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Supporting Information

Ba_2BS_3Cl and $Ba_5B_2S_8Cl_2$: First alkaline-earth metal thioborate halides with $[BS_3]$ units

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Supporting Information (SI)

1 .Syntheses of the Ba_2BS_3Cl and $Ba_5B_2S_8Cl_2$ Crystals

(1) The Ba_2BS_3Cl crystals for single crystal X-ray diffraction were obtained by the flux method. The starting reagents are lead chloride (99.9 %), barium sulfide (98 %), and boron powder (99.9 %), sulfur powder (99.9 %), purchased from Aladdin Bio-chemical Technology Co., Ltd. The lead chloride was used as the source of halogen and fluxing agent. A total of 0.5 g of $PbCl_2$, BaS, B and S in a molar ratio of 1: 4: 2: 2 was weighted in an argon atmosphere glove box, and then loaded into a graphite crucible, sealed in a quartz tube under a vacuum of about $\sim 10^{-3}$ Pa. After that, the tube was put into a temperature program-controlled furnace, heated to 900 °C in 200 h and kept at this temperature for 100 h, then cooled to room temperature at a rate of 3 °C/h. After the quartz tube was broken, the Ba_2BS_3Cl crystals with secondary phases like $PbCl_2$ and PbS were harvested in the graphite crucible.

(2) $Ba_5B_2S_8Cl_2$ crystals for single crystal X-ray diffraction were obtained by the flux method with the similar temperature procedure for the synthesis of Ba_2BS_3Cl. The used starting materials are $PbCl_2$: BaS : B : S = 1: 5: 2: 3 (molar ratio).

2. Structural Refinement and Crystal Data

The single crystal data of Ba_2BS_3Cl and $Ba_5B_2S_8Cl_2$ were collected using a Bruker SMART APEX II 4K CCD diffractometer equipped with Mo *Ka* radiation (λ = 0.71073Å) at room temperature. The single crystals were selected by using a microscope and fixed on the top of a glass fiber with epoxy and mounted on the machine. The data were refined base on Lorentz and polarization factors, and the

face-indexed absorption corrections were implemented by XPREP Program, the structure was solved with SHELXTL program package[1] and refined by full-matrix least-squares fitting on F^2. The space group *Pbcm* for Ba_2BS_3Cl and *C2/c* for $Ba_5B_2S_8Cl_2$ were recommended during the refinements. The finale structures were checked with PLATON[2], no other higher symmetry elements were found. The structure refinement details and crystallographic data are list in Table S1, atomic coordinates, isotropic displacement parameters and selected bond lengths and angles are given in Tables S3-S7.

3.Experimental and Computational Characterizations

Powder X-ray Diffraction. The powder XRD data were recorded on an automated Bruker D2 X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å) in the 2θ range of 10−70 ° with a step of 0.02 ° and a fixed counting time of 1 s/ step.

Elemental Analysis.

The semiquantitative elemental analysis was carried on the surface of an individual single crystal using a field emission scanning electron microscopy (SEM, SUPRA 55VP) equipped with an energy dispersive X-ray spectroscope (EDX, BRUKER x-flash-sdd-5010).

Raman Spectroscopy.

To investigate the Raman spectra, a LABRAM HR Evolution spectrometer equipped with a CCD detector by a 532 nm radiation was used to record Raman

scattering spectroscopy data in the 1000−100 cm^{-1} region. High-quality single crystals of the title compounds were put on a glass slide and located by using a 50 × objective lens for the measurements. The laser with 532 nm radiation was applied for the characterizations, the maximum power was 60 Mw and keep 15 s to complete the measurements.

Computational Description

The plane-wave pseudopotential method was used which was implemented in the CASTEP,[3, 4] the electronic structures of title compounds were performed. Ba_2BS_3Cl and $Ba_5B_2S_8Cl_2$ were optimized by The Perdew-Burke-Ernzerhof (PBE) exchange-correlation of Generalized Gradient Approximation (GGA).[5] Optimized norm-conserving pseudopotential (NCP)[6] in the Kleinman–Bylander form was employed and the valance electrons of the related atoms were: Ba $5s^2$ $5p^6$ $6s^2$, B $2s^2$ $2p^1$, S $3s^2$ $3p^4$, and Cl $3s^2$ $3p^5$, respectively. Also, kinetic energy cut-offs were set to be 830.0 eV and Monkhorst-Pack *k*-point meshes (3 × 3 × 3) with a density of fewer than 0.04 $Å^{-1}$ in the Brillouin zone (BZ) was adopted. The default values of the CASTEP code were used on the aspect of the other calculation parameters and convergence criteria.

To detect birefringence controlled by the fundamental building units, a response electron distribution anisotropy (REDA) method[7] can be employed, which reflects that the optical anisotropy is proportional to the REDA index: $\Delta n \sim \sum_i [N_c Z_a \Delta \rho^b] i/(n_1 E_g)$, where N_c is the coordination number of the nearest neighbor cations to the central

anion, Z_a is the formal chemical valence of the anion, $\Delta\rho^b$ is the difference of covalent electron density of the covalent bond i on the optical principal axes of a crystal, n_1 is the minimal refractive index, E_g is the optical bandgap.

Table S1. Crystal Data and Structure Refinements for Ba_2BS_3Cl and $Ba_5B_2S_8Cl_2$.

Empirical formula	Ba_2BS_3Cl	$Ba_5B_2S_8Cl_2$
Formula weight	417.12	1035.7
Crystal system	Orthorhombic	Monoclinic
Crystal color	Colorless	Light green
Space group	*Pbcm* (No. 57)	*C*2/*c* (No. 15)
a (Å)	8.617(2)	23.318(11)
b (Å)	8.999(3)	8.609(4)
c (Å)	9.323(3)	8.942(4)
β (deg.)	90	94.033(6)
V (Å^3)	723.0(3)	1790.6(15)
Z	4	4
D_c (g.cm^{-3})	3.832	3.842
μ (mm^{-1})	11.939	12.035
F(000)	728	1808
GOOF on F^2	1.074	1.026
R_1, wR_2 ($I > 2\sigma(I)$) [α]	0.0222, 0.0475	0.0277, 0.0588
R_1, wR_2 (all data) [α]	0.0267, 0.0491	0.0330, 0.0609
Largest diff peak/hole, e·Å^{-3}	0.648/−0.986	1.030/−1.329

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

Table S2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters of Ba_2BS_3Cl.

Atom	Oxidation	Wyckoff	*Occ.*	*x*	*y*	*z*	[a]*U* (eq)
Ba1	+2	4*c*	1.0	0.07146(5)	0.25	0.5	0.019(1)
Ba2	+2	4d	1.0	0.60463(4)	0.38173(4)	0.75	0.016(1)
B1	+3	4d	1.0	0.1925(8)	0.5366(7)	0.75	0.014(1)
S1	−2	8e	1.0	0.29070(15)	0.57065(14)	0.91807(11)	0.025(1)
S2	−2	4d	1.0	−0.01158(17)	0.47834(17)	0.75	0.018(1)
Cl1	−1	4d	1.0	0.31343(18)	0.20553(16)	0.75	0.023(1)

[a]U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $Ba_5B_2S_8Cl_2$.

Atom	Oxidation	Wyckoff	*Occ.*	*x*	*y*	*z*	^aU (eq)
Ba1	+2	4e	1.0	0.5	0.56405(5)	0.75	0.016(1)
Ba2	+2	8f	1.0	0.40189(2)	1.11164(4)	0.60198(3)	0.016(1)
Ba3	+2	8f	1.0	0.29893(2)	0.59642(4)	0.73421(4)	0.014(1)
B1	+3	8f	1.0	0.3950(3)	0.6787(7)	0.4433(6)	0.012(1)
S1	−2	8f	1.0	0.46307(6)	0.77279(18)	0.41838(15)	0.019(1)
S2	−2	8f	1.0	0.22887(6)	0.35424(16)	0.52420(15)	0.015(1)
S3	−2	8f	1.0	0.39496(6)	0.47851(16)	0.51762(15)	0.016(1)
S4	−2	8f	1.0	0.32690(6)	0.76929(18)	0.38969(17)	0.022(1)
Cl1	−1	8f	1.0	0.40761(6)	0.81905(16)	0.77496(14)	0.018(1)

$^aU_{eq}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Selected Bond Lengths [Å] and Angles [°] for Ba_2BS_3Cl.

Ba(1)-Cl(1)	3.1529(13)	Cl(1)-Ba(1)-S(2)#10	127.37(4)	Cl(1)#3-Ba(2)-S(1)#7	78.85(2)
Ba(1)-Cl(1)#10	3.1529(13)	Cl(1)-Ba(1)-S(2)#13	134.03(4)	Cl(1)-Ba(2)-S(1)#4	77.29(4)
Ba(1)-S(1)#5	3.5327(14)	Cl(1)-Ba(1)-S(2)	71.93(4)	Cl(1)#3-Ba(2)-S(1)	73.42(4)
Ba(1)-S(1)#11	3.5956(16)	S(1)#5-Ba(1)-S(1)#10	115.34(5)	Cl(1)#3-Ba(2)-S(1)#4	138.82(3)
Ba(1)-S(1)#10	3.5327(14)	S(1)#12-Ba(1)-S(1)#11	59.55(4)	Cl(1)-Ba(2)-S(1)#7	107.75(2)
Ba(1)-S(1)#12	3.5956(16)	S(1)#10-Ba(1)-S(1)#11	141.71(3)	Cl(1)-Ba(2)-S(1)#5	67.21(4)
Ba(1)-S(2)#10	3.1887(12)	S(1)#5-Ba(1)-S(1)#12	141.71(3)	Cl(1)-Ba(2)-S(1)#6	107.75(2)
Ba(1)-S(2)	3.1887(12)	S(1)#10-Ba(1)-S(1)#12	98.25(3)	Cl(1)#3-Ba(2)-S(1)#5	73.42(4)
Ba(1)-S(2)#12	3.4170(13)	S(1)#5-Ba(1)-S(1)#11	98.25(3)	Cl(1)#3-Ba(2)-S(1)#6	78.85(2)
Ba(1)-S(2)#13	3.4170(13)	S(2)-Ba(1)-S(1)#5	55.64(3)	Cl(1)-Ba(2)-S(2)#2	162.44(4)
Ba(2)-Cl(1)	2.9684(17)	S(2)#13-Ba(1)-S(1)#5	69.14(3)	Cl(1)#3-Ba(2)-S(2)#2	61.65(4)
Ba(2)-Cl(1)#3	2.9982(17)	S(2)#13-Ba(1)-S(1)#11	53.33(3)	S(1)#8-Ba(2)-S(1)	144.50(3)
Ba(2)-S(1)#4	3.3326(14)	S(2)#10-Ba(1)-S(1)#5	143.56(3)	S(1)#6-Ba(2)-S(1)#5	74.27(4)
Ba(2)-S(1)#5	3.5586(15)	S(2)#10-Ba(1)-S(1)#11	86.51(4)	S(1)#8-Ba(2)-S(1)#4	56.10(4)
Ba(2)-S(1)#6	3.2518(13)	S(2)-Ba(1)-S(1)#12	86.51(4)	S(1)#4-Ba(2)-S(1)	113.58(3)
Ba(2)-S(1)	3.5587(15)	S(2)-Ba(1)-S(1)#10	143.56(3)	S(1)#4-Ba(2)-S(1)#5	144.50(3)
Ba(2)-S(1)#7	3.2518(13)	S(2)#10-Ba(1)-S(1)#12	70.80(3)	S(1)#5-Ba(2)-S(1)	52.25(4)
Ba(2)-S(1)#8	3.3326(14)	S(2)-Ba(1)-S(1)#11	70.81(3)	S(1)#7-Ba(2)-S(1)#5	124.54(2)
Ba(2)-S(2)#2	3.4196(18)	S(2)#12-Ba(1)-S(1)#12	53.33(3)	S(1)#6-Ba(2)-S(1)#8	65.68(4)
S(1)-B(1)	1.807(4)	S(2)#12-Ba(1)-S(1)#11	109.57(3)	S(1)#8-Ba(2)-S(1)#5	113.58(3)
S(2)-B(1)	1.835(7)	S(2)#13-Ba(1)-S(1)#12	109.57(3)	S(1)#7-Ba(2)-S(1)#6	144.23(5)
Cl(1)-Ba(1)-Cl(1)#10	97.20(5)	S(2)#13-Ba(1)-S(1)#10	121.18(3)	S(1)#6-Ba(2)-S(1)#4	118.89(3)
Cl(1)-Ba(1)-S(1)#5	65.81(4)	S(2)#10-Ba(1)-S(1)#10	55.64(3)	S(1)#7-Ba(2)-S(1)#8	118.89(3)
Cl(1)#10-Ba(1)-S(1)#12	142.00(3)	S(2)#12-Ba(1)-S(1)#10	69.14(3)	S(1)#6-Ba(2)-S(1)	124.54(3)
Cl(1)#10-Ba(1)-S(1)#11	111.10(3)	S(2)#12-Ba(1)-S(1)#5	121.18(3)	S(1)#7-Ba(2)-S(1)#4	65.68(4)
Cl(1)#10-Ba(1)-S(1)#5	72.69(3)	S(2)-Ba(1)-S(2)#13	90.21(2)	S(1)#7-Ba(2)-S(1)	74.27(4)
Cl(1)-Ba(1)-S(1)#11	142.00(3)	S(2)-Ba(1)-S(2)#12	85.90(2)	S(1)#4-Ba(2)-S(2)#2	87.24(3)
Cl(1)-Ba(1)-S(1)#10	72.69(3)	S(2)#12-Ba(1)-S(2)#13	162.63(5)	S(1)#7-Ba(2)-S(2)#2	72.44(2)
Cl(1)#10-Ba(1)-S(1)#10	65.81(4)	S(2)#10-Ba(1)-S(2)#12	90.21(2)	S(1)#6-Ba(2)-S(2)#2	72.44(2)
Cl(1)-Ba(1)-S(1)#12	111.10(3)	S(2)#10-Ba(1)-S(2)#13	85.90(2)	S(1)#8-Ba(2)-S(2)#2	87.24(3)
Cl(1)#10-Ba(1)-S(2)#13	60.31(4)	S(2)-Ba(1)-S(2)#10	154.06(6)	S(2)#2-Ba(2)-S(1)	127.86(3)
Cl(1)-Ba(1)-S(2)#12	60.31(4)	Cl(1)-Ba(2)-Cl(1)#3	135.91(4)	S(2)#2-Ba(2)-S(1)#5	127.86(3)
Cl(1)#10-Ba(1)-S(2)#10	71.93(4)	Cl(1)-Ba(2)-S(1)#8	77.29(4)	S(1)#5-B(1)-S(1)	120.3(4)
Cl(1)#10-Ba(1)-S(2)#12	134.03(4)	Cl(1)-Ba(2)-S(1)	67.21(4)	S(1)-B(1)-S(2)	119.8(2)
Cl(1)#10-Ba(1)-S(2)	127.37(4)	Cl(1)#3-Ba(2)-S(1)#8	138.82(3)	S(1)#5-B(1)-S(2)	119.8(2)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,-z+3/2 #2 x+1,y,z #3 -x+1,y+1/2,-z+3/2
#4 -x+1,y-1/2,z #5 x,y,-z+3/2 #6 -x+1,-y+1,z-1/2
#7 -x+1,-y+1,-z+2 #8 -x+1,y-1/2,-z+3/2
#9 x,y,-z+1/2 #10 x,-y+1/2,z-1/2
#11 -x,-y+1,z-1/2 #12 -x,y-1/2,-z+3/2
#13 -x,-y+1,-z+1 #14 -x,-y+1,z+1/2
#15 x-1,y,z

Table S5. Selected Bond Lengths [Å] and Angles [°] for $Ba_5B_2S_8Cl_2$.

Ba(1)-Cl(1)	3.0949(18)	S(1)#5-Ba(1)-S(1)#7	138.78(4)	S(2)#4-Ba(2)-S(1)	107.81(4)
Ba(1)-Cl(1)#7	3.0949(18)	S(1)#5-Ba(1)-S(1)#1	63.26(6)	S(2)#4-Ba(2)-S(1)#9	147.13(4)
Ba(1)-S(1)	3.5221(19)	S(1)#7-Ba(1)-S(1)	118.64(6)	S(2)#4-Ba(2)-S(3)#10	78.32(4)
Ba(1)-S(1)#7	3.5221(19)	S(1)#1-Ba(1)-S(1)#7	96.70(5)	S(2)#4-Ba(2)-S(4)#2	73.00(5)
Ba(1)-S(1)#5	3.406(2)	S(1)#1-Ba(1)-S(1)	138.78(4)	S(3)#10-Ba(2)-S(1)	132.91(4)
Ba(1)-S(1)#1	3.406(2)	S(1)#5-Ba(1)-S(1)	96.70(5)	S(3)#10-Ba(2)-S(1)#9	74.20(4)
Ba(1)-S(3)#1	3.5616(18)	S(1)#5-Ba(1)-S(3)#5	53.71(3)	S(3)#10-Ba(2)-S(4)#2	82.04(4)
Ba(1)-S(3)	3.1849(17)	S(1)-Ba(1)-S(3)#1	118.63(4)	S(4)#2-Ba(2)-S(1)	144.99(4)
Ba(1)-S(3)#5	3.5616(18)	S(1)#1-Ba(1)-S(3)#1	53.71(3)	Cl(1)-Ba(3)-S(2)#3	72.64(4)
Ba(1)-S(3)#7	3.1849(18)	S(1)#1-Ba(1)-S(3)#5	114.62(4)	Cl(1)-Ba(3)-S(2)#1	106.05(4)
Ba(2)-Cl(1)#8	2.9966(19)	S(1)#5-Ba(1)-S(3)#1	114.62(4)	Cl(1)-Ba(3)-S(2)	146.68(4)
Ba(2)-Cl(1)	2.9540(18)	S(1)#7-Ba(1)-S(3)#5	118.63(4)	Cl(1)-Ba(3)-S(3)#1	62.66(4)
Ba(2)-S(1)#9	3.319(2)	S(1)-Ba(1)-S(3)#5	68.02(4)	Cl(1)-Ba(3)-S(3)	71.15(4)
Ba(2)-S(1)	3.6837(19)	S(1)#7-Ba(1)-S(3)#1	68.02(4)	Cl(1)-Ba(3)-S(4)	69.53(4)
Ba(2)-S(1)#2	3.2345(19)	S(3)-Ba(1)-S(1)	55.76(4)	Cl(1)-Ba(3)-S(4)#1	111.95(4)
Ba(2)-S(2)#4	3.189(2)	S(3)-Ba(1)-S(1)#5	73.83(4)	Cl(1)-Ba(3)-S(4)#4	120.95(5)
Ba(2)-S(3)#10	3.249(2)	S(3)#7-Ba(1)-S(1)#1	73.83(4)	S(2)-Ba(3)-S(2)#1	107.23(5)
Ba(2)-S(4)#2	3.3704(18)	S(3)#7-Ba(1)-S(1)#7	55.77(4)	S(2)-Ba(3)-S(2)#3	137.27(3)
Ba(3)-Cl(1)	3.1778(18)	S(3)-Ba(1)-S(1)#7	142.99(4)	S(2)#1-Ba(3)-S(2)#3	38.54(5)
Ba(3)-S(2)#3	3.1953(17)	S(3)#7-Ba(1)-S(1)#5	83.39(4)	S(2)-Ba(3)-S(3)	77.80(5)
Ba(3)-S(2)	3.1798(17)	S(3)#7-Ba(1)-S(1)	142.99(4)	S(2)#1-Ba(3)-S(3)#1	76.24(5)
Ba(3)-S(2)#1	3.1890(18)	S(3)-Ba(1)-S(1)#1	83.39(4)	S(2)-Ba(3)-S(3)#1	127.84(4)
Ba(3)-S(3)	3.2258(17)	S(3)-Ba(1)-S(3)#5	94.10(5)	S(2)#1-Ba(3)-S(3)	161.28(4)
Ba(3)-S(3)#1	3.3247(18)	S(3)-Ba(1)-S(3)#7	153.26(5)	S(2)#3-Ba(3)-S(3)	143.79(4)
Ba(3)-S(4)#4	3.2734(19)	S(3)#1-Ba(1)-S(3)#5	168.19(5)	S(2)#3-Ba(3)-S(3)#1	77.13(4)
Ba(3)-S(4)#1	3.485(2)	S(3)-Ba(1)-S(3)#1	83.16(5)	S(2)-Ba(3)-S(4)#1	73.57(5)
Ba(3)-S(4)	3.523(2)	S(3)#7-Ba(1)-S(3)#5	83.16(5)	S(2)#3-Ba(3)-S(4)#4	76.34(4)
S(1)-B(1)	1.810(6)	S(3)#7-Ba(1)-S(3)#1	94.10(5)	S(2)#1-Ba(3)-S(4)	142.34(4)
S(2)-S(2)#11	2.107(3)	Cl(1)-Ba(2)-Cl(1)#8	132.63(3)	S(2)#1-Ba(3)-S(4)#1	83.58(4)
S(3)-B(1)	1.847(6)	Cl(1)#8-Ba(2)-S(1)#2	138.17(4)	S(2)-Ba(3)-S(4)	83.08(5)
S(4)-B(1)	1.803(6)	Cl(1)#8-Ba(2)-S(1)#9	77.25(4)	S(2)#3-Ba(3)-S(4)#1	113.52(5)
Cl(1)-Ba(1)-Cl(1)#7	89.64(7)	Cl(1)#8-Ba(2)-S(1)	71.19(4)	S(2)#3-Ba(3)-S(4)	110.89(5)
Cl(1)#7-Ba(1)-S(1)#7	64.44(4)	Cl(1)-Ba(2)-S(1)#9	106.04(4)	S(2)-Ba(3)-S(4)#4	67.71(5)
Cl(1)-Ba(1)-S(1)#1	111.91(4)	Cl(1)-Ba(2)-S(1)	63.48(5)	S(2)#1-Ba(3)-S(4)#4	74.33(5)
Cl(1)-Ba(1)-S(1)#7	73.00(4)	Cl(1)-Ba(2)-S(1)#2	78.66(5)	S(3)-Ba(3)-S(3)#1	86.44(5)
Cl(1)-Ba(1)-S(1)#5	146.59(4)	Cl(1)#8-Ba(2)-S(2)#4	75.13(4)	S(3)#1-Ba(3)-S(4)#1	54.80(3)
Cl(1)#7-Ba(1)-S(1)#1	146.59(4)	Cl(1)-Ba(2)-S(2)#4	105.70(4)	S(3)-Ba(3)-S(4)	55.18(4)
Cl(1)#7-Ba(1)-S(1)	73.00(4)	Cl(1)-Ba(2)-S(3)#10	161.86(4)	S(3)-Ba(3)-S(4)#1	80.61(4)
Cl(1)#7-Ba(1)-S(1)#5	111.91(4)	Cl(1)#8-Ba(2)-S(3)#10	65.46(4)	S(3)-Ba(3)-S(4)#4	123.47(5)
Cl(1)-Ba(1)-S(1)	64.44(4)	Cl(1)-Ba(2)-S(4)#2	82.32(5)	S(3)#1-Ba(3)-S(4)	126.32(4)
Cl(1)#7-Ba(1)-S(3)#1	129.54(4)	Cl(1)#8-Ba(2)-S(4)#2	138.19(4)	S(4)#4-Ba(3)-S(3)#1	150.01(4)

Cl(1)#7-Ba(1)-S(3)	128.63(4)	S(1)#2-Ba(2)-S(1)	118.20(5)	S(4)#4-Ba(3)-S(4)#1	126.32(3)
Cl(1)-Ba(1)-S(3)#7	128.63(4)	S(1)#9-Ba(2)-S(1)	79.30(5)	S(4)#4-Ba(3)-S(4)	76.79(4)
Cl(1)-Ba(1)-S(3)#5	129.54(4)	S(1)#2-Ba(2)-S(1)#9	66.05(4)	S(4)#1-Ba(3)-S(4)	133.59(4)
Cl(1)-Ba(1)-S(3)#1	60.62(4)	S(1)#2-Ba(2)-S(3)#10	85.17(4)	S(1)-B(1)-S(3)	119.0(3)
Cl(1)#7-Ba(1)-S(3)#5	60.62(4)	S(1)#2-Ba(2)-S(4)#2	57.28(5)	S(4)-B(1)-S(1)	122.5(4)
Cl(1)-Ba(1)-S(3)	72.77(4)	S(1)#9-Ba(2)-S(4)#2	119.72(4)	S(4)-B(1)-S(3)	118.5(3)
Cl(1)#7-Ba(1)-S(3)#7	72.77(4)	S(2)#4-Ba(2)-S(1)#2	129.27(4)		

Symmetry transformations used to generate equivalent atoms:

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

Table S6. Anisotropic Displacement Parameters (Å^2) for Ba_2BS_3Cl.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	0.0129(2)	0.0151(3)	0.0185(2)	0.00000	−0.00257(18)	0.00000
Ba2	0.01762(19)	0.0167(2)	0.01327(17)	0.00009(14)	−0.00003(13)	0.00464(12)
Ba3	0.01278(18)	0.01629(19)	0.01413(17)	0.00061(13)	0.00057(12)	−0.00362(12)
B1	0.013(3)	0.017(3)	0.006(3)	0.001(2)	−0.001(2)	0.000(2)
S1	0.0118(7)	0.0256(8)	0.0193(7)	−0.0029(6)	0.0021(5)	0.0027(6)
S2	0.0142(7)	0.0149(7)	0.0153(7)	−0.0020(5)	0.0001(5)	-0.0010(5)
S3	0.0169(7)	0.0118(7)	0.0189(7)	0.0009(6)	-0.0030(5)	-0.0017(5)
S4	0.0135(7)	0.0260(9)	0.0270(8)	0.0073(6)	-0.0004(6)	0.0086(6)
Cl1	0.0276(8)	0.0140(7)	0.0134(6)	0.0006(6)	0.0030(5)	0.0001(5)

Table S7. Anisotropic Displacement Parameters (Å^2) for $Ba_5B_2S_8Cl_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	0.0129(2)	0.0151(3)	0.0185(2)	0.00000	−0.00257(18)	0.00000
Ba2	0.01762(19)	0.0167(2)	0.01327(17)	0.00009(14)	−0.00003(13)	0.00464(12)
Ba3	0.01278(18)	0.01629(19)	0.01413(17)	0.00061(13)	0.00057(12)	−0.00362(12)
B1	0.013(3)	0.017(3)	0.006(3)	0.001(2)	−0.001(2)	0.000(2)
S1	0.0118(7)	0.0256(8)	0.0193(7)	−0.0029(6)	0.0021(5)	0.0027(6)
S2	0.0142(7)	0.0149(7)	0.0153(7)	−0.0020(5)	0.0001(5)	-0.0010(5)
S3	0.0169(7)	0.0118(7)	0.0189(7)	0.0009(6)	-0.0030(5)	-0.0017(5)
S4	0.0135(7)	0.0260(9)	0.0270(8)	0.0073(6)	-0.0004(6)	0.0086(6)
Cl1	0.0276(8)	0.0140(7)	0.0134(6)	0.0006(6)	0.0030(5)	0.0001(5)

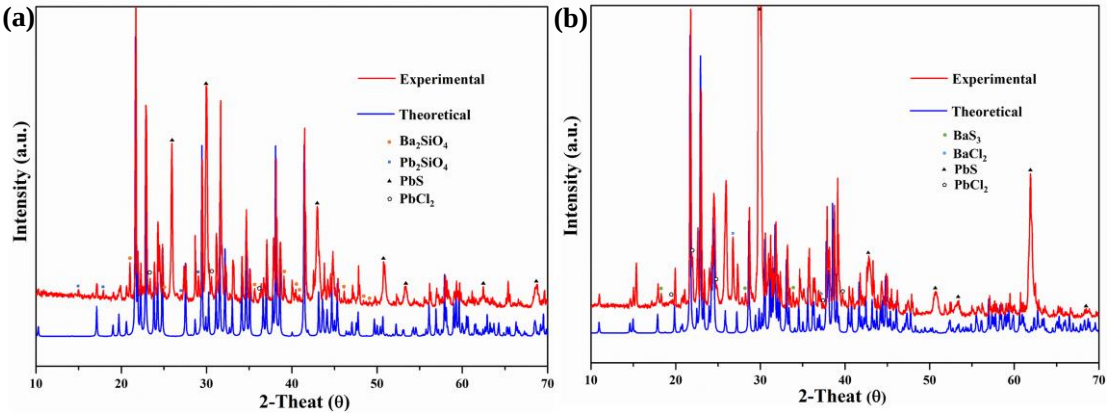

Fig. S1. Experimental and theoretical X-ray diffraction patterns of Ba_2BS_3Cl (a) and $Ba_5B_2S_8Cl_2$ (b).

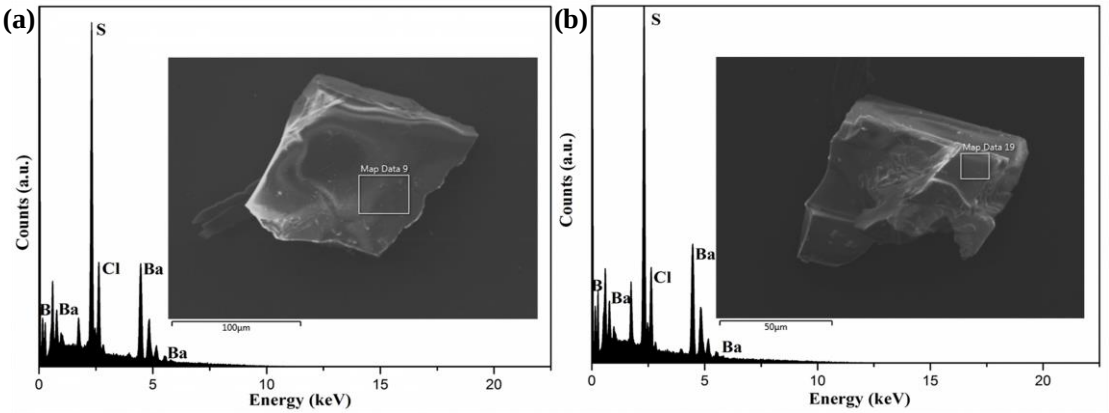

Fig. S2. The Energy-dispersive X-ray Spectroscopy of Ba_2BS_3Cl (a) and $Ba_5B_2S_8Cl_2$ (b). The results confirm the existence of the Ba, B, S and Cl elements in the title compounds.

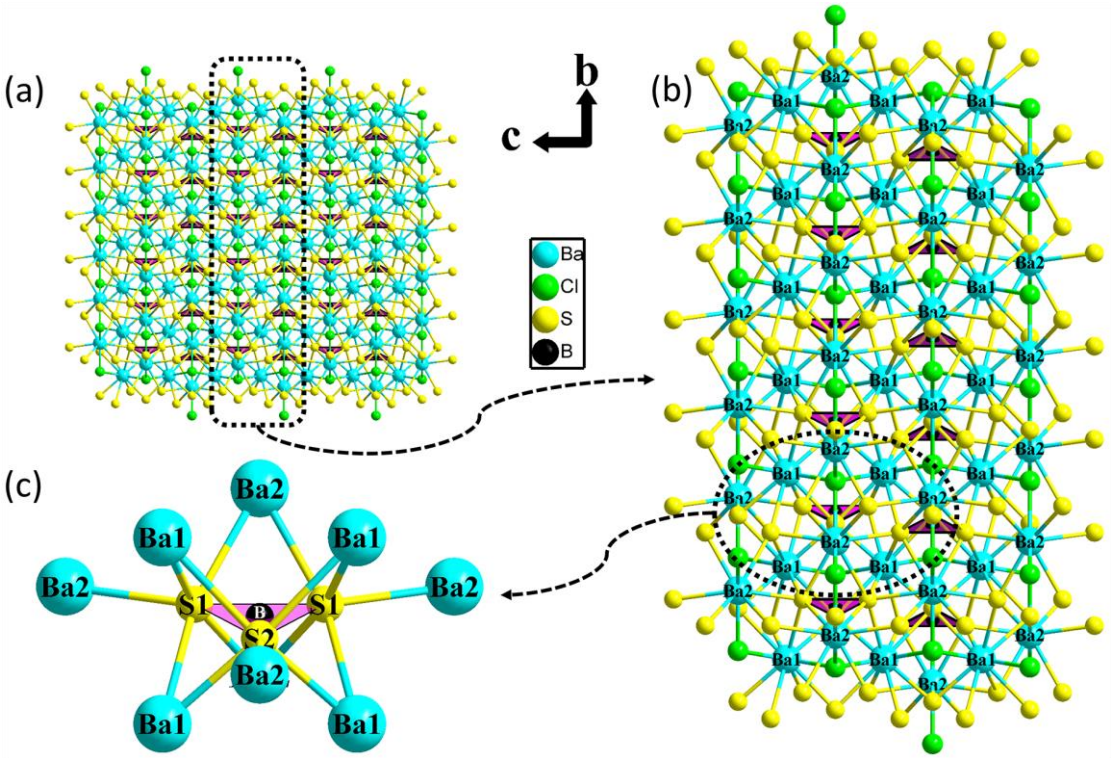

Fig. S3. (a) The 3D network structure of Ba_2BS_3Cl; (b) The $[BS_3]$ pseudo-layers connected with Ba-S-Cl group by corner-sharing; (c) The connection between $[BS_3]$ units and Ba atoms.

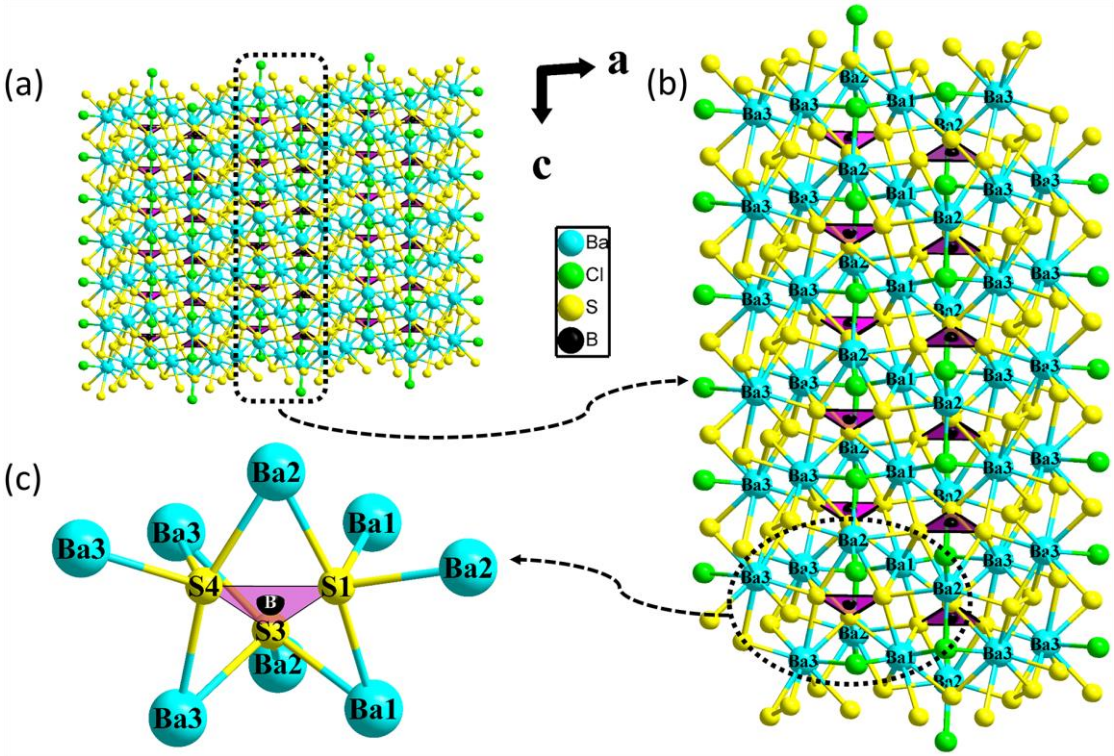

Fig. S4. (a) The 3D network structure of $Ba_5B_2S_8Cl_2$; (b) The $[BS_3]$ pseudo-layers connected with Ba-S-Cl group by corner-sharing; (c) The connection between $[BS_3]$ units and Ba atoms.

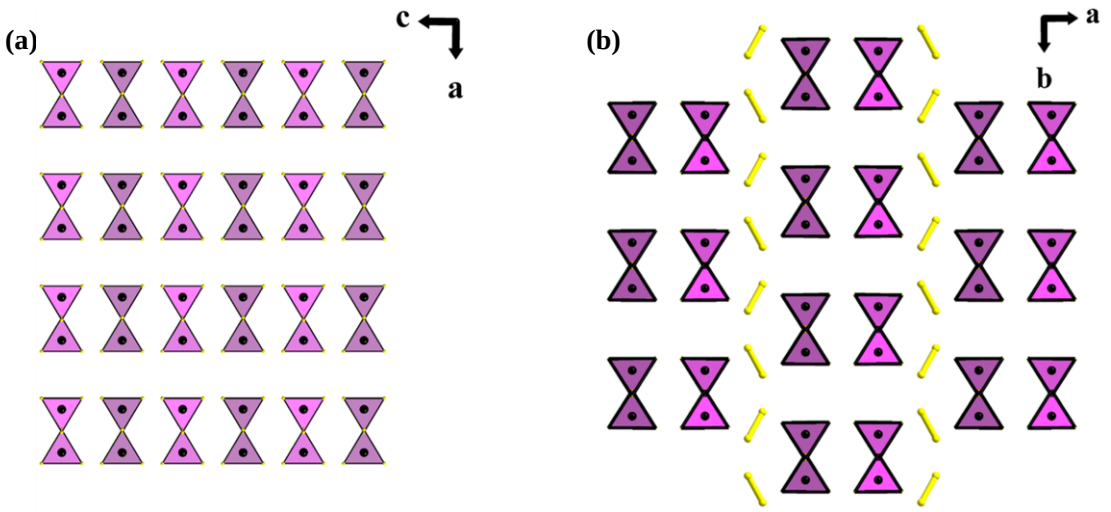

Fig. S5. (a) The square array-like arrangement of [BS_3] units in Ba_2BS_3Cl viewed along the *b* axis; (b) The honeycomb-like arrangement of [BS_3] units in $Ba_5B_2S_8Cl_2$ viewed along the *c* axis.

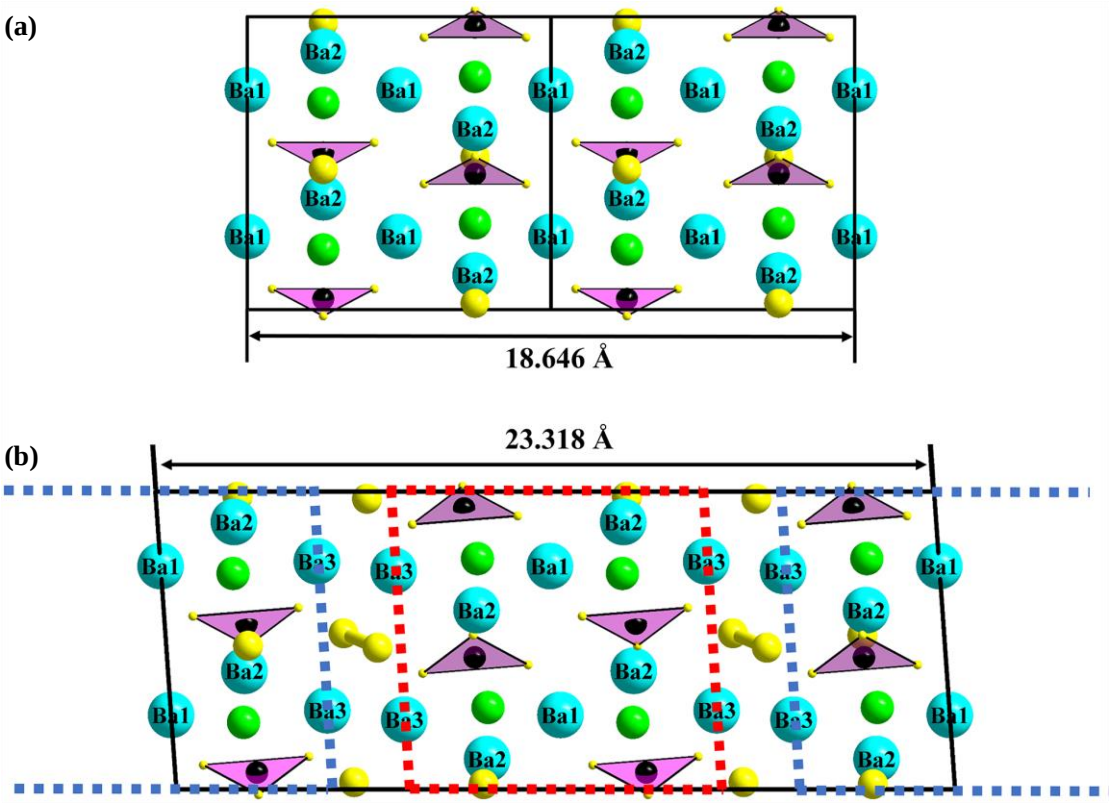

Fig. S6. Crystal structure comparison between Ba_2BS_3Cl (a) and $Ba_5B_2S_8Cl_2$ (b).

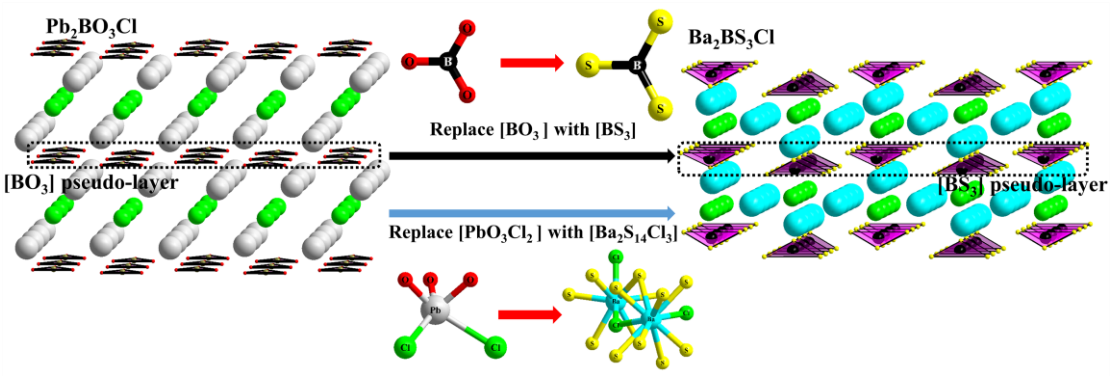

Fig. S7. Crystal structure comparison between Ba_2BS_3Cl and Pb_2BO_3Cl.

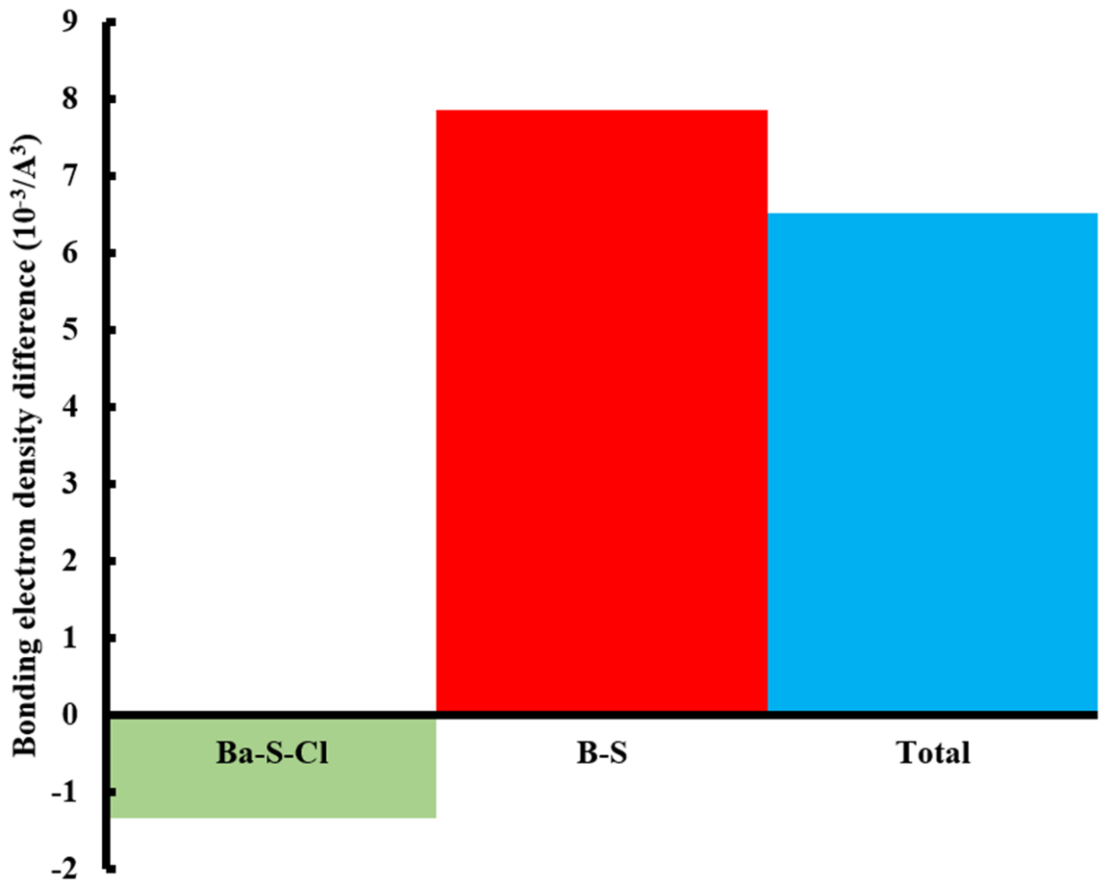

Fig. S8. Calculated bonding electron density difference (Δρ) of the covalent bonds along the optical principal axes, which is derived from Ba-S-Cl group and B-S group of Ba_2BS_3Cl.

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