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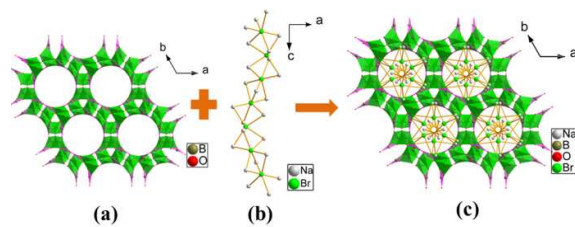
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They consist of the B<sub>4</sub>O<sub>9</sub> framework and [Na<sub>3</sub>Br] chain which hasn't been found in other alkali metal borate halides.

## ARTICLE

# Na<sub>3</sub>B<sub>4</sub>O<sub>7</sub>X (X = Cl, Br): two new borate halides with 1D Na-X (X = Cl, Br) chain formed by the face-sharing XNa<sub>6</sub> octahedra

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**Abstract:** Two new sodium borate halides, namely, Na<sub>3</sub>B<sub>4</sub>O<sub>7</sub>X (X = Cl, Br), have been successfully synthesized through high-temperature solid state reactions. Single-crystal X-ray diffraction analysis reveals that both of them crystallize in the same space group *P*6<sub>3</sub>22 of the hexagonal system. And in their crystal structures, the B<sub>4</sub>O<sub>9</sub> groups link with each other by oxygen-sharing to form a three dimensional (3D) framework containing channels viewing along [001] direction, in which the 1D helical [Na<sub>3</sub>X] chain formed by the face-sharing XNa<sub>6</sub> octahedra is resided. To the best of our knowledge, the 1D helical [Na<sub>3</sub>X] chain has not been found in other alkali metal borate halides. From another perspective, the two compounds can also be regarded as NaX salt inclusion borates. In addition, the infrared (IR) spectroscopy spectra and bond valence sums (BVS) calculations are used to verify the validity of the structures. The differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD) results prove that both of them are incongruently melting compounds. And the electronic structures have been calculated by the first-principle method based on the density-functional theory.

## Introduction

Borates<sup>1-8</sup>, owing to the possible 3- or 4-fold coordination of boron atoms, form a great number of compounds having diverse structures. The diverse structures make them own the interesting and excellent properties for technical applications, which attract the attention of material scientists. After much research effort, many excellent borate crystals have been obtained, such as  $\alpha$ -BaB<sub>2</sub>O<sub>4</sub> ( $\alpha$ -BBO)<sup>9</sup>,  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> ( $\beta$ -BBO)<sup>10</sup>, KBe<sub>2</sub>BO<sub>3</sub>F<sub>2</sub> (KBBF)<sup>11</sup>.

Studies of alkali metal borates have also produced a large family of compounds with outstanding physical properties, such as LiB<sub>3</sub>O<sub>5</sub> (LBO)<sup>12</sup>, CsB<sub>3</sub>O<sub>5</sub><sup>13</sup>, CsLiB<sub>6</sub>O<sub>10</sub><sup>14</sup>, Li<sub>4</sub>Cs<sub>3</sub>B<sub>7</sub>O<sub>24</sub><sup>15</sup> and Li<sub>6</sub>Rb<sub>5</sub>B<sub>11</sub>O<sub>22</sub><sup>16</sup>, the crystals of which have wide range transparency. In addition, it is well-known that combination of halogen with borate can widen band gaps<sup>17</sup>. In our group, by introducing halogen atoms into borate, a series of new crystals consisting of the similar XM<sub>6</sub> (X = Cl, Br; M = alkali metals) octahedra have been successfully synthesized, such as K<sub>3</sub>B<sub>6</sub>O<sub>10</sub>X<sup>18</sup>, Na<sub>3</sub>B<sub>6</sub>O<sub>10</sub>X<sup>19</sup>, K<sub>3-x</sub>Na<sub>x</sub>B<sub>6</sub>O<sub>10</sub>Br (x = 0.13, 0.67, 1.30, 2.20)<sup>20</sup> and RbNa<sub>2</sub>B<sub>6</sub>O<sub>10</sub>X<sup>19a</sup>. Interestingly, although these crystals have similar stoichiometry and comprise the B<sub>6</sub>O<sub>13</sub> groups and XM<sub>6</sub> (X = Cl, Br; M = alkali metals) octahedra, their properties have great difference owing to the different XM<sub>6</sub> (X = Cl, Br; M = alkali metals) octahedra. Inspired by the above work, we believe that it is significant to continue an investigation of alkali-metal borate halides containing XM<sub>6</sub> octahedra. After extensive efforts, we successfully synthesized two new alkali metal borate halides Na<sub>3</sub>B<sub>4</sub>O<sub>7</sub>X (X = Cl, Br) containing a 1D helical [Na<sub>3</sub>X] chain of face-sharing XNa<sub>6</sub> octahedra, which has not been found in other alkali metal borate halides. From another perspective, the two compounds can also be regarded as NaX salt inclusion borates. This paper describes the syntheses, crystal and electronic structures and optical properties of Na<sub>3</sub>B<sub>4</sub>O<sub>7</sub>X (X = Cl, Br). These results give a

hint of the very extensive crystal chemistry of alkali-metal borate halides containing XM<sub>6</sub> (X = Cl, Br; M = alkali metals) octahedra system, which continues to provide a rich source of new compounds.

## Experimental

### Reagents

NaCl (Tianjin BaiShi Chemical Reagent Co., 99.0%), NaBr (Tianjin HongYan Chemical Reagent Co., Ltd., 99.0%), Na<sub>2</sub>CO<sub>3</sub> (Tianjin HongYan Chemical Co., Ltd., 99.5%) and H<sub>3</sub>BO<sub>3</sub> (Tianjin HongYan Chemical Co., Ltd., 99.5%) were used as received.

### Crystal growth

Single crystals of Na<sub>3</sub>B<sub>4</sub>O<sub>7</sub>X (X = Cl, Br) were grown by spontaneous crystallization. A mixture of 0.424 g (4.00 mmol) of Na<sub>2</sub>CO<sub>3</sub>, 0.234 g (4.00 mmol) of NaCl (or 0.411 g (4.00 mmol) of NaBr), and 0.7420 g (12.00 mmol) of H<sub>3</sub>BO<sub>3</sub> was thoroughly ground for Na<sub>3</sub>B<sub>4</sub>O<sub>7</sub>X (X = Cl, Br). The mixture was then placed in a platinum crucible that was placed into a vertical, programmable-temperature furnace. The crucible was gradually heated to 750 °C in air, held for 12 h until the solution became transparent and clear. The homogenized solution was cooled rapidly to 700 °C and then slowly cooled to 600 °C at a rate of 2 °C/h, followed by rapid cooling to room temperature. The crystals were separated mechanically from the crucible for the further characterization by single-crystal X-ray measurements.

### Structure determination

The single crystals of Na<sub>3</sub>B<sub>4</sub>O<sub>7</sub>X (X = Cl, Br) with dimensions 0.245 mm × 0.126 mm × 0.109 mm and 0.200 mm × 0.172 mm × 0.091

mm were selected for the structure determination, respectively. Their crystal structures were determined by single-crystal XRD on an APEX II CCD diffractometer using monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293(2) K and integrated with the SAINT program<sup>21</sup>. Numerical absorption corrections were carried out using the SCALE program for area detector. All calculations were performed with programs from the SHELXTL crystallographic software package<sup>22</sup>. All atoms were refined using full matrix least-squares techniques; final least-squares refinement is on  $F_o^2$  with data having  $F_o^2 \geq 2\sigma(F_o^2)$  ( $F_o$ : observed structure factors,  $\sigma$ : standard uncertainty). The structures were checked for missing symmetry elements by the program PLATON<sup>23</sup>. Crystal data and structure refinement information are presented in Table 1. The final refined atomic positions, isotropic thermal parameters and bond valence sums (BVS)<sup>24</sup> of each atom are summarized in Table 2. Selected bond lengths (in  $\text{\AA}$ ) and angles (in deg.) are listed in Tables S1 and S2 in the Supporting Information.

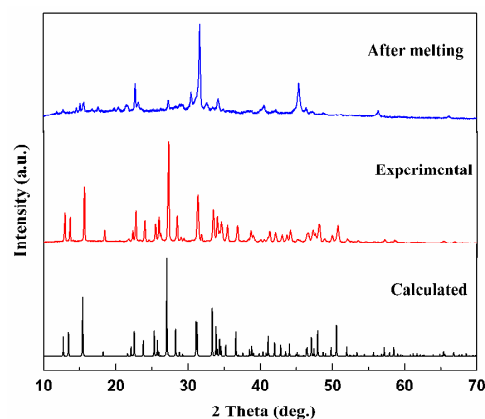
**Table 1** Crystal data and structures refinement for  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  (X = Cl, Br).

Empirical formula	$\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$	$\text{Na}_3\text{B}_4\text{O}_7\text{Br}$
Formula weight	259.66	304.12
Crystal system	Hexagonal	Hexagonal
Space group, Z	$P6_322, 6$	$P6_322, 6$
Unit cell dimensions	$a = 8.031(1) \text{ \AA}$ $c = 20.369(3) \text{ \AA}$	$a = 8.146(5) \text{ \AA}$ $c = 20.24(3) \text{ \AA}$
Volume	$1137.7(2) \text{ \AA}^3$	$1163.1(18) \text{ \AA}^3$
Density (calculated)	$2.274 \text{ Mg/m}^3$	$2.605 \text{ Mg/m}^3$
Theta range for data collection	$2.93^\circ$ to $24.96^\circ$	$2.89^\circ$ to $27.50^\circ$
Limiting indices	$-9 \leq h \leq 8, -7 \leq k \leq 9, -24 \leq l \leq 20$	$-9 \leq h \leq 10, -7 \leq k \leq 10, -23 \leq l \leq 26$
Reflections collected / unique	5755 / 671 [ $R(\text{int}) = 0.0408$ ]	7065 / 896 [ $R(\text{int}) = 0.0502$ ]
Completeness to theta	100 %	99.8%
Goodness-of-fit on $F^2$	1.184	1.100
Final R indices	$R_1 = 0.0609, wR_2 = 0.1809$	$R_1 = 0.0482, wR_2 = 0.1304$
$[F_o^2 > 2\sigma(F_o^2)]^{\text{a}}$	$R_1 = 0.0636, wR_2 = 0.1822$	$R_1 = 0.0548, wR_2 = 0.1343$
R indices (all data) <sup>a</sup>	0.0636, 0.1822	0.0548, 0.1343
Absolute structure parameter	0.0(4)	0.06(3)
Extinction coefficient	0.031(10)	0.005(3)
Largest diff. peak and hole	0.819 and $-0.356 \text{ e} \cdot \text{\AA}^{-3}$	0.938 and $-0.883 \text{ e} \cdot \text{\AA}^{-3}$

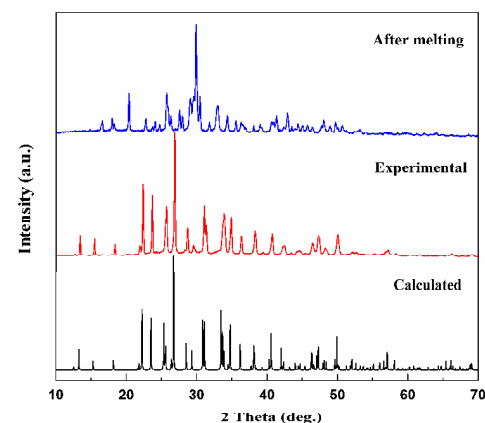
<sup>a</sup> $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$  and  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$  for  $F_o^2 > 2\sigma(F_o^2)$

### Solid-state synthesis

The polycrystalline powders of  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  (X = Cl, Br) were synthesized by high temperature solid-state reactions. The stoichiometric mixtures of  $\text{Na}_2\text{CO}_3$ , NaX (X = Cl, Br) and  $\text{H}_3\text{BO}_3$  at a molar ratio 1:1:4 for  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  (X = Cl, Br) were ground well and packed into Pt crucibles, respectively. The raw materials were heated to  $400^\circ\text{C}$  to decompose the carbonate and eliminate the water, then the compounds were gradually heated up to  $650^\circ\text{C}$  for  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  (X = Cl, Br) and kept at this temperature for 72 h. During the sintering steps, the samples were cooled to room temperature and ground. The powders of  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  (X = Cl, Br) were obtained. The powder X-ray diffraction (XRD) data were collected at room temperature in the angular range of  $2\theta = 10\text{--}70^\circ$  with a scan step width of  $0.02^\circ$  and a fixed counting time of 1 s/step by using an automated Bruker D2 X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The diffraction patterns are well agreeable with the calculated ones (Figure 1).



(a)  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$



(b)  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$

**Figure 1.** Powder XRD patterns of calculated, before melting and after melting for (a)  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$ , (b)  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ .

### IR spectroscopy

IR spectra of  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  (X = Cl, Br) were recorded on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the  $400\text{--}4000 \text{ cm}^{-1}$  range. The samples were mixed thoroughly with dried KBr, and the characteristic absorption peaks were shown in Figure S1 in the Supporting Information.

### UV–Vis–NIR diffuse reflectance spectra

Optical diffuse reflectance spectra of  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  (X = Cl, Br) were measured at room temperature with a Shimadzu SolidSpec-3700DUV spectrophotometer. Data were collected in the wavelength range  $190\text{--}2600 \text{ nm}$ . Also, reflectance spectra were converted to absorbance with the Kubelka–Munk function<sup>25–26</sup>.

### Thermal analysis

The melting behaviors of  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  (X = Cl, Br) were carried out on NETZSCH STA 449C simultaneous analyzer instrument in an atmosphere of flowing  $\text{N}_2$ . The sample heated from  $25$  to  $1000^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ .

### Elemental analysis

Elemental analysis of single crystal was measured by a VISTA-PRO CCD simultaneous ICP-OES. The crystal samples were dissolved in nitric acid. The elemental analysis results are listed in Table S3.

### Theoretical calculations

The electronic structures of the title crystals, including the band structure and full/partial density of states (DOS/PDOS), were performed by a plane-wave pseudopotential package employed in CASTEP<sup>27</sup>. Norm-conserving pseudopotentials (NCP)<sup>28</sup> were used. The exchange-correlation functional was Perdew-Burke-Ernzerhoff (PBE) functional within the generalized gradient approximation (GGA)<sup>29</sup>. The plane-wave energy cutoff was set at 750 eV. The numerical integration of the Brillouin zone was performed using a  $4 \times 4 \times 2$  Monkhorst-Pack  $k$ -point sampling.

## Results and discussion

### Crystal structures

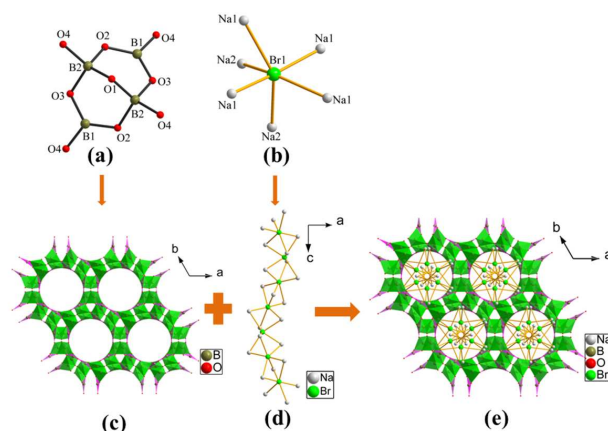
$\text{Na}_3\text{B}_4\text{O}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) have similar 3D framework, except that the  $\text{ClNa}_6$  group is replaced by  $\text{BrNa}_6$  group. Hence only the structure of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$  will be discussed in detail as a representation. X-ray analysis reveals that  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$  crystallizes in the chiral space group  $P6_322$  of the hexagonal system. In the asymmetric unit of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ , there are two unique Na atoms, two unique B atoms, four unique O atoms and one unique Br atom (Table 2).

**Table 2** Atomic coordinates, equivalent isotropic displacement parameters and bond valence analyses for  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ).

atom	wyc $k$	x	y	z	U(eq) <sup>a</sup>	BVS <sup>b,c</sup>
$\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$						
Na(1)	12c	0.5438(5)	0.7980(5)	0.5576(2)	0.049(1)	0.838
Na(2)	6a	0	0.8478(6)	0.6667(0)	0.034(1)	0.979
B(1)	12c	0.5134(11)	0.3563(10)	0.5298(3)	0.017(2)	3.072
B(2)	12c	0.8631(10)	0.5462(11)	0.5479(4)	0.018(2)	3.088
O(1)	6b	0.5131(4)	0.4869(4)	0.5833(0)	0.017(1)	1.906
O(2)	12c	0.7133(7)	0.4383(7)	0.5050(2)	0.023(1)	2.048
O(3)	12c	0.4374(7)	0.1675(6)	0.5546(2)	0.022(1)	2.105
O(4)	12c	0.3994(8)	0.3529(7)	0.4734(2)	0.024(1)	2.057
Cl(1)	6b	0.9023(2)	0.0977(2)	0.5833(0)	0.049(1)	0.693
$\text{Na}_3\text{B}_4\text{O}_7\text{Br}$						
Na(1)	12c	0.4667(4)	0.2071(3)	0.0555(1)	0.034(1)	0.926
Na(2)	6a	0.8454(5)	0	0	0.035(1)	0.961
B(1)	12c	0.1428(7)	0.4548(8)	0.0477(3)	0.010(1)	3.058
B(2)	12c	0.4878(8)	0.6284(7)	0.0296(2)	0.008(1)	3.043
O(1)	6b	0.4896(3)	0.5104(3)	0.0833(0)	0.011(1)	1.933
O(2)	12c	0.2895(5)	0.5581(5)	0.0054(2)	0.013(1)	1.904
O(3)	12c	0.5635(6)	0.8252(5)	0.0536(2)	0.014(1)	2.032
O(4)	12c	0.5991(5)	0.6398(6)	0.9719(8)	0.016(1)	1.995
Br(1)	6b	0.1055(1)	0.8945(1)	0.0833(0)	0.042(1)	0.890

The structure of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$  is illustrated in Figure 2. The structure consists of the  $\text{B}_4\text{O}_9$  groups and  $\text{BrNa}_6$  polyhedra as structure building units (Figures 2(a) and (b)). Interestingly, a notable feature in the structure is the 1D helical  $[\text{Na}_3\text{Br}]$  chain

formed by the face-sharing  $\text{BrNa}_6$  polyhedra, which has not been found in other alkali metal borate halides. In general,  $\text{XM}_6$  octahedron ( $\text{A} = \text{alkali metals}; \text{X} = \text{halogen}$ ) exists in the structure as the 3D framework, such as  $\text{K}_3\text{B}_6\text{O}_{10}\text{X}^{18}$ ,  $\text{Na}_3\text{B}_6\text{O}_{10}\text{X}^{19}$ ,  $\text{K}_3\text{Na}_x\text{B}_6\text{O}_{10}\text{Br}$  ( $x = 0.13, 0.67, 1.30, 2.20$ )<sup>20</sup>,  $\text{RbNa}_2\text{B}_6\text{O}_{10}\text{X}^{19a}$ . The  $\text{B}_4\text{O}_9$  group is built of two  $\text{BO}_4$  tetrahedra (T) and two  $\text{BO}_3$  triangles ( $\Delta$ ) through corner-sharing, which is the typical tetraborate block with notation  $4:[2\Delta+2\text{T}]$  introduced by Christ and Clark<sup>30</sup>. Each  $\text{B}_4\text{O}_9$  group is connected by sharing its four terminal oxygens to form a 3D network with channels pointing along the  $c$  axis (Figure 2(c), Figure S3 in the Support Information), where the  $[\text{Na}_3\text{Br}]$  chains are filled. The tetraborate  $\text{B}_4\text{O}_9$  group is also found in many anhydrous as well as hydrous borates. It can be found that the  $\text{B}_4\text{O}_9$  groups can exist as isolated groups or further linked with each other to form 3D frameworks. For example, it can exist as, an isolated  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  group in Borax  $\text{Na}_2\text{B}_4\text{O}_7(\text{OH})_4 \cdot 8\text{H}_2\text{O}^{31}$ , as a  $[\text{B}_4\text{O}_7(\text{OH})_2]^{2-}$  group with a  $[\text{MnB}_4\text{O}_7(\text{OH}_2)]^{2-}$  chain in Roweite  $\text{Ca}_2\text{Mn}_2(\text{OH})_4\text{B}_4\text{O}_7(\text{OH})_2^{32}$ , as an isolated  $\text{B}_4\text{O}_9$  group in  $\text{Na}_3\text{GaB}_4\text{O}_9^{33}$ ,  $\text{Cs}_2\text{GeB}_4\text{O}_9^{34}$  and as a 3D  $[\text{B}_4\text{O}_9]^{2-}$  network in  $\text{Li}_2\text{B}_4\text{O}_7^{35}$  and  $\text{LiNaB}_4\text{O}_7^{36}$ .



**Figure 2.** Crystal structure of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ : (a) the  $\text{B}_4\text{O}_9$  group, (b) the  $\text{BrNa}_6$  polyhedron, (c) the  $\text{B}_4\text{O}_9$  network, (d) the  $[\text{Na}_3\text{Br}]$  chain, (e) the crystal structure of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ . (The  $\text{BO}_3$  triangles are shown in rose, the  $\text{BO}_4$  tetrahedra are shown in green).

The Na atoms have one kind of coordinated environment: both Na(1) and Na(2) atoms are coordinated by the four O atoms and two Br atoms (Figure S2 in the Supporting Information). The Na–O bond distances have a wide region varying from 2.282(5) to 2.928(5) Å, and Na–Br distances vary from 2.822(3) to 3.346(4) Å. The B atoms have two kinds of coordinated environments: the B(1) atoms are coordinated by three O atoms to form  $\text{BO}_3$  triangles while the B(2) atoms are coordinated to four O atoms to form  $\text{BO}_4$  tetrahedra. The B–O distances range from 1.356(6) to 1.501(6) Å. All of the bond lengths are consistent with those observed in other compounds<sup>19,20</sup>. The results of bond valence calculations (Na, 0.926–0.961; B, 3.043–3.058; Br, 0.890) indicate that the Na, B, and Br atoms are in oxidation states of +1, +3, and -1, respectively<sup>24,37</sup>.

The difference between the two crystal structures is mainly in the size and the coordination environment of the Cl and Br atoms. In  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$ , the Na–Cl bond lengths are range from 2.725(3) to 3.402(5) Å, while in  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ , the Na–Br bond lengths are range from 2.822(3) to 3.346(4) Å.

It is of some interest to find that the Na(1) and Cl (Br) atoms have large thermal factors in the two crystals during the refinement (Table 2), either indicating diffuse positioned atoms or site deficiencies.



Such phenomenon has been observed in some salt inclusion borates, such as  $\text{Ba}_4\text{Ga}_2\text{B}_8\text{O}_{18}\text{Cl}_2\cdot\text{NaCl}$ <sup>38</sup>,  $\text{Ba}_4(\text{BO}_3)_3(\text{SiO}_4)\cdot\text{Ba}_3\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ )<sup>39</sup>. From the bond length calculation, in  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$ , the Na(1)-O distances are in the range of 2.406(6) to 2.940(6) Å with an average length of 2.558(2) Å. It is found that the Na(1)-O bond length of 2.558(2) Å is significantly longer than the sum of their ionic radii (2.40 Å), whereas that of Na(1)-Cl (2.725(3) Å) is much shorter than the sum (2.83 Å). Such observation may indicate that, Na(1) and Cl are more or less forms of the NaCl molecule, and because it is weakly bonded to the rest of the lattice with a bond valence sum for Na(1) of only +0.84 and that for Cl of -0.69. In the same way, the average bond length of the Na(1)-O bonds in  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$  is 2.553(7) Å, which is longer than the sum of their ionic radii (2.40 Å), whereas that of Na(1)-Br (2.822(3) Å) is much shorter than the sum (2.98 Å), which further indicate that weak interaction between NaBr and the rest of the lattice. Therefore, from another perspective,  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) also can be regarded as salt inclusion borates<sup>40</sup>.

### IR spectra

Figure S1 in the Supporting Information presents the IR spectra of  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and they are similar. The assignments of IR spectra of the two compounds are listed in Table S4 in the Supporting Information. Referring to the literatures<sup>41-42</sup>, the peaks at 1346-1338  $\text{cm}^{-1}$  and 950  $\text{cm}^{-1}$  can be assigned to the asymmetric stretching and symmetric stretching vibrations of  $\text{BO}_3$ , respectively. The peaks located at 1140 and 862-753  $\text{cm}^{-1}$  arise from the asymmetric stretching and symmetric stretching vibrations of  $\text{BO}_4$ , respectively. The peaks observed in the regions of 663-654  $\text{cm}^{-1}$  are attributed to the out-of-plane bending of  $\text{BO}_3$ . The peaks at 520  $\text{cm}^{-1}$  characterize the bending of  $\text{BO}_3$  and  $\text{BO}_4$ . The peaks observed in the regions of 475-465  $\text{cm}^{-1}$  are attributed to the bending of  $\text{BO}_4$ . The IR spectra further confirm the existence of the  $\text{BO}_3$  triangles and  $\text{BO}_4$  tetrahedra, which is consistent with the results obtained from the single crystal X-ray structural analyses.

### UV-Vis-NIR diffuse reflectance spectroscopy

The UV-Vis-NIR diffuse reflectance spectra of  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in the region 190-2600 nm are shown in Figure S4 in the Supporting Information. It is clear that the two compounds have no obvious absorption from 340 to 2600 nm, but the absorption sharply increases below 340 nm and the cut-off edges for the two compounds are below 200 nm.

### Thermal analysis

The DSC/TG curves of the two crystals are shown in Figure 3. It can be seen that there is one endothermic peak at 745 and 766 °C on the DSC curves for  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$ , and  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ , respectively, along with weight loss on the TG curves. Analysis of the powder XRD pattern of the solidified melt reveal that the entire solid product exhibits a diffraction pattern different from that of the initial pure powder for the two compounds, as shown in Figure 1. It demonstrates that the two compounds are incongruently melting compounds.

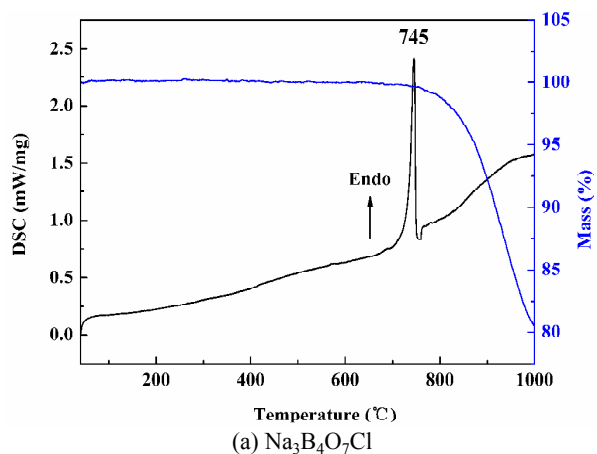
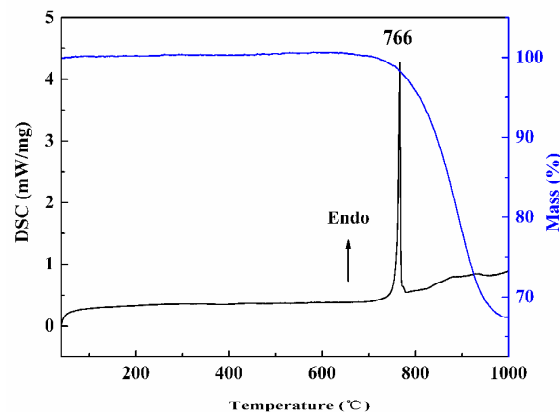
(a)  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$ (b)  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ 

Figure 3. TG/DSC curves for (a)  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$ , (b)  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ .

### Theoretical calculations

The electronic band structure of  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$  calculated by GGA method is plotted along high symmetry  $k$ -points in Figure 4 (The electronic band structure of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$  is in Figure S5 in the Support Information). All the two crystals are direct band gap materials with the calculated band gap of 4.53 eV ( $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$ ) and 4.16 eV ( $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ ), which are relatively smaller than experimental optical gaps (> 6.2 eV) due to a typical disadvantage in density functional theory (DFT) calculations.

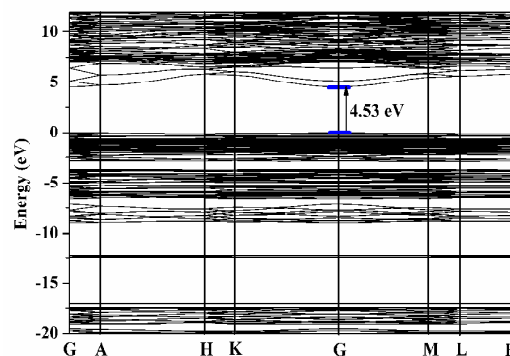
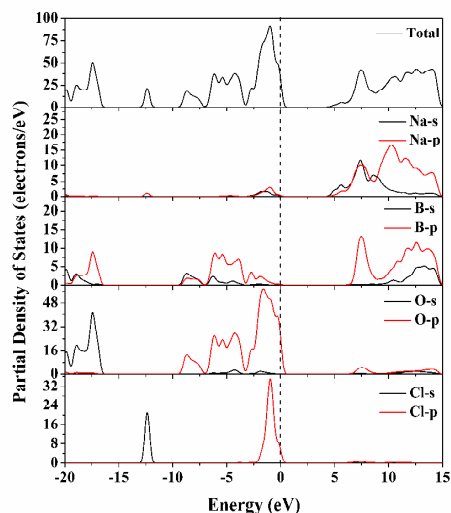


Figure 4. Calculated band structure of  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$ .

The PDOS of  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$  can be divided into four major distinct regions, as can be seen from Figure 5. The lowest part located from  $-23.0$  to  $-16.0$  eV contains contributions mainly from the O 2p orbital, with a small amount of B 2s and B 2p orbitals. The next region, around  $-12.5$  eV, is contributed by Cl 3s orbital with very sharp and narrow shape. The third region extends in a wide range from  $-9.5$  eV to VBM, that is, the Fermi level. This band mostly originates from the O 2p, B 2p and Cl 3p states, with some mixing of B 2s state. For the lowest conduction band, the main components are the Na 2p, Na s, and B 2p states. The PDOS of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$  (Figure S6 in the Support Information) is similar to that of  $\text{Na}_3\text{B}_6\text{O}_{10}\text{Cl}$  due to the two crystals having the similar building units and chemical environments.



**Figure 5.** The total and partial densities of states of  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$ .

## Conclusion

This study is a continuation of systematic investigation of the alkali-metal borate halides containing  $\text{XM}_6$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{M} =$  alkali metals) octahedra system. In this system, two new alkali metal borate halides  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) have been reported for the first time. The compounds exhibit a 3D structure consisting of  $\text{XNa}_6$  ( $\text{X} = \text{Cl}, \text{Br}$ ) polyhedra and  $\text{B}_4\text{O}_9$  groups. The  $\text{B}_4\text{O}_9$  group is connected by sharing its four terminal oxygens to form a 3D network with channels pointing along the  $c$  axis, where the 1D helical  $[\text{Na}_3\text{X}]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) chains are filled. In addition, the two compounds also can be regarded as  $\text{NaX}$  salt inclusion borates. The DSC/TG curves show that  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) melt incongruently. The formation of  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) provides another example that alkali-metal borate halides containing  $\text{XM}_6$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{M} =$  alkali metals) octahedra system possess very extensive crystal chemistry, which continues to provide a rich source of new compounds. In the future, the research on the alkali-metal borate halides containing  $\text{XM}_6$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{M} =$  alkali metals) octahedra system will be further expanded.

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## Notes and references

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† CCDC-number 1039806-1039807 for  $\text{Na}_3\text{B}_4\text{O}_7\text{Cl}$  and  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$  Crystal datas (CIF file); Checkcif; selected bond lengths (Å) and angles (deg.); The element analysis of  $\text{Na}_3\text{B}_4\text{O}_7\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ); The assignment of infrared spectra; Infrared spectra; The coordination environments of the cations in  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ ; The boron-oxygen framework in the crystal structure of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$  in  $bc$  plane; UV-Vis-NIR diffuse-reflectance spectra; Calculated band structure of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ ; The total and partial densities of states of  $\text{Na}_3\text{B}_4\text{O}_7\text{Br}$ .

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