and final least-squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The structures were checked for missing symmetry elements by the program PLATON [52]. Crystal data and structure refinement information are

given in Table 1. The final refined atomic positions and isotropic thermal parameters are listed in Table S2. Selected bond distances (Å) and angles (deg) for the compounds are listed in Table S3.

Infrared and UV-vis-NIR spectrum measurements

Infrared (IR) spectra were recorded with a Shimadzu IR Affinity-1 Fourier transform IR spectrometer in the 400–4,000 cm^{-1} wave number range using KBr pellets (400 mg of KBr, 4 mg of the sample). UV-vis-NIR diffuse reflectance spectra were measured at room temperature with a Shimadzu SolidSpec-3700DUV spectrophotometer. Data were collected in the wavelength range of 190–2,600 nm. And reflectance spectrum was converted to absorbance with the Kubelka-Munk function [53,54].

Thermal analysis

The thermal properties of the compounds are studied on a NETZSCH STA 449C simultaneous analyzer under nitrogen gas, heated from the room temperature to 1,400°C at a rate of 5°C min^{-1} for $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$.

Figure 2 The pseudo-layers composed of CO_3 and BO_3 groups are stacked along the b direction for $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$).

Theoretical calculations

The electronic structures and optical properties of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ were calculated by the CASTEP package based on the density functional theory (DFT) [55]. The Perdew-Burke-Ernzerhof (PBE) method in generalized gradient approximation (GGA) was chosen to describe the exchange-correlation potential [56], and the norm-conserving pseudopotential (NCP) [57] was used for the following valence electrons, Ba ($5s^2 5p^6 6s^2$), B ($2s^2 2p^1$), C ($2s^2 2p^2$), O ($2s^2 2p^4$). The kinetic energy cutoff was set as 830 eV, and the Monkhorst-Pack scheme was set as $4 \times 2 \times 3$ for the Brillouin zone. Other calculation parameters were set as the default values in the CASTEP.

RESULTS AND DISCUSSION

Crystal structure

$\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$) crystallize in the same space group $Pnma$ of the orthorhombic system. Since two compounds are iso-structural, only the structure of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ is discussed in detail. In its asymmetric unit, there are three unique Ba atoms, one unique C atom, two unique B atoms and seven unique O atoms (Table S1). Both the B and C atoms are coordinated by three O atoms to form isolated planar triangles, respectively, which are perfectly aligned to a direction forming the pseudo-layers (Fig. 2). The Ba atoms are inserted into the inter-layer and intra-layer. Among them, Ba(1) is located in the inter-layer and shared by the $[\text{CO}_3]$ pseu-

do-layers to build $[\text{BaCO}_3]$ layers, while the Ba(2) and Ba(3) atoms are located in the inter-layer and intra-layer shared by the BO_3 triangles to construct $[\text{Ba}_3(\text{BO}_3)_2]$ layers. Thus, the structure of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ can be described as the three-dimensional framework composed of the $[\text{Ba}_3(\text{BO}_3)_2]$ layers and $[\text{BaCO}_3]$ layers stacked alternately along the b direction. Furthermore, the Ba(2) atoms in the intra-layer of $[\text{Ba}_3(\text{BO}_3)_2]$ are substituted by the Sr atoms to form the crystal structure of $\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$ (Fig. 2). Thus, $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ and $\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$ can be written as $[\text{Ba}_3(\text{BO}_3)_2] \cdot 2[\text{BaCO}_3]$ and $[\text{Ba}_2\text{Sr}(\text{BO}_3)_2] \cdot 2[\text{BaCO}_3]$ based on above structure analysis. In addition, the substitution of the Ba atoms by the Sr atoms is always observed in the borate and can keep the structure symmetry. For example, $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}$ [58] and $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ [59], $\text{Ba}_3\text{B}_6\text{O}_{11}\text{F}_2$ [60] and $\text{Sr}_3\text{B}_6\text{O}_{11}\text{F}_2$ [61] are synthesized. In the structure of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$, three types of Ba atoms are all coordinated by eight O atoms to form bicapped trigonal prisms (Fig. S2). Similarly, in $\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$, two types of Ba atoms and one type of Sr atom are all coordinated by eight O atoms to form the BaO_8 or SrO_8 polyhedra (Fig. S2). In both structures, the Ba–O bond lengths have a wide range varying from 2.605(6) to 3.066(7) Å. The Sr–O bond lengths are in the range of 2.457(7)–2.780(5) Å. For the BO_3 triangles, the B–O bond distance varies from 1.325(6) to 1.353(14) Å. The triangularly coordinated boron atoms maintain O–B–O bond angles within 4° of the 3-fold symmetrical 120° angle, which is corresponding to the sp^2 hybridiza-

tion of the B atoms. For the CO_3 triangles, the C–O bond lengths are in the range of 1.298(7)–1.327(9) Å, the O–C–O bond angles are within 2° of the 3-fold symmetrical 120° angle (Table S2). These results are consistent with those observed in other compounds [62–65].

Other borate-carbonates

Based on the ICSD, there are 120 borate-carbonates. Except five anhydrous borate-carbonates, the remaining borate-carbonates are synthesized by hydrothermal reaction or obtained from a geologic or geologic-like environment. For example, natural minerals borcarite $\text{Ca}_4\text{MgB}_4\text{O}_6(\text{OH})_6(\text{CO}_3)_2$ [66], sakhaite $\text{Ca}_3\text{Mg}(\text{BO}_3)_2(\text{CO}_3)_2 \cdot (\text{H}_2\text{O})_{0.36}$ [67], $\text{Ca}_{48}\text{Mg}_{16}(\text{BO}_3)_{24.96}(\text{CO}_3)_{16}\text{Cl}_{5.28}(\text{OH})_{13.84}(\text{H}_2\text{O})_{3.4}$ [68], and $\text{Ca}_{12}\text{Mg}_4(\text{BO}_3)_7(\text{CO}_3)_4(\text{OH})\text{Cl} \cdot \text{H}_2\text{O}$ [69]. Their formation is at high temperature and high pressure hydrothermal environments. $\text{Pb}_7\text{O}(\text{OH})_3(\text{CO}_3)_3(\text{BO}_3)$ is an NLO material, and also synthesized by the hydrothermal method [70]. Obviously, the closed but relatively high-temperature or high pressure conditions in geologic or hydrothermal environments favor the formation of these borate-carbonates. However, among the anhydrous borate-carbonates, $\text{Ca}_4\text{Mn}_3(\text{BO}_3)_3(\text{CO}_3)_3\text{O}_3$, $\text{Ca}_8\text{Mn}_6((\text{BO}_3)_6(\text{CO}_3)_2\text{O}_6)$ [71], $\text{Li}_9\text{BaB}_{15}\text{O}_{27}(\text{CO}_3)$ [72], $\text{Sr}_2\text{CuO}_2[(\text{CO}_3)_{0.85}(\text{BO}_3)_{0.15}]$, and $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$, the former two are mineral; $\text{Li}_9\text{BaB}_{15}\text{O}_{27}(\text{CO}_3)$ is synthesized by the hydrothermal reaction; $\text{Sr}_2\text{CuO}_2[(\text{CO}_3)_{0.85}(\text{BO}_3)_{0.15}]$ and $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$ are synthesized by high temperature solution/solid state reaction. However, the syntheses of $\text{Sr}_2\text{CuO}_2[(\text{CO}_3)_{0.85}(\text{BO}_3)_{0.15}]$ need the CO_2 atmosphere. More importantly, in these two structures, the BO_3 and CO_3 anions statistically occupy the same sites. Thus, the two compounds can be seen as a carbonate with a small amount of CO_3 groups substituted by BO_3 or a borate with a small amount of BO_3 groups substituted by CO_3 , respectively. However, it is noteworthy that in $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$), the BO_3 and CO_3 anionic groups have a molar ratio of 1:1 and respectively occupy their own sites. Therefore, in this sense, $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ and $\text{Ba}_4\text{Sr}(\text{CO}_3)_2(\text{BO}_3)_2$ represent the first example of borate-carbonate complex salts synthesized in an open system. And their formulas can be written as $[\text{Ba}_3(\text{BO}_3)_2] \cdot 2[\text{BaCO}_3]$ and $[\text{Ba}_2\text{Sr}(\text{BO}_3)_2] \cdot 2[\text{BaCO}_3]$. $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$) can be synthesized by high temperature solution method in an open system. This is mainly because of their special structure. In $[\text{Ba}_3(\text{BO}_3)_2] \cdot 2[\text{BaCO}_3]$ and $[\text{Ba}_2\text{Sr}(\text{BO}_3)_2] \cdot 2[\text{BaCO}_3]$, the BO_3 and CO_3 triangles are respectively arranged in different $[\text{Ba}_3(\text{BO}_3)_2]/[\text{Ba}_2\text{Sr}(\text{BO}_3)_2]$ or $[\text{BaCO}_3]$ layers, which makes them adopt their own symmetry and ar-

rangement without affecting each other. This is the reason that the BO_3 and CO_3 groups can co-exist in one structure. These results show that the layer intergrowth is an effective method to synthesize the complex salts, containing multi-anionic-groups (e.g., CO_3 and NO_3) [40,44]. The layer structure feature has also been observed in KSrCO_3F , which contains the flat SrCO_3 layers and K-F layers, that is, the intergrowth SrCO_3 and KF layers (Fig. S3). Also, in $\text{Ca}_4\text{Mn}_3\text{O}_3(\text{BO}_3)_3\text{CO}_3$, the BO_3 groups and the CO_3 groups alternately stack along the a direction (Fig. S1a). In $\text{Pb}_2(\text{BO}_3)(\text{NO}_3)$, the BO_3 groups and the NO_3 groups also have the layer arrangement in (100) plane (Fig. S2b). These results suggest that the intergrowth layer structure is beneficial for the formation of complex salts containing multiple anion groups. In $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$, they also refer the intergrowth layer structure. $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$ can be viewed as an intergrowth along the (001) direction of the slab $[\text{Ba}_2(\text{BO}_3)_2]^{2-}$ in trigonal $\text{Ba}_2\text{Mg}(\text{BO}_3)_2$ and the (111) slab $[\text{Ba}_2\text{Cl}_2]^{2+}$ of the cubic fluorite BaCl_2 structures [73]. Compared with $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$, $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ can be seen as $[\text{Ba}_2\text{Cl}_2]^{2+}$ layers in $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$ substituted by BaCO_3 ; the $[\text{Ba}_2(\text{BO}_3)_2]$ layers are substituted by the $[\text{Ba}_3(\text{BO}_3)_2]$ layers to constitute an intergrowth of $[\text{Ba}_3(\text{BO}_3)_2]$ and $[\text{BaCO}_3]$ layers along the (001) direction (Fig. 3).

IR spectroscopy

To confirm the existence of CO_3 and BO_3 groups in the structure, IR spectra of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ and BaCO_3 were collected and shown in Fig. 4. It is clear that the peaks at 1,446, 1,160, 854 and 694 cm^{-1} can be attributed to the CO_3 vibrations. Exhaustively, the bands at 1,446 and $1,160\text{ cm}^{-1}$ are assigned to the asymmetric and symmetric stretching modes of the CO_3 group. The bands observed at 854 and 694 cm^{-1} are designated as the bending vibrations of CO_3 group, which are very similar to those in BaCO_3 , while the peaks at 762 and 577 cm^{-1} can be assigned as the bending of the BO_3 groups, which confirms the existence of the CO_3 and BO_3 groups, respectively.

Furthermore, to confirm the existence of the CO_3 groups, 1.0 g of polycrystalline sample of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ was ground and put into 10 mL of diluted HCl solution (2 mol L^{-1}). When the polycrystalline samples were added into the diluted HCl solution, a large number of bubbles were observed (Fig. S4). After the mixture was stirred for 30 min to ensure the decomposition of carbonate, 0.091 g of weight loss for $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ was found, which is in good agreement with the decomposition of the CO_3 groups in the structure. These results further confirm that

Figure 3 The structure of $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$ and $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ (the Ba–O and Ba–Cl bonds are omitted for clarity).

Mode description	$\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ (cm^{-1})	BaCO_3 (cm^{-1})
Asymmetric stretching $\text{C}_3\text{--O}$	1,446	1,458
Symmetric stretching vibration $\text{C}_3\text{--O}$	1,160	1,080
Bending out of plane vibration $\text{C}_3\text{--O}$	854	854
Bending in plane vibration $\text{C}_3\text{--O}$	694	694
Bending of $\text{B}_3\text{--O}$	577, 762	

Figure 4 The IR spectra and the assignments of the infrared absorption peaks of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ and BaCO_3 .

the CO_3 group and the BO_3 group simultaneously exist in $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$.

TG/DSC analyses

The thermal behavior of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ was also measured (Fig. S5). It is clear that there is one endothermic peak at 1,113°C on the differential scanning calorimetry (DSC) curve and there is no weight loss on thermal gravimetric (TG) curve until 920°C. These results show that $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ is thermodynamically stable below 920°C, which is consistent with the other reported anhydrous borate-carbonates [45].

UV-vis-NIR diffuse reflectance spectroscopy

The optical diffuse reflectance spectrum of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ is shown in Fig. 5. The result indicates that $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ has a wide transmission window from 190–2,500 nm (UV cut-off edges <190 nm), which is comparable to the absorption edges of other borates or carbonates such as $\text{Ba}_2(\text{BO}_3)_{1-x}(\text{CO}_3)_x\text{Cl}_{1+x}$ (~220 nm), $\text{KBa}_2(\text{CO}_3)_2\text{F}$ (~245 nm) and $\text{RbBa}_2(\text{CO}_3)_2\text{F}$ (~220 nm) [74].

Theoretical analyses

The electronic band structure is plotted in Fig. 6. $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ is a direct band gap compound, with a band gap of 4.30 eV. This value is smaller than the experimental band gap (5.11 eV) based on the conversion of Kubelka-Munk function, which is due to the inaccuracy

Figure 5 The diffuse reflectance spectrum for $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$.

of the exchange correlation energy calculated by PBE functional within GGA [75,76]. The partial and total densities of states (PDOS and TDOS) for $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ are exhibited in Fig. 6. Since the optical properties are mainly determined by electronic transition among the states near Fermi level. The electronic states at the top of valence-band (VB) and the bottom of conduction band (CB) are analyzed. As shown in Fig. 6, from -10 to 0 eV, the main occupants are O 2p orbitals, and the bottom of the CB is occupied by Ba 5d and C 2p orbitals. Accordingly, the absorption spectrum can be assigned to the charge transfer from the O 2p states to the Ba 5d and C 2p states.

CONCLUSIONS

The borate-carbonates, $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$), have been synthesized by open high temperature solution method. Both compounds crystallize in orthorhombic space group, $Pnma$. In their structures, they both possess the isolated BO_3 and CO_3 groups to form the $[\text{Ba}_3(\text{BO}_3)_2]$ layers and $[\text{BaCO}_3]$ layers stacked alternately along the b direction. Based on the structure analysis of anhydrous borate-carbonates, the results show that the intergrowth layer structure is beneficial for the synthesis of $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ ($\text{M} = \text{Ba}, \text{Sr}$). The IR measurements confirm the coexistence of the BO_3 and CO_3 groups in $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$. UV-vis-NIR diffuse reflectance spectrum suggests that $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$ has a wide transmission window. The first principle calculation reveals that the O 2p states and the Ba 5d and C 2p states are the major contribution to the optical property for $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$.

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Figure 6 The band structure PDOS and TDOS of $\text{Ba}_5(\text{CO}_3)_2(\text{BO}_3)_2$.

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Author contributions Wu H, Zhang X and Yu H performed the experiments and data analysis, and wrote the paper; Yang Z performed the theoretical data analysis; Pan S designed and supervised the experiments. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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$\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ (M=Ba, Sr): 在开放体系下通过高温溶液法合成两种硼酸-碳酸盐

张雪艳, 吴红萍, 俞洪伟, 杨志华, 潘世烈*

摘要 本文中, 我们成功合成了两种复合的硼酸-碳酸盐 $\text{Ba}_4\text{M}(\text{CO}_3)_2(\text{BO}_3)_2$ (M = Ba, Sr). 这是第一例在开放体系下合成的硼酸-碳酸盐. 它们的结构由单晶X射线衍射确定, 结晶在相同的 $Pnma$ 空间群. 它们的晶体结构是由 BaO_8 多面体(SrO_8 多面体)、孤立的 BO_3 和 CO_3 三角形组成的三维网络结构. 详细的结构分析表明, 共生长的 $[\text{Ba}_3(\text{BO}_3)_2]/[\text{Ba}_2\text{Sr}(\text{BO}_3)_2]$ 和 $[\text{BaCO}_3]$ 层是利于这两种硼酸-碳酸盐的合成. 此外, 还研究了它们的合成、光谱性质和热行为.