Electronic Supplementary Information

Ba$_3$B$_{10}$O$_{17}$Br$_2$: A New Barium Borate Halide with B-O Layered Structure

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Experimental Section

Synthesis

$Ba_3B_{10}O_{17}Br_2$ was obtained in the sealed system. First, the raw materials (BaF_2, KBr and B_2O_3 at the mole of 1 : 1 : 3) were put into a Pt crucible to be preheated at 350 °C for 5 h, then cooled to room temperature and ground. After that, we loaded the preheated mixture into a tidy quartz tube which was washed using deionized water and dried at high temperature, and then the tube was flame-sealed under 10^{-3} Pa. The tube was heated to 650 °C, held at 650 °C for 20 h. Subsequently, it was cooled to 550 °C at a rate of 1.5 °C/h, then cooled to 350 °C at a rate of 2.5 °C/h, finally lowered to 30 °C at a rate of 10 °C/h. During the cooling process, the crystals were obtained. Colorless crystal was separated from the tube for structural characterization.

The polycrystalline sample of $Ba_3B_{10}O_{17}Br_2$ was prepared through solid-state reaction in the sealed system. The mixture ($BaBr_2$, $Ba(NO_3)_2$ and B_2O_3 at the molar ratio of 1 : 2 : 5) was preheated at 300 °C for 3 h, then elevated to 400 °C and held at 400 °C for 10 h. Before and after sintering at 400 °C, the sample was cooled to room temperature and ground. Then the preheated mixture was loaded into a tidy quartz tube, which was flame-sealed under 10^{-3} Pa. The tube was heated to 565 °C and held for 65 h.

The purity of the polycrystalline was confirmed by powder X-ray diffraction. The data were carried out through a Bruker D2 PHASER diffractometer using Cu Kα radiation (λ = 1.5418 Å). The diffraction patterns were set in the range of 10°-70° (2θ), its scan step width and fixed counting time are 0.02° and 1s/step, respectively. The diffraction patterns are well consistent with the calculated ones except several impurity peaks (Figure S1 in the Supporting Information (SI)).

Structural Determination.

Collection of the single-crystal XRD data was done at 296(2) K using a Bruker SMART APEX II 4K CCD diffractometer with Mo Kα radiation (λ=0.71073 Å), and the data were integrated with a SAINT program.[1] The direct methods and SHELXTL system were used to solve and refine the crystal structure, respectively.[2] All of the atoms positions were refined by full matrix least-squares techniques. The information of crystal data and structural refinements is summarized in Table S1, the atomic coordinates and the equivalent isotropic displacement parameters are given in Table S2. Table S3 lists the selected bond lengths and angles.

Optical Characterization.

The infrared (IR) spectrum was measured to specify the coordination of boron. And it was recorded using Shimadzu IRAffinity^{-1} Fourier transform IR spectrometer with the range: 400-4000 cm^{-1}. The sample was mixed with dried KBr.

For determining the UV cutoff edge of $Ba_3B_{10}O_{17}Br_2$, the UV diffuse reflectance spectrum was measured using Shimadzu SolidSpec-3700DUV spectrophotometer. Data were collected in the wavelength range 190 to 2500 nm. And the reflectance spectrum was converted to absorbance with the Kubelka–Munk function.[3]

Theoretical Calculations.

The electronic and band structures as well as linear optical property calculations were performed by employing CASTEP,[4] a plane-wave pseudopotential density functional theory (DFT) package, with the norm-conserving pseudopotentials (NCPs).[5-7] The exchange-correlation functional was Perdew−Burke−Emzerhof (PBE) functional within the generalized gradient approximation (GGA).[8] The plane-wave energy cutoff was set at 830.0 eV. Self-consistent field (SCF) calculations were performed with a convergence criterion of 5×10^{-7} eV/atom on the total energy. The Monkhorst-

Pack Scheme k-points grid sampling was set at 2×2×1 for the Brillouin zone (BZ). The valence electrons of the elements in $Ba_3B_{10}O_{17}Br_2$ were calculated as follows: Ba $5s^25p^66s^2$, B $2s^22p^1$, O $2s^22p^4$ and Br $4s^25p^5$, respectively. The empty bands were set as 3 times the valence bands in the calculation to ensure the convergence of optical properties. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique was employed in geometry optimization during the calculation and the converged criteria are that the residual forces on the atoms, the displacements and the energy change of atoms are less than 0.01 eV /Å, 5×10^{-4} Å and 5.0×10^{-6} eV, respectively. The default values of the CASTEP code were retained for other parameters and convergent criteria.

Table S1 Crystal data and structure refinement for $Ba_3B_{10}O_{17}Br_2$.

Empirical formula	$Ba_3B_{10}O_{17}Br_2$
Formula weight	951.94
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Monoclinic, $C2/c$
a (Å), α (deg.)	11.656(10), 90
b (Å), β (deg.)	6.647(6), 102.93(2)
c (Å), γ (deg.)	22.485(19), 90
Volume (Å3)	1698(3)
Z, Calculated density	4, 3.724 g/cm^3
Absorption coefficient	11.678 mm^{-1}
F(000)	1696
Theta range for data collection	3.55 to 27.58 deg.
Limiting indices	$-15 \leq h \leq 14$, $-8 \leq k \leq 8$, $-28 \leq l \leq 20$
Reflections collected/unique	5069/1949 [Rint = 0.0404]
Completeness to theta = 27.58	99.30%
Max. and min. transmission	0.7456 and 0.5249
Refinement method	Full-matrix least-squares on F_o^2
Data/restraints/parameters	1949/24/147
Goodness-of-fit on F_o^2	1.093
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	$R_1 = 0.0296$, $wR_2 = 0.0688$
R indices (all data)[a]	$R_1 = 0.0373$, $wR_2 = 0.0732$
Extinction coefficient	0.00020(6)
Largest diff. peak and hole	0.987 and -1.209 eÅ^{-3}

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

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $Ba_3B_{10}O_{17}Br_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ba(1)	1135(1)	2194(1)	554(1)	9(1)
Ba(2)	0	3526(1)	2500	27(1)
B(1)	4685(5)	12211(9)	869(3)	5(1)
B(2)	3372(5)	9145(9)	730(3)	5(1)
B(3)	3880(5)	5569(9)	1073(3)	5(1)
B(4)	1803(5)	6781(10)	715(3)	7(1)
B(5)	4765(6)	13328(9)	1907(3)	8(1)
O(1)	4166(3)	7746(6)	982(2)	7(1)
O(2)	2572(3)	5307(6)	906(2)	8(1)
O(3)	5616(3)	11370(6)	583(2)	6(1)
O(4)	4461(3)	14322(6)	701(2)	4(1)
O(5)	2171(3)	8636(6)	565(2)	10(1)
O(6)	5000	12735(8)	2500	11(1)
O(7)	4968(3)	11874(6)	1516(2)	8(1)
O(8)	3590(3)	11050(5)	584(2)	5(1)
O(9)	4295(3)	5161(6)	1725(2)	8(1)
Br(1)	2249(1)	809(1)	1946(1)	33(1)

Table S3. Selected bond lengths and angles for $Ba_3B_{10}O_{17}Br_2$.

Ba(1)-O(5)#1	2.653(4)	Ba(2)-Br(1)	3.626(2)
Ba(1)-O(2)	2.669(4)	B(1)-O(7)	1.436(7)
Ba(1)-O(1)#2	2.704(4)	B(1)-O(4)	1.462(7)
Ba(1)-O(4)#3	2.801(4)	B(1)-O(3)	1.489(7)
Ba(1)-O(3)#2	2.845(4)	B(1)-O(8)	1.507(7)
Ba(1)-O(8)#4	2.894(4)	B(2)-O(1)	1.345(7)
Ba(1)-O(4)#4	2.929(4)	B(2)-O(8)	1.347(7)
Ba(1)-O(8)#1	2.947(4)	B(2)-O(5)	1.407(7)
Ba(1)-O(3)#4	3.044(4)	B(3)-O(4)#1	1.450(7)
Ba(1)-Br(1)	3.242(3)	B(3)-O(9)	1.462(7)
Ba(2)-O(6)#2	2.798(6)	B(3)-O(2)	1.497(7)
Ba(2)-O(9)#5	2.842(4)	B(3)-O(1)	1.509(7)
Ba(2)-O(9)#2	2.842(4)	B(4)-O(2)	1.332(7)
Ba(2)-O(7)#5	3.131(4)	B(4)-O(5)	1.372(7)
Ba(2)-O(7)#2	3.131(4)	B(4)-O(3)#2	1.376(7)
Ba(2)-Br(1)#6	3.514(3)	B(5)-O(6)	1.358(7)
Ba(2)-Br(1)#7	3.514(3)	B(5)-O(9)#9	1.361(7)
Ba(2)-Br(1)#8	3.626(2)	B(5)-O(7)	1.362(8)
O(5)#1-Ba(1)-O(1)#2	122.57(12)	O(7)#5-Ba(2)-Br(1)	134.54(8)
O(1)#2-Ba(1)-O(4)#3	51.81(12)	Br(1)#8-Ba(2)-Br(1)	120.25(6)
O(4)#3-Ba(1)-O(8)#1	121.32(11)	O(7)-B(1)-O(3)	110.9(4)
O(4)#4-Ba(1)-O(8)#1	87.30(10)	O(4)-B(1)-O(8)	107.2(4)
O(5)#1-Ba(1)-O(3)#4	120.35(12)	O(3)-B(1)-O(8)	104.6(4)
O(5)#1-Ba(1)-Br(1)	69.81(10)	O(1)-B(2)-O(8)	127.1(5)
O(2)-Ba(1)-Br(1)	81.03(10)	O(1)-B(2)-O(5)	119.7(5)
O(1)#2-Ba(1)-Br(1)	83.32(10)	O(8)-B(2)-O(5)	113.1(5)
O(4)#4-Ba(1)-Br(1)	142.15(9)	O(4)#1-B(3)-O(9)	112.3(4)
O(3)#4-Ba(1)-Br(1)	161.38(7)	O(9)-B(3)-O(2)	108.6(4)
O(6)#2-Ba(2)-O(9)#5	141.93(8)	O(4)#1-B(3)-O(1)	108.9(4)
O(9)#2-Ba(2)-O(7)#5	161.53(10)	O(9)-B(3)-O(1)	106.3(4)
O(6)#2-Ba(2)-O(7)#2	44.72(8)	O(2)-B(3)-O(1)	108.7(4)
O(9)#2-Ba(2)-O(7)#2	99.79(12)	O(2)-B(4)-O(3)#2	119.7(5)
O(7)#5-Ba(2)-O(7)#2	89.45(16)	O(5)-B(4)-O(3)#2	118.6(5)
O(6)#2-Ba(2)-Br(1)#6	64.42(3)	O(6)-B(5)-O(9)#9	122.3(6)
O(9)#2-Ba(2)-Br(1)	61.91(9)	O(6)-B(5)-O(7)	113.7(5)

Symmetry transformations used to generate equivalent atoms:

#1 x, y-1, z   #2 x-1/2, y-1/2, z   #3 x-1/2, y-3/2, z   #4 -x+1/2, -y+3/2, -z
#5 -x+1/2, y-1/2, -z+1/2   #6 -x+1/2, y+1/2, -z+1/2   #7 x-1/2, y+1/2, z
#8 -x, y, -z+1/2   #9 x, y+1, z   #10 x+1/2, y+1/2, z
#11 x+1/2, y+3/2, z   #12 -x+1, y, -z+1/2   #13 x+1/2, y-1/2, z

Table S4. The barium borate halogenides.

No.	Compounds	Space group	B-O anionic framework	Cation /Boron	ref
1	$Ba_7(BO_3)_3F_5$	$P3_1c$	Isolated BO_3	2.33	9
2	$Ba_7B_{3.51}O_{10.53}F_{3.47}$	$P6_3$	Isolated BO_3	1.99	10
3	$Ba_5(BO_3)_3F$	$Pnma$	Isolated BO_3	1.67	11
4	$Ba_5(B_2O_5)_2F_2$	$C2/c$	Isolated B_2O_5	1.25	12
5	$Ba_3B_6O_{11}F_2$	$P2_1$	3D framework	0.5	13, 14
6	$Ba_4B_{11}O_{20}F$	$Cmc2_1$	3D framework	0.36	15
7	$Ba_2B_5O_9Cl$	$Pnn2$	3D framework	0.4	16
8	$Ba_2B_5O_9Br$	$Pmm2$	3D framework	0.4	16
9	$Ba_5(BO_3)_3Cl$	$C222_1$	Isolated BO_3	1.67	17
10	$Ba_5(BO_3)_3Br$	$C222_1$	Isolated BO_3	1.67	17
11	Ba_2BO_3Br	$P\bar{3}m1$	Isolated BO_3	2	18
12	$Ba_3BO_3Br_3$	$P\bar{1}$	Isolated BO_3	3	18
13	$Ba_3B_{10}O_{17}Br_2$	$C2/c$	2D $(B_{10}O_{17})_\infty$ double layer	0.3	This work

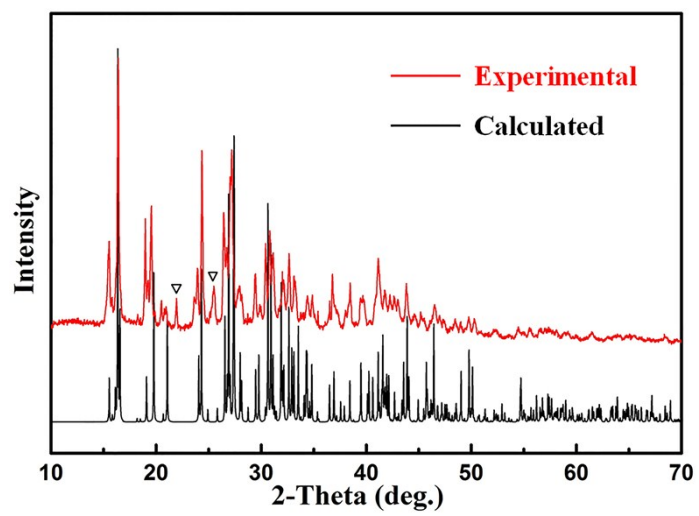Figure S1. Experimental and calculated XRD patterns of $Ba_3B_{10}O_{17}Br_2$.

Figure S2. (a) The arrangement of Ba(1)O_9Br; (b) The arrangement of Ba(2)O_5Br_4; (c) The 3D Ba-O-Br framework.

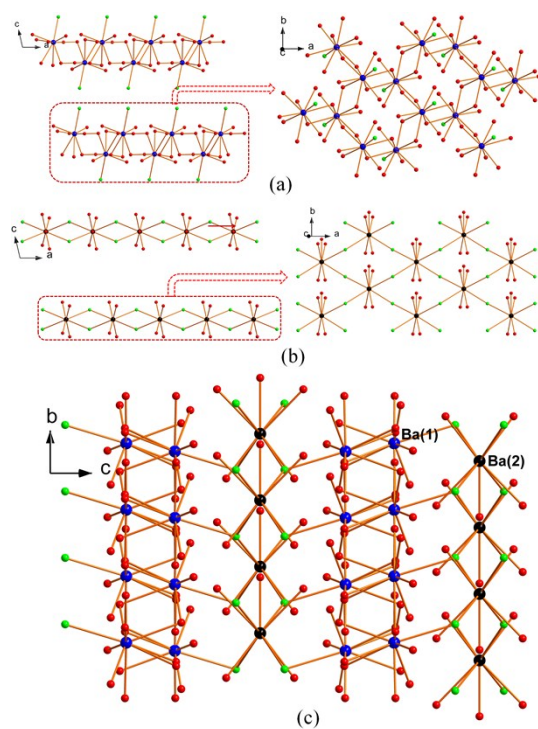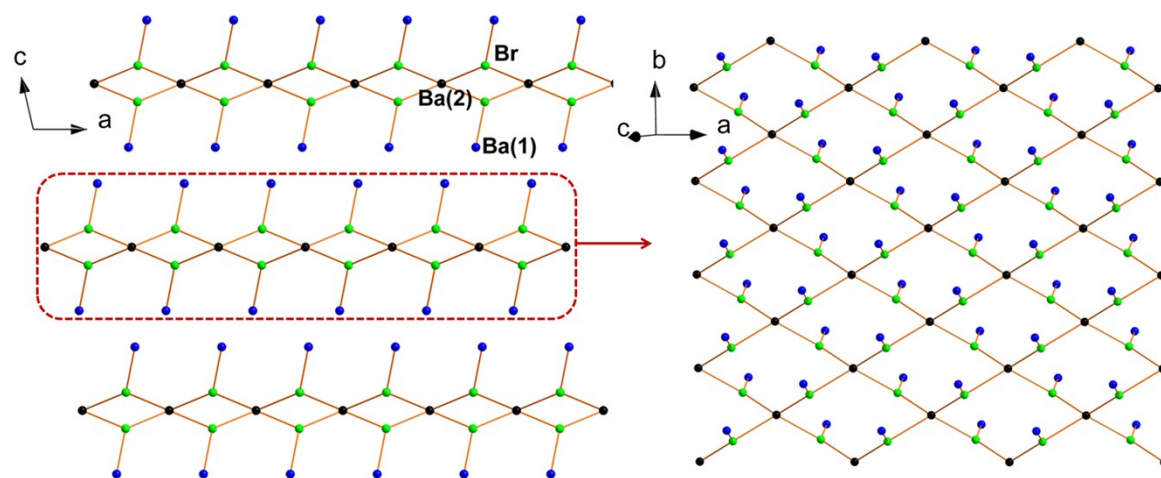Figure S3. The 2D layer formed by BrBa$_3$.

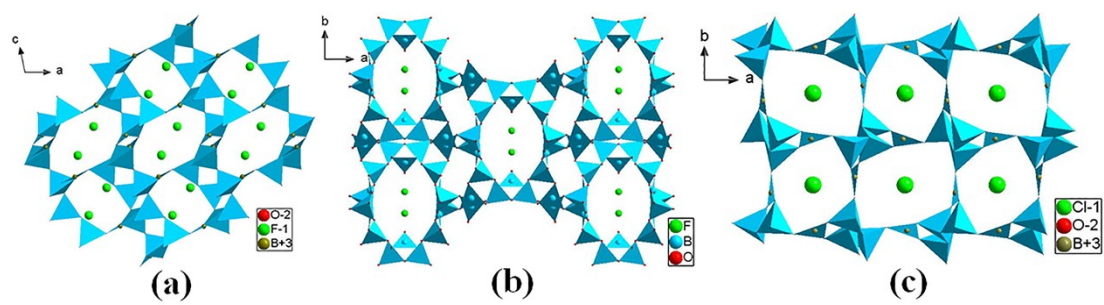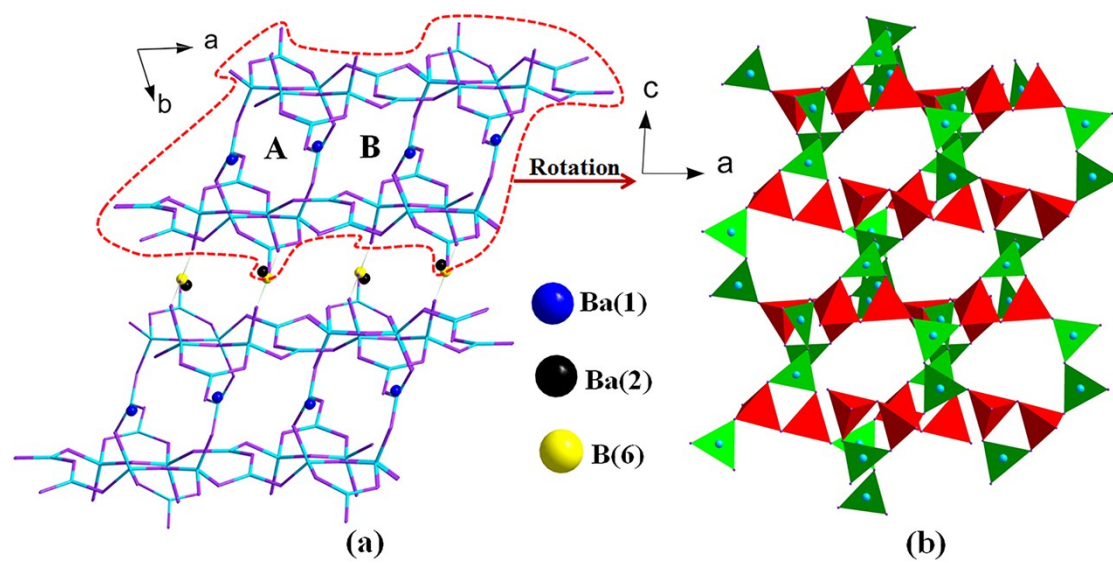Figure S4. The structures of $Ba_3B_6O_{11}F_2$, $Ba_4B_{11}O_{20}F$ and $Ba_2B_5O_9Cl$.

Figure S5. The structure of $Ba_2B_{10}O_{17}$.

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